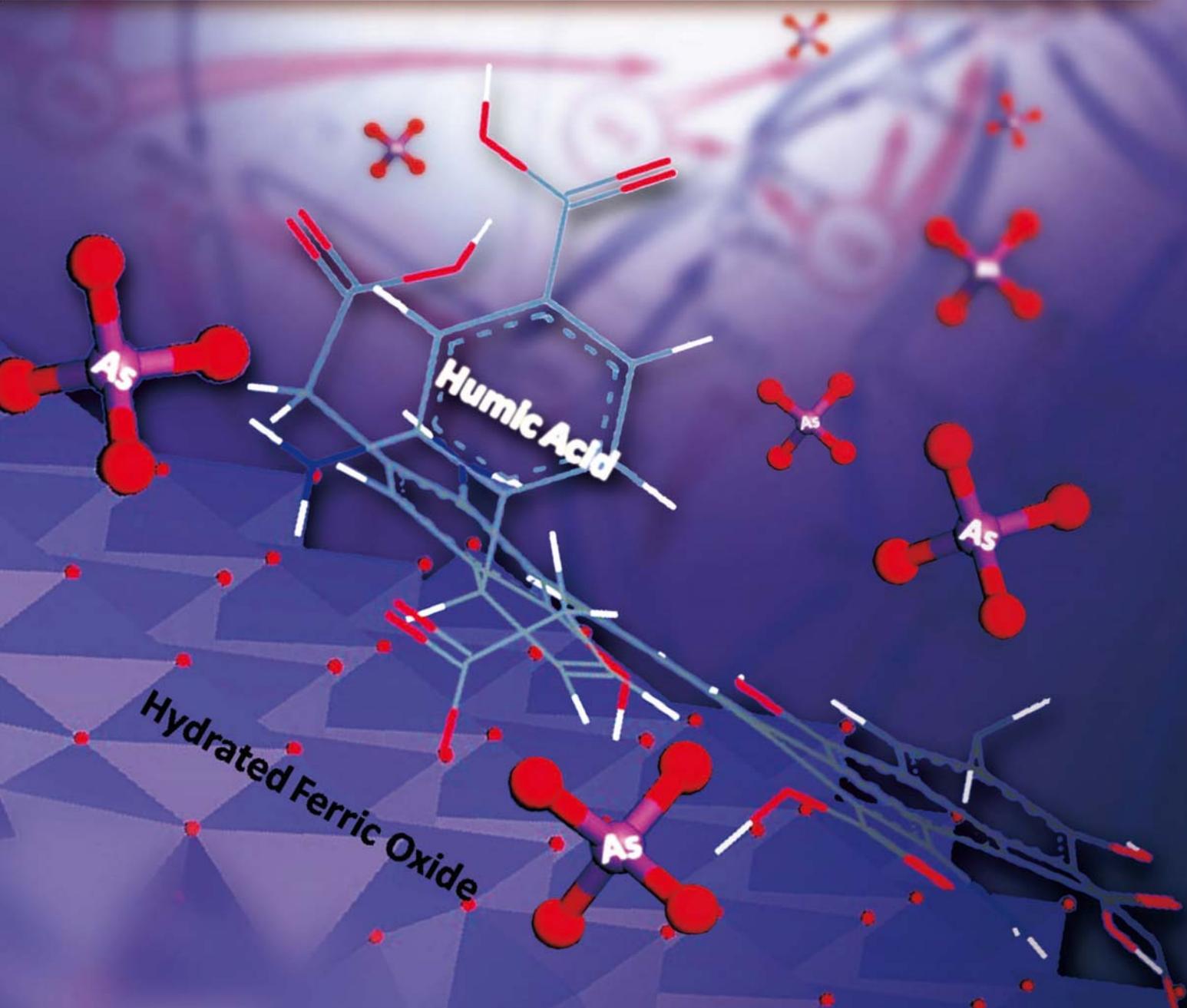


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CONTENTS

Aquatic environment

- Removal of total cyanide in coking wastewater during a coagulation process: Significance of organic polymers
Jian Shen, He Zhao, Hongbin Cao, Yi Zhang, Yongsheng Chen 231
- Removal of arsenate with hydrous ferric oxide coprecipitation: Effect of humic acid
Jingjing Du, Chuanyong Jing, Jinming Duan, Yongli Zhang, Shan Hu 240
- Arsenic removal from groundwater by acclimated sludge under autohydrogenotrophic conditions
Siqing Xia, Shuang Shen, Xiaoyin Xu, Jun Liang, Lijie Zhou 248
- Characteristics of greenhouse gas emission in three full-scale wastewater treatment processes
Xu Yan, Lin Li, Junxin Liu 256
- Effect of temperature on anoxic metabolism of nitrites to nitrous oxide by polyphosphate accumulating organisms
Zhijia Miao, Wei Zeng, Shuying Wang, Yongzhen Peng, Guihua Cao, Dongchen Weng, Guisong Xue, Qing Yang 264
- Efficacy of two chemical coagulants and three different filtration media on removal of *Aspergillus flavus* from surface water
Hamid Mohammad Al-Gabr, Tianling Zheng, Xin Yu 274
- Beyond hypoxia: Occurrence and characteristics of black blooms due to the decomposition of the submerged plant
Potamogeton crispus in a shallow lake
Qiushi Shen, Qilin Zhou, Jingge Shang, Shiguang Shao, Lei Zhang, Chengxin Fan 281
- Spatial and temporal variations of two cyanobacteria in the mesotrophic Miyun reservoir, China
Ming Su, Jianwei Yu, Shenling Pan, Wei An, Min Yang 289
- Quantification of viable bacteria in wastewater treatment plants by using propidium monoazide combined with quantitative PCR (PMA-qPCR)
Dan Li, Tiezheng Tong, Siyu Zeng, Yiwen Lin, Shuxu Wu, Miao He 299
- Antimony(V) removal from water by hydrated ferric oxides supported by calcite sand and polymeric anion exchanger
Yangyang Miao, Feichao Han, Bingcai Pan, Yingjie Niu, Guangze Nie, Lu Lv 307
- A comparison on the phytoremediation ability of triazophos by different macrophytes
Zhu Li, Huiping Xiao, Shuiping Cheng, Liping Zhang, Xiaolong Xie, Zhenbin Wu 315
- Biostability in distribution systems in one city in southern China: Characteristics, modeling and control strategy
Pinpin Lu, Xiaojian Zhang, Chiqian Zhang, Zhangbin Niu, Shuguang Xie, Chao Chen 323

Atmospheric environment

- Characteristics of ozone and ozone precursors (VOCs and NO_x) around a petroleum refinery in Beijing, China
Wei Wei, Shuiyuan Cheng, Guohao Li, Gang Wang, Haiyang Wang 332
- Identification of sources of lead in the atmosphere by chemical speciation using X-ray absorption near-edge structure (XANES) spectroscopy
Kohei Sakata, Aya Sakaguchi, Masaharu Tanimizu, Yuichi Takaku, Yuka Yokoyama, Yoshio Takahashi 343
- Online monitoring of water-soluble ionic composition of PM₁₀ during early summer over Lanzhou City
Jin Fan, Xiaoying Yue, Yi Jing, Qiang Chen, Shigong Wang 353
- Effect of traffic restriction on atmospheric particle concentrations and their size distributions in urban Lanzhou, Northwestern China
Suping Zhao, Ye Yu, Na Liu, Jianjun He, Jinbei Chen 362

Environmental health and toxicology

- A review on completing arsenic biogeochemical cycle: Microbial volatilization of arsines in environment
Peipei Wang, Guoxin Sun, Yan Jia, Andrew A Meharg, Yongguan Zhu 371
- Alginate modifies the physiological impact of CeO₂ nanoparticles in corn seedlings cultivated in soil
Lijuan Zhao, Jose R. Peralta-Videa, Bo Peng, Susmita Bandyopadhyay, Baltazar Corral-Diaz, Pedro Osuna-Avila, Milka O. Montes, Arturo A. Keller, Jorge L. Gardea-Torresdey 382
- Humification characterization of biochar and its potential as a composting amendment
Jining Zhang, Fan Lü, Chenghao Luo, Liming Shao, Pinjing He 390
- Immigrant *Pantoea agglomerans* embedded within indigenous microbial aggregates: A novel spatial distribution of epiphytic bacteria
Qing Yu, Anzhou Ma, Mengmeng Cui, Xuliang Zhuang, Guoqiang Zhuang 398
- Remediation of nutrient-rich waters using the terrestrial plant, *Pandanus amaryllifolius* Roxb.
Han Ping, Prakash Kumar, Bee-Lian Ong 404

Construction of a dual fluorescence whole-cell biosensor to detect <i>N</i> -acyl homoserine lactones Xuemei Deng, Guoqiang Zhuang, Anzhou Ma, Qing Yu, Xuliang Zhuang.....	415
Digestion performance and microbial community in full-scale methane fermentation of stillage from sweet potato-shochu production Tsutomu Kobayashi, Yueqin Tang, Toyoshi Urakami, Shigeru Morimura, Kenji Kida.....	423
Health risk assessment of dietary exposure to polycyclic aromatic hydrocarbons in Taiyuan, China Jing Nie, Jing Shi, Xiaoli Duan, Beibei Wang, Nan Huang, Xiuge Zhao	432
Acute toxicity formation potential of benzophenone-type UV filters in chlorination disinfection process Qi Liu, Zhenbin Chen, Dongbin Wei, Yuguo Du	440
Exposure measurement, risk assessment and source identification for exposure of traffic assistants to particle-bound PAHs in Tianjin, China Xiaodan Xue, Yan You, Jianhui Wu, Bin Han, Zhipeng Bai, Naijun Tang, Liwen Zhang.....	448

Environmental catalysis and materials

Fabrication of Bi ₂ O ₃ /TiO ₂ nanocomposites and their applications to the degradation of pollutants in air and water under visible-light Ashok Kumar Chakraborty, Md Emran Hossain, Md Masudur Rhaman, K M A Sobahan	458
Comparison of quartz sand, anthracite, shale and biological ceramsite for adsorptive removal of phosphorus from aqueous solution Cheng Jiang, Liyue Jia, Bo Zhang, Yiliang He, George Kirumba	466
Catalytic bubble-free hydrogenation reduction of azo dye by porous membranes loaded with palladium nanoparticles Zhiqian Jia, Huijie Sun, Zhenxia Du, Zhigang Lei	478
Debromination of decabromodiphenyl ether by organo-montmorillonite-supported nanoscale zero-valent iron: Preparation, characterization and influence factors Zhihua Pang, Mengyue Yan, Xiaoshan Jia, Zhenxing Wang, Jianyu Chen.....	483

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Antimony(V) removal from water by hydrated ferric oxides supported by calcite sand and polymeric anion exchanger

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ABSTRACT

We fabricated and characterized two hybrid adsorbents originated from hydrated ferric oxides (HFOs) using a polymeric anion exchanger D201 and calcite as host. The resultant adsorbents (denoted as HFO-201 and IOCCS) were employed for Sb(V) removal from water. Increasing solution pH from 3 to 9 apparently weakened Sb(V) removal by both composites, while increasing temperature from 293 to 313 K only improved Sb(V) uptake by IOCCS. HFO-201 exhibited much higher capacity for Sb(V) than for IOCCS in the absence of other anions in solution. Increasing ionic strength from 0.01 to 0.1 mol/L NaNO₃ would result in a significant drop of the capacity of HFO-201 in the studied pH ranges; however, negligible effect was observed for IOCCS under similar conditions. Similarly, the competing chloride and sulfate pose more negative effect on Sb(V) adsorption by HFO-201 than by IOCCS, and the presence of silicate greatly decreased their adsorption simultaneously, while calcium ions were found to promote the adsorption of both adsorbents. XPS analysis further demonstrated that preferable Sb(V) adsorption by both hybrids was attributed to the inner sphere complexation of Sb(V) and HFO, and Ca(II) induced adsorption enhancement possibly resulted from the formation of HFO-Ca-Sb complexes. Column adsorption runs proved that Sb(V) in the synthetic water could be effectively removed from 30 µg/L to below 5 µg/L (the drinking water standard regulated by China), and the effective treatable volume of IOCCS was around 6 times as that of HFO-201, implying that HFO coatings onto calcite might be a more effective approach than immobilization inside D201.

Introduction

Antimony (Sb) is widely used in various industries such as flame retardants, catalyst in plastics, batteries, pigments ceramics and glass (Filella et al., 2002a). However, it has been proved to impose great threat to human health and ecosystems (Gardea-Torresdey et al., 2001). Now, it has been listed as a priority pollutant by US EPA and European Union. US EPA established the concentration limit for Sb in drinking water as 6 µg/L. In China, the corresponding limit value for Sb is 5 µg/L, as same as that proposed by WHO and European Union (Guo et al., 2009; Kolbe et al.,

2011). In non-polluted waters, antimony is usually present less than 1 µg/L. Nevertheless, in the water body near various antimony-related ore fields, it could even reach as high as 53.6 ± 46.7 µg/L (Fu et al., 2010).

Similar to arsenic, antimony possesses s^2p^3 outer orbital electron configurations, and thus exists as two valence states, Sb(III) and Sb(V). In natural waters, it occurs as oxyanions, that is, Sb(OH)₃ and Sb(OH)₆⁻, and most of inorganic antimony exists as Sb(OH)₆⁻ in water (Filella et al., 2002b). Various methods have been reported for Sb removal, including adsorption (Mitsunobu et al., 2009), coagulation/flocculation and precipitation (Wu et al., 2010; Guo et al., 2009; Kang et al., 2003), solvent extraction (Navarro et al., 1999), ion exchange (Riveros et al., 2008) and membrane separation (Kang et al., 2000). Coagu-

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lation/flocculation and precipitation are widely used for Sb removal from drinking water, however, they usually cannot sequester Sb to meet the stringent regulations particularly when the initial Sb is high (Kang et al., 2003). In the past years, various adsorbents have been fabricated for Sb removal, including rice husks (Khalid et al., 2000), river sands (Hasany and Chaudhary, 1996), hydrous ferric oxides (HFOs) (Thanabalasingam and Pickering, 1990), hydroxyapatite (Leyva et al., 2001), and clay (Ilgen and Trainor, 2012). Among the adsorbents, HFOs exhibit outstanding performance for their specific inner sphere complexation with Sb(V) (Mitsunobu et al., 2010). Besides, they also exist extensively in nature and can be readily available (Tighe et al., 2005).

However, the powder state of HFOs inhibits their widespread use in water treatment since it is difficult to separate them from water and dispose of the excessive sludge formed during operation (Benjamin et al., 1996). To overcome the above problems, an effective approach is to coat HFOs inside or onto solid supports of large particle size to obtain hybrid adsorbents (Biswas et al., 2009; Chang et al., 2010; Xiong and Peng, 2008). Such hybrid materials combine the excellent handling, flow characteristics of the porous supports with the specific affinity of HFOs toward targeted pollutants. In our recent studies (Zhang et al., 2008; Pan et al., 2009), we impregnated HFO nanoparticles into a porous polystyrene anion exchange resin (D201) to fabricate a new hybrid adsorbent (HFO-201). The resultant composite exhibited excellent removal of arsenic and phosphate from aqueous solution. Besides, some other minerals of low cost could also serve as the host for HFO, such as sand (Benjamin et al., 1996) and diatomite (Jang et al., 2006).

As one of the most common minerals in the Earth's crust, calcite has exhibited considerable potential for water remediation (Bardelli et al., 2011; Sawada et al., 2003; Song et al., 2006). Different from sand (Benjamin et al., 1996) and diatomite (Jang et al., 2006), its possibility to serve as the host for HFO loadings has not been explored yet. In this study, we employed calcite as the support to prepare a new composite adsorbent, that is, iron-oxide coated calcite sands (IOCCS). Sb(V) removal onto HFO-201 and IOCCS was compared as functions of solution pH, temperature, ionic strength, and coexisting anions. The primary purpose of the study is to elucidate how to obtain a more efficient HFO-based composite for efficient Sb(V) removal from contaminated waters.

1 Materials and methods

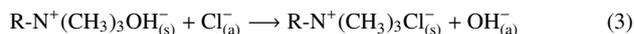
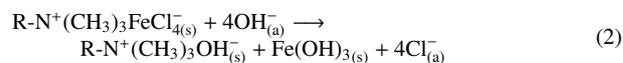
1.1 Materials

The stock Sb(V) solution was prepared by dissolving K₂Sb(OH)₆ (Aldrich-Sigma, China) into deionized water

(resistivity, 18.25 MΩ·cm). Other chemicals were analytical grade and obtained from Shanghai Chemical Reagent Station (Shanghai, China). Calcite sands were provided by Nanfeng Powder Factory (Nanjing, China). The polymeric anion exchanger D201 was provided by Zhengguang Resin Co. Ltd. (Hangzhou, China). Prior to use, the spherical D201 beads and irregular shape of calcite sands were screened to obtain those ranging from 0.6 to 0.7 mm and 0.45 to 0.9 mm in diameter, respectively.

1.2 Preparation of HFO-201 and IOCCS

The preparation of HFO-201 followed the procedures mentioned in our previous study (Zhang et al., 2008; Pan et al., 2009). In detail, the D-201 beads were added into the binary FeCl₃ (0.6 mol/L)-HCl (1.2 mol/L) solution so that the FeCl₄⁻ anions were preferably ion exchanged by D201. Afterwards, the FeCl₄⁻ preloaded D-201 beads were decomposed and simultaneously *in situ* precipitated onto the inner-pore surface of D-201 by adding NaOH-NaCl solution. Finally, the solid beads were washed with ultrapure water till neutral pH and thermally treated at 328 K for 12 hr, and we obtained the hybrid HFO-201. The above process could be represented by the following equations:



To prepare IOCCS, FeCl₃ solution (30% in mass) was added into a large conical flask containing 50 g raw calcite sands (RCS) and shaken continuously. After RCS was adequately immersed, NaOH solution (5.0% in mass) was added dropwise until solution pH reached 10–11, where Fe(OH)₃ was gradually and sufficiently precipitated onto the surface of RCS. The mixture kept quiescent for 30 min. Afterwards, 1.0 mol/L HCl solution was added dropwise to reach neutral pH of the mixture, just neutralizing the residual alkaline inside or onto RCS particles. The final product was washed by ultrapure water for several times, and then thermally stored at 328 K to obtain the hybrid adsorbent IOCCS.

1.3 Adsorption experiments

In batch adsorption, 0.050 g adsorbent was added into Erlenmeyer flasks, followed by 100 mL Sb(V) solution with known concentration. NaNO₃ was added to adjust the ionic strength of the solution when necessary. Meanwhile, 0.1 mol/L HNO₃ or 0.1 mol/L NaOH was added into

solution every 4 hr to adjust solution pH into the range of 3–9 until adsorption equilibrium was achieved. Except for being noted, initial Sb(V) concentration was set as 10 mg/L and the ambient temperature was controlled at 303 K. Desired amount of NaCl, Na₂SO₄, Na₂SiO₃, or Ca(NO₃)₂ was added into the test solution to evaluate the effect of ubiquitous ions including Cl⁻, SO₄²⁻, SiO₃²⁻, and Ca²⁺ on Sb(V) adsorption, where initial Sb(V) concentration was set as 0.10 mmol/L (12.2 mg/L), the initial pH was 6.0, and the competitive ions was 1.0 mmol/L. In addition, desorption of the used adsorbents was also attempted by using the binary NaOH (2.0%)-NaCl (5.0%) solution as eluent.

1.4 Fixed-bed adsorption

Fixed-bed adsorption experiments were carried out with a polyethylene column (12 mm in diameter and 130 mm in length) packed with water bath to control the ambient temperature. Five milliliters of HFO-201 and IOCCS beads were packed within two columns, respectively. The simulated water was prepared by adding Sb(V) solution into tap water and employed as feeding solution. Detailed hydraulic parameters were mentioned in the related figures. A BT100-2J pump (Baoding, China) was used to ensure a constant flow rate.

1.5 Characterization and analyses

HFO loadings of both hybrid adsorbents was determined by a flame atomic absorption spectrometer (Thermal Co., US) after digesting desired amount of adsorbent into 6 mol/L HCl solution for 6 hr and filtering the residue solids. Sb in solution was determined by an atomic fluorescence spectroscope equipped with an online reducing unit (AF-610A, China) by using KBH₄ and HCl. The samples were reduced with 10% thiourea and acidified with concentrated HCl before analysis. The specific surface area and the pore size distribution of adsorbents were determined by N₂ adsorption at 77 K (ASAP-2020 Micromeritics, USA). The appearance was observed by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM-

EDX, S-3400N HITACHI, Japan). The HFO particles loaded on both adsorbents were observed with transmission electron microscope (Model PS-800 HITACHI, Japan). The hybrid adsorbents were also subjected to an X-ray diffraction analysis (XTRA, Switzerland) equipped with a graphite monochromator and Cu-K α radiation. X-ray photo-electron spectroscopy (XPS) spectra of samples were obtained on a PHI 5000 Versaprobe system to assay Fe and Sb on the adsorbents. All the binding energies were referenced to the C 1s peak at 284.8 eV. The XPS data were correlated using XPS peak fit version 4.1.

2 Results and discussion

2.1 Characterization of HFO-201 and IOCCS

Figure 1 depicts the transmission electron microscopy images of two composites, and their SEM image are provided in **Fig. S1**. One can see that nanosized HFOs were coated inside D201 or onto calcite. Some basic properties of the host materials (D201 and RCS) as well as the corresponding hybrid adsorbents (HFO-201 and IOCCS) are summarized in **Table 1**. The HFO loading amount of HFO-201 was 16.0% (in Fe mass), and that for IOCCS was 19.5%. For both hybrid adsorbents, surface areas increased significantly after HFO loadings. We assumed that, the acidic FeCl₃ solution was expected to erode the RCS particles during preparation, resulting in a conspicuous increase of IOCCS in pore volume and surface area. As for HFO-201, the loaded HFO nanoparticles of high surface area-to-mass ratio were expected to increase the total surface area of the resultant HFO-201 composite, although they would occupy some pore volume. The X-ray diffraction spectra of HFO-201, RCS and IOCCS depicted in **Fig. S2** showed that HFOs are amorphous in nature since no new distinct peaks were observed after HFO loadings. Peak intensity variation before and after HFO loadings might be attributed to the acidic erosion of calcite surface during the preparation of IOCCS.

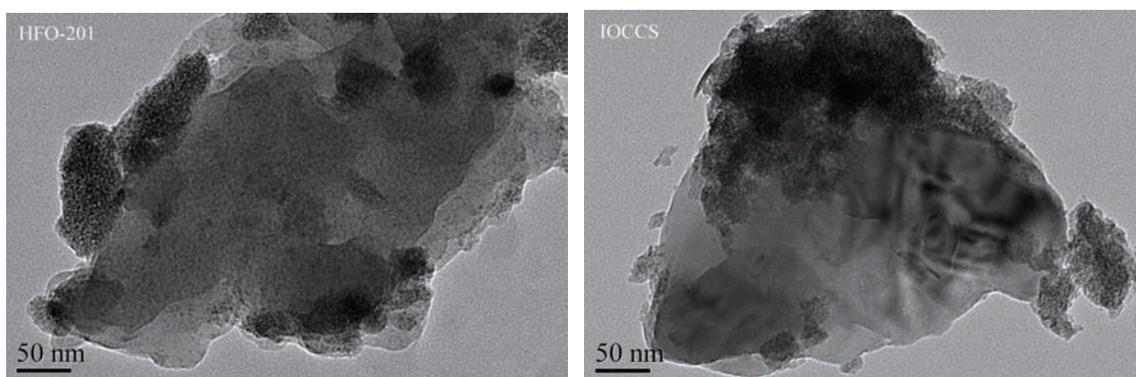


Fig. 1 TEM images of HFO-201 and IOCCS.

Table 1 Physicochemical properties of the sorbents and their host materials

Adsorbent	D201	HFO-201	RCS	IOCCS
Matrix structure	Poly (styrene-divinylbenzene)		Calcite	
BET surface area (m ² /g)	13.2	35.4	4.4	87.6
Pore volume (cm ³ /g)	0.039	0.037	0.008	0.062
HFO content (Fe mass%)	0	16.0	0.1	19.5
Bulk density (g/cm ³)	0.52	0.79	1.46	1.00

2.2 Effect of solution pH and ionic strength

The effect of solution pH on Sb(V) removal by HFO-201 and IOCCS at different ionic strength levels is described in **Fig. 2**. For both adsorbents, the removal efficiency decreased as solution pH increased. This is reasonable because Sb(V) mainly exists as $\text{Sb}(\text{OH})_6^-$ at $\text{pH} > 3$ (Biswas et al., 2009b), and positively charged surface are favorable for Sb(V) uptake. Given that HFOs have two $\text{p}K_a$ values, 6.5 and 9.0 (Cumbal and Sengupta, 2005),

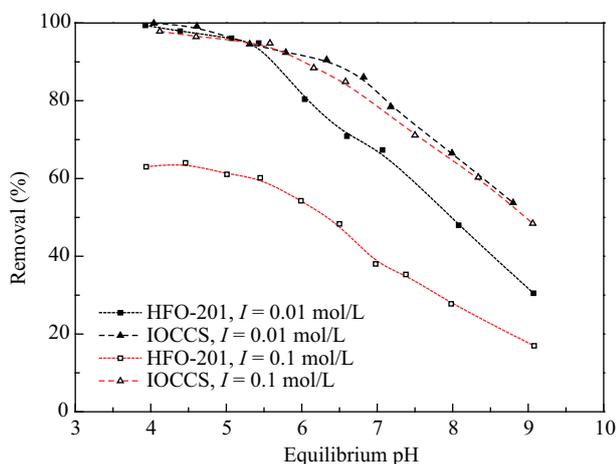


Fig. 2 Effect of solution pH on Sb(V) adsorption by HFO-201 and IOCCS at different ionic strengths. Experimental conditions: $C_0 = 10$ mg/L; temperature (T) = 303 K; shaking time 24 hr.

increasing pH from 6 to 9 or higher values would result in a significant drop in the fraction of positively charged HFO species. Therefore, Sb(V) removal would decrease accordingly.

Effect of ionic strength at two levels (0.01 and 0.1 mol/L NaNO_3) was also described in **Fig. 2**. For IOCCS, different ionic strengths did not pose any significant effect on Sb(V) removal in the studied pH ranges. Considering that RCS, the host of IOCCS, could not adsorb Sb(V) effectively (**Fig. 3b**), we suggest that Sb(V) adsorption mainly resulted from the coated HFOs, which interacted specifically with Sb(V) through formation of inner sphere complexes (Mitsunobu et al., 2010). Generally, increasing ionic strength was expected to have a competitive effect on the formation of outer sphere complexes but not inner sphere complexes, since the former is nonspecific (Tighe et al., 2005). As for HFO-201, increasing ionic strength from 0.01 to 0.10 mol/L decreased Sb(V) removal considerably. This is because that HFO-201 could sequester Sb(V) through two different pathways, the encapsulated HFOs of specific interaction with Sb(V) and the host exchanger D201 of nonspecific interaction with Sb(V), i.e., Columbic interaction or formation of outer sphere complexes, and the latter would be greatly affected by the added nitrate ions.

2.3 Adsorption isotherms

The adsorption isotherms of Sb(V) by both hybrids under three temperatures are illustrated in **Fig. 3**, and their

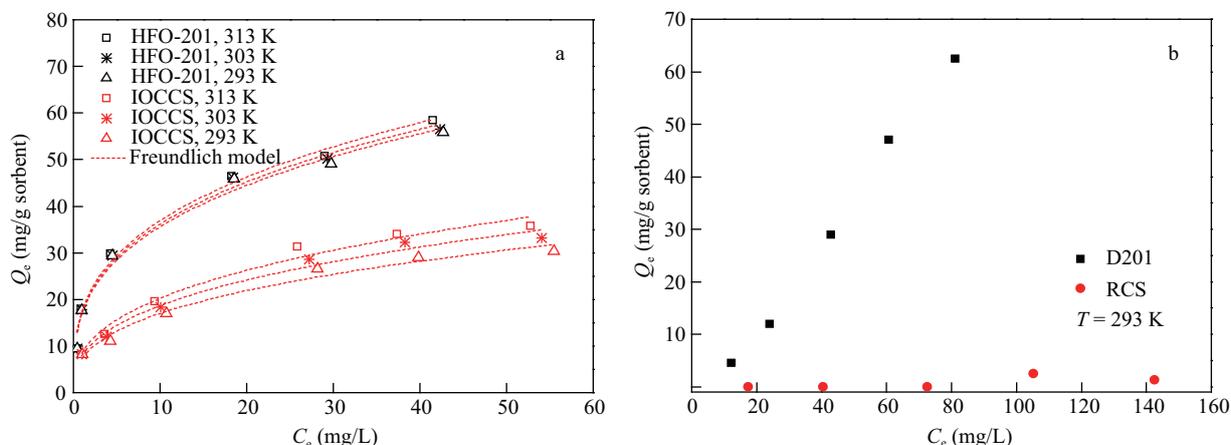


Fig. 3 Sb(V) adsorption isotherms onto (a) HFO-201 and IOCCS; (b) D201 and RCS. Experimental conditions: $C_0 = 5$ –70 mg/L; $\text{pH} = 6.0$; shaking time 24 hr.

hosts, D201 and RCS, were also employed for reference. Freundlich and Langmuir models described in Eq. (4) and (5) were employed to fit the isotherm data. For comparison purpose, the normalized sorption capacity, Q_m (mg/g), was used for modeling.

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

$$Q_e = K_F C_e^{1/n} \quad (5)$$

where, C_e (mg/L) is the equilibrium concentration, Q_e (mg/g) is the equilibrium adsorption capacity, K_L (L/mg) is a binding constant, K_F is the Freundlich adsorption affinity coefficient, and n is indicative of the homogeneity of the adsorbent. As seen in Fig. 3a, Sb(V) removal by IOCCS increased slightly as temperature increased from 293 to 313 K, indicating that Sb(V) adsorption onto IOCCS was endothermic in nature. In contrast, little influence was observed for Sb(V) adsorption by HFO-201. Different temperature dependence of both Fe-bearing hybrids might be associated with their different adsorption mechanisms towards Sb(V). For HFO-201, the main species of Sb(V), $\text{Sb}(\text{OH})_6^-$, could be sequestered not only by the encapsulated by HFO, but also by the D201 matrix through ion exchange process. On the contrary, the calcite matrix of

IOCCS could not adsorb any Sb(V) anions, as seen in Fig. 3b. Such different adsorption also resulted in much higher capacity of HFO-201 than that of IOCCS for sorption to the single Sb(V), as shown in Table 2.

2.4 Adsorption kinetics

Adsorption kinetics of Sb(V) onto HFO-201 and IOCCS are depicted in Fig. 4a, and were simulated by the intraparticle diffusion model (Eq. (6)).

$$Q_t = K_i t^{0.5} + C \quad (6)$$

where, Q_t (mg/g) is the amount of Sb(V) adsorbed at time t (min), K_i ($\text{mg}/(\text{g}\cdot\text{min}^{-0.5})$) is the diffusion rate constant and C (mg/g) is the intercept for any experiment.

Consistent with the results mentioned above, Sb(V) adsorption on HFO-201 seemed independent upon the ambient temperature, and increasing temperature was favorable for Sb(V) adsorption by IOCCS. The intraparticle diffusion model was employed to fit the kinetic curves of both hybrids at 303 K, and the results in Fig. 4b indicated that multiple steps affected and even controlled Sb(V) adsorption onto both hybrids at different time intervals. Based on the results in Fig. 4b, we assume that prior to effective sequestration by HFO-201, Sb(V) would diffuse inside the inner pore of D201 to the outer surface of

Table 2 Langmuir fit and Freundlich fit of the adsorption isotherms

Sorbent	T (K)	Freundlich			Langmuir		
		K_F	$1/n$	R^2	Q_m (mg/g)	K_L (L/mg)	R^2
HFO-201	313	17.5	0.325	0.986	62.5	0.273	0.980
	303	17.2	0.322	0.984	60.9	0.275	0.983
	293	17.0	0.321	0.982	60.2	0.271	0.984
IOCCS	313	8.55	0.374	0.977	42.7	0.123	0.981
	303	7.94	0.372	0.980	39.9	0.117	0.975
	293	7.33	0.366	0.977	36.7	0.112	0.971

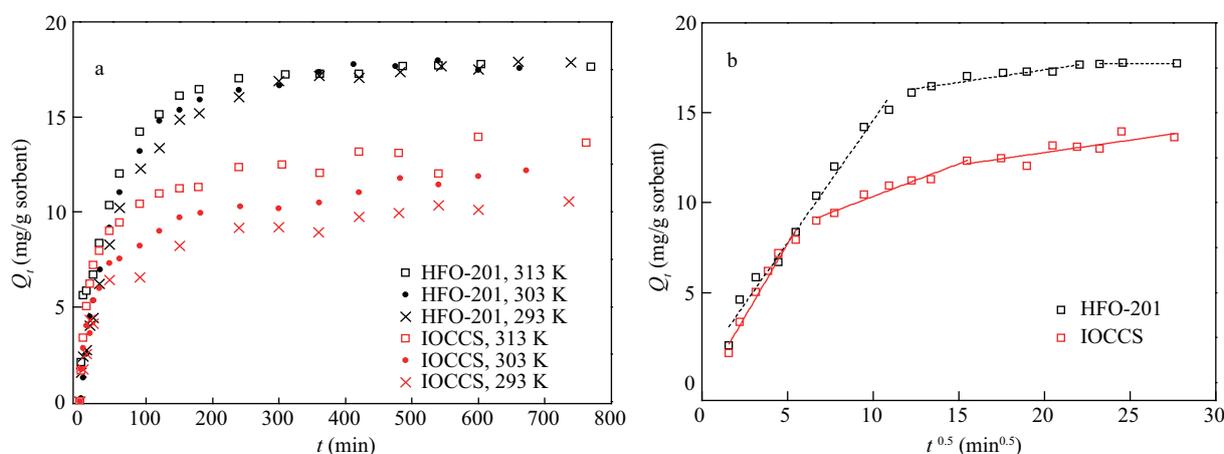


Fig. 4 (a) Adsorption kinetics of Sb(V) onto HFO-201 and IOCCS at different temperatures. Experimental conditions: $C_0 = 10$ mg/L; pH = 6.0. (b) Intraparticle diffusion modeling for the Sb(V) adsorption by HFO-201 and IOCCS at 303 K.

HFOs, and then diffuse into the inner region of HFO nanoparticles to react with the active sites. For IOCCS, Sb(V) would diffuse from the solution to the active sites of the external HFO surface. Also, it would diffuse within the inner regions of HFO nanoparticles to react with the inside active sites. Similar kinetic performance as well as the underlying mechanism was reported in our recent study (Wang et al., 2011).

2.5 Effect of coexisting ions

Considering the ubiquitous ions are present with Sb(V) in contaminated water, we examined the effect of some coexisting ions on Sb(V) adsorption by HFO-201 and IOCCS, and the results are illustrated in Fig. 5. As for IOCCS, the added anions including NO_3^- , SO_4^{2-} , and Cl^- did not pose any significant effect on Sb(V) sequestration, while SiO_3^{2-} would greatly inhibit Sb(V) adsorption. It is possibly because the former three anions could mainly form outer-sphere complexes with HFOs and thus affected Sb(V) adsorption insignificantly (Cumbal and Sengupta, 2005), while SiO_3^{2-} could compete with Sb(V) for the active sites of the coated HFOs through specific adsorption, similar to its inhibition on arsenic removal by goethite (Waltham and Eick, 2002). However, we could observe that NO_3^- , SO_4^{2-} , and Cl^- could inhibit Sb(V) adsorption by HFO-201 to a considerable extent. This is because HFO-201 could effectively sequester Sb(V) through two separate pathways, the ammonium groups of the host D201 binding Sb(V) through nonspecific electrostatic attraction, and the loaded HFO capturing Sb(V) through specific complexation. Similar to effect of other solution chemistry discussed above, the above three anions would effectively occupy the active sites of D201 through Columbic interaction. As for SiO_3^{2-} , it inhibited Sb(V) adsorption by HFO-201 most significantly because it could compete for the active sites of both HFOs and D201.

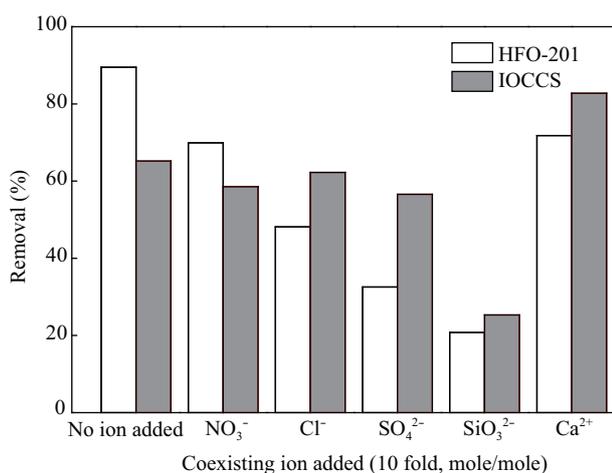


Fig. 5 Effect of coexisting ions on the removal of Sb(V) by HFO-201 and IOCCS. Experimental conditions: $C_0 = 0.1$ mmol/L; $T = 303$ K; shaking time 24 hr.

Of note is that the added Ca^{2+} would promote Sb(V) adsorption by both hybrids, when the negative effect of its counter anion, nitrate, on adsorption was involved (Fig. S3). On one hand, Sb(V) may form secondary minerals with Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , of which Ca antimonates (romeites, $\text{Ca}[\text{Sb}(\text{OH})_6]_2$) have the lowest solubility ($K_{sp} = -12.55$) (Cornelis et al., 2011). Precipitation of calcium salts in the adsorption process of arsenate by Fe-Mn binary oxides was also found (Zhang et al., 2012). Another possible reason is that interaction between Ca^{2+} and HFO might result in HFO-Ca-Sb complex and thus enhanced the adsorption. Similar observations were also found by Guan et al. (2009), who illustrated that formation of $\text{Fe}(\text{OH})_3$ -Ca-As complex might formed during the coagulation-flocculation process.

To further probe the specific interaction between Sb(V) and HFO, we obtained XPS spectra of Sb(V) adsorbed onto HFO in the absence or presence of calcium ions, and the results are depicted in Fig. 6. As compared to the non-adsorbed Sb(V) (i.e., $\text{KSb}(\text{OH})_6$), the $3d_{3/2}$ peak of Sb(V) adsorbed by HFO was increased from 539.6 to 540 eV. It is known that the binding energy of a given atom is dominated by its oxidation state and the chemical environment (Salim et al., 1995), and the shift in $3d_{3/2}$ peak of Sb(V) adsorbed by HFO should be attributed to the formation of inner sphere Fe-O-Sb complexes, since the outer sphere Fe-O-Sb complexes cannot change the binding energy significantly (Pan et al., 2010). When calcium ions were added, it was further increased to 540.4 eV, implying the formation of HFO-Ca-Sb complexes, just as illustrated above.

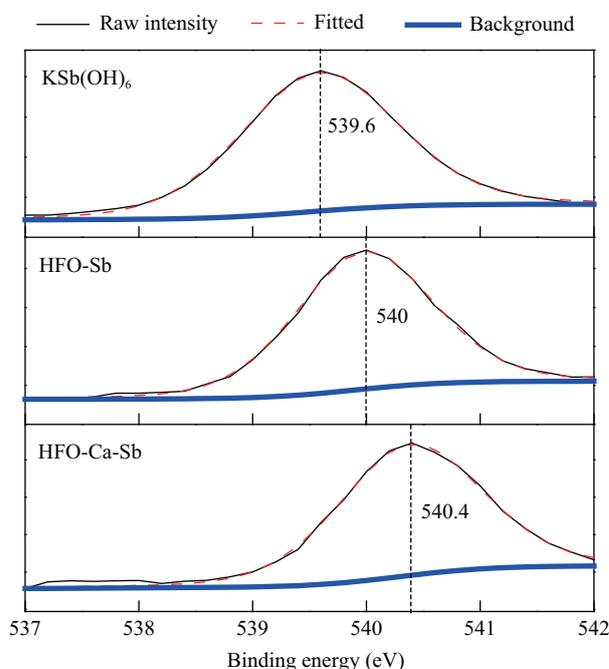


Fig. 6 XPS spectra of Sb $3d_{3/2}$ region of $\text{KSb}(\text{OH})_6$ and that adsorbed by HFO in the absence or presence of calcium ions.

2.6 Fixed-bed column experiments

Two separate columns filled with HFO-201 beads or IOCCS particles were employed to evaluate the potential performance of the hybrid sorbents for practical use (Fig. 7). The synthetic feeding solution was prepared by adding Sb(V) stock solution into tap water, simulating the natural Sb(V)-contaminated river water, and its basic composition is mentioned as follows (in mg/L): Sb(V) 0.03; Ca²⁺ 36.9; Mg²⁺ 4.23; Al³⁺ 0.017; Na⁺ 12.0; K⁺ 7.23; SO₄²⁻ 40.4; NO₃⁻ 3.8; Cl⁻ 10.1; SiO₃²⁻ 10.62; and PO₄³⁻ 0.08 (the Sb(V) concentration in the original contaminated river water was 30 µg/L in the locate). The breakthrough curves from both columns are depicted in Fig. 7. One can obviously see that IOCCS performed much better than HFO-201, and the effective treatable volume of IOCCS is around 6 times as that of HFO-201. Sb(V) can be removed effectively by IOCCS within 4000 BV until the effluent concentration of Sb(V) exceeded 5 µg/L, while for HFO-201 it was 700 BV. All the above results further validated that IOCCS was less sensitive than HFO-201 to the coexisting ions in water. Considering that HFO loadings of HFO-201 (16.0%) were similar to IOCCS (19.5%), such quite different behavior of both hybrids in column adsorption implied that the efficiency of HFOs coated onto RCS was much higher than those inside D201. HFOs coated onto RCS greatly increased the surface area from 4.4 m²/g of RCS to 87.6 m²/g of IOCCS, while those inside D201 only increased from 13.2 to 35.4 m²/g, suggesting that HFO coated onto RCS would provide much higher accessible surface than immobilized inside D201 to react with Sb(V). However, further study is still required to confirm the assumption.

After column adsorption, we used the binary NaOH-NaCl solution to regenerate the exhausted HFO-201 and IOCCS. Unfortunately but reasonably, the regeneration efficiency for both columns was only about 10%, because effective Sb(V) adsorption by HFO-based hybrids was

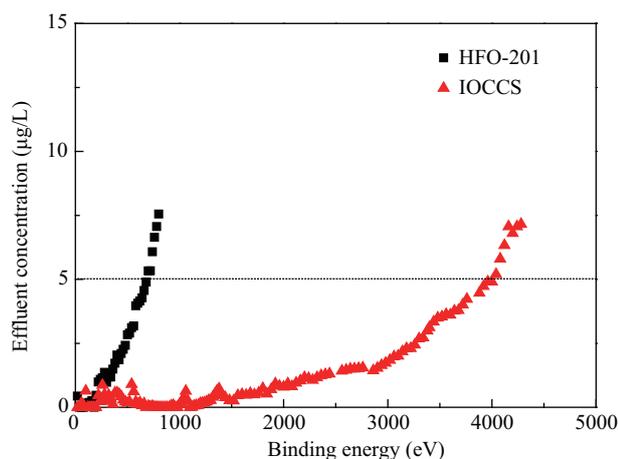


Fig. 7 Sb(V) retention by two separate column beds packed with HFO-201 and IOCCS respectively from a synthetic feeding solution. Experimental conditions: $C_0 = 30 \mu\text{g/L}$, $\text{pH} = 7.0\text{--}7.5$, empty bed contact time = 3 min, superficial liquid velocity = 0.9 m/hr.

mainly achieved through specific inner-sphere complexation. Given that IOCCS is more economically desirable than HFO-201, the former hybrid should be a potential choice for treatment of Sb(V) contaminated water in water supply system. As for HFO-201, how to further improve the efficiency of the inside HFOs is still a question to be solved.

3 Conclusions

We demonstrated that HFO nanoparticles coated onto calcite or inside D201 would exhibit satisfactory removal of Sb(V) from water under different solution chemistry, and column adsorption demonstrated that adsorption onto both hybrids could result in a distinct decrease of Sb(V) from 30 µg/L to less than 5 µg/L (the drinking standard recommended by WHO). Such attractive performance mainly resulted from the formation of inner sphere complexes of Sb(V) and HFO nanoparticles. In addition, HFOs coated onto calcite were much less sensitive to the coexisting anions than those inside D201 and simultaneously, more efficient for Sb(V) removal from contaminated water. Unfortunately, how to regenerate both of the exhausted composite adsorbents is still a challenging task, and as for HFO-201, how to further improve the efficiency of the encapsulated HFOs is another problem to be solved.

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Supporting materials

Supplementary data associated with this article can be found in the online version.

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Supporting materials

The spectrum of HFO-201 suggested that HFO encapsulated in D201 was amorphous in nature (Zhang et al., 2008). The XRD spectra of RCS and IOCCS was in accordance with calcite, although a little impurities appeared (Cave and Talens-Alesson, 2005).

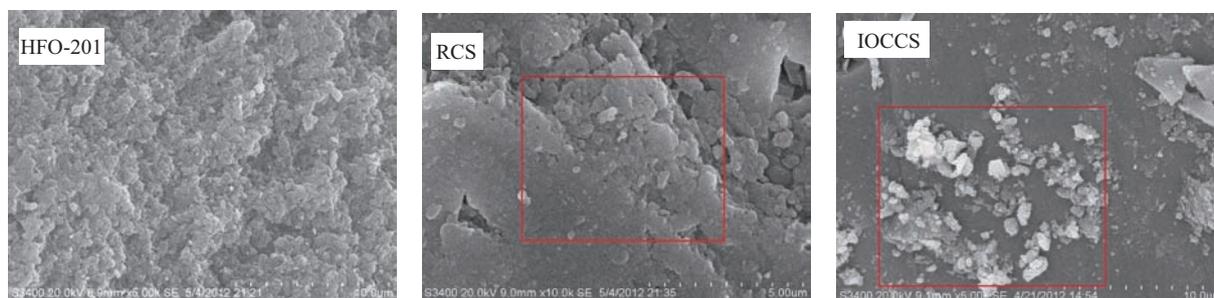


Fig. S1 SEM images of the hybrid sorbents.

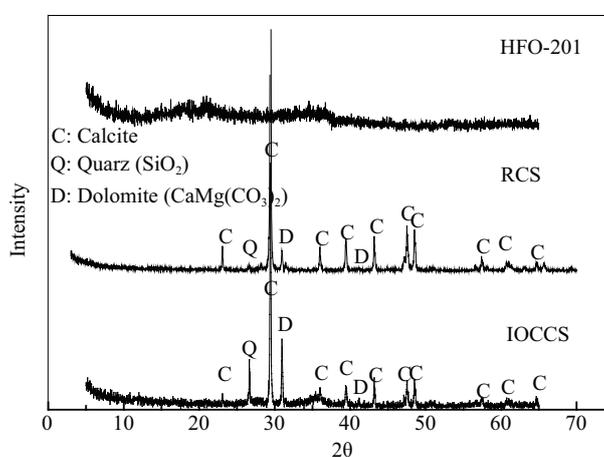


Fig. S2 XRD image of HFO-201, RCS and IOCCS.

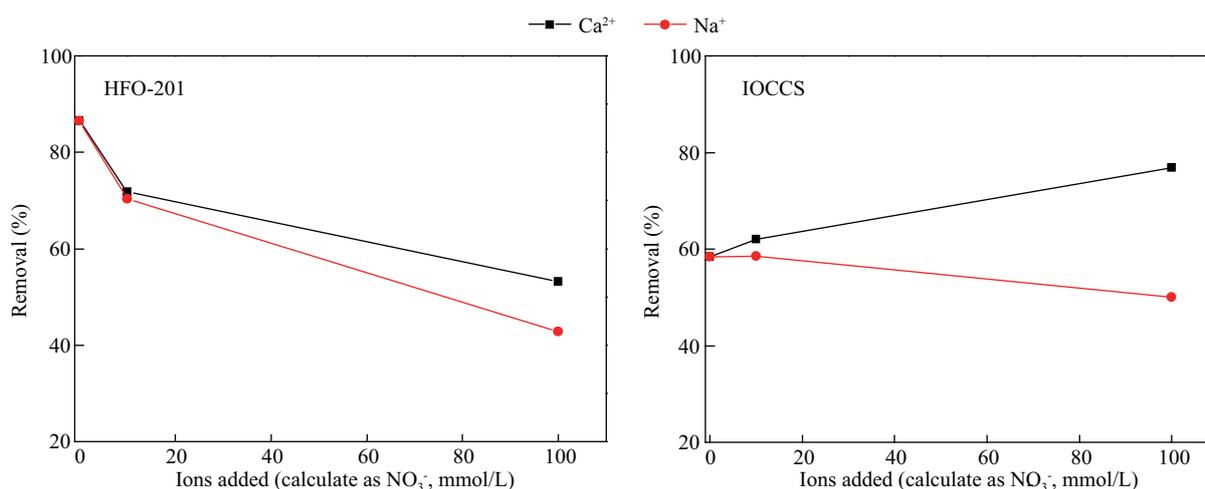


Fig. S3 Effect of Ca²⁺ compared to Na⁺ in Sb(V) removal by HFO-201 and IOCCS.

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