



Preparation, characterization and application of a copper (II)-bound polymeric ligand exchanger for selective removal of arsenate from water

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ABSTRACT

A copper (II)-bound polymeric ligand exchanger named WH-425-Cu was prepared by loading Cu²⁺ onto poly (4-vinylpyridine) resin. The performance of WH-425-Cu as the ligand exchanger to remove arsenate [As (V)] from aqueous solution was also investigated by using static equilibrium and dynamic adsorption experiments. Results of static experiments indicated that WH-425-Cu had higher adsorption selectivity for As (V) than other ubiquitous anions in nature water body such as SO₄²⁻, Cl⁻, SiO₃²⁻, and PO₄³⁻. The optimal pH for adsorption of As (V) on WH-425-Cu was in the range of 6.0–8.0. The As (V) adsorbed on WH-425-Cu could be easily eluted with 7BV of 6% NaCl solution (at pH=9.0) with elution efficiency above 99%. The prepared WH-425-Cu could be used as a highly selective and reusable ligand exchanger for selective removal of As (V) from water.

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1. Introduction

Arsenic (As) has been recognized as a poison that negatively impacts on public health and environment. Arsenic pollution in the groundwater has been reported in South Asia, North America, Taiwan, Inner Mongolia and Shanxi of China [1–7]. Due to the toxicity and carcinogenicity, the World Health Organization (WHO) has stringently regulated the allowable maximum arsenic contamination in drinking water to be no more than 0.01 mg L⁻¹ [8]. Many approaches have been proposed in literatures for the removal of arsenic from water body such as precipitation [9], reverse osmosis [10], ion exchange [11,12], and adsorption [13]. Evaluation studies of various arsenic removal methods were also reported in recent review literatures [14–16]. Among the various proposed arsenic removal methods, adsorption and ion exchange have been most widely investigated for arsenic removal from water because of their versatile advantages over other methods such as simple operation and easy regeneration. Various types of adsorbents such as activated carbons, iron oxyhydroxides and mixed metal oxides [17–21] have been reported for the removal of arsenic in aqueous solutions. However, due to their poor mechanical strength and capacity loss during the recovery process, these adsorbents were often used as ‘disposable’ sorbents. Therefore, the adsorption process might result in large volumes of As-laden sorbents, which would require further safely treated.

Ion exchange is currently an EPA-identified best available technology (BAT) for removing As (V) because of the high efficiency to remove these ions almost quantitatively from aqueous solution [22], the insensitivity of the process to solution pH, and the long effective lifetime of the resins. However, for ion exchange, the capacity of traditional anion exchange resins for removing As (V) is severely retarded and its selectivity is low due to the competition from other anions such as sulfate ions that are ubiquitously abundant in natural water body [23–25].

To overcome the drawback of the traditional anion exchange resins, increasing interests have been focused on developing polymeric ligand exchanger (PLE), which is composed of a polymer (supporting matrix) and a transition metal cation (Lewis acid) as its terminal functional groups [26,27]. To achieve selective removal of As (V), many transition metal cations such as Zr⁴⁺, Fe³⁺, Mo³⁺, La³⁺ and Al³⁺ were loaded by many research groups onto polymer to attain ligand exchangers [28–32]. A few studies indicated that Cu²⁺ might be the best Lewis acid metal cation to attain high capacity and selective ligand exchanger [33]. The properties of the metal hosting polymer are of critical importance in preparation of a novel ligand exchanger. The metal hosting polymer should possess the stable physical, chemical properties, high metal-loading capacity as well as strong bonding force to metal ion [33,34]. It is well known that polymers based on vinylpyridine have high mechanical strength and can form polymer–metal complex [35,36].

In this study, poly (4-vinylpyridine) resin was prepared by suspension polymerization of 4-vinylpyridine and divinylbenzene, and copper (II)-bound polymeric ligand exchanger (WH-425-Cu) was obtained by loading Cu²⁺ onto poly (4-vinylpyridine) resin. The

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objectives of this study were to explore the feasibility of WH-425-Cu as novel ligand exchanger for As (V) removal from the aqueous solution. The batch equilibrium experiments were carried out to evaluate the effect of pH, coexisting foreign anions, humic acid on As (V) removal. The regenerability of the As (V) saturated WH-425-Cu was also studied.

2. Experimental

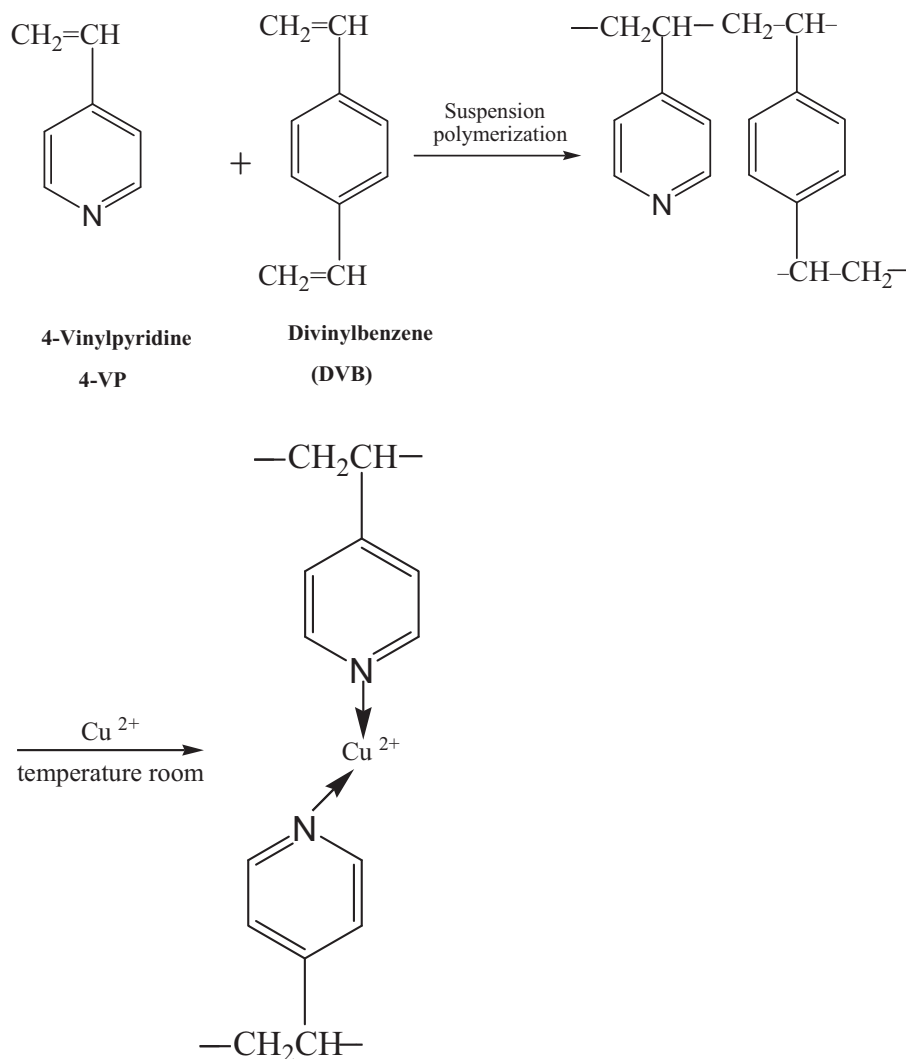
2.1. Materials

4-Vinylpyridine (4-VP, supplied by Alfa Aesar, John Matthey Company, Lancashire, England) was dried over CaH₂ and distilled under reduced pressure prior to use. Divinylbenzene was obtained from Dongda Chemical Co. (Shandong Province, China). A commercial strong base anion exchanger (D201) with quaternary ammonium functional groups was kindly provided by Jiangsu N&G Environmental Technology Co. Ltd. (Jiangsu Province, China). Sodium arsenate (Na₂HAsO₄·7H₂O, A.R.) was purchased from Aldrich Sigma (Shanghai, China). The stock solution of 100.0 mg L⁻¹ As (V) was prepared by dissolving Na₂HAsO₄·7H₂O in distilled water. All solutions for test were prepared by appropriate dilution of the freshly prepared stock solution. Copper sulfate pentahydrate, sodium chloride, sodium sulfate, sodium silicate and sodium

phosphate dodecahydrate were purchased from Shanghai Chemical Reagent Plant (Shanghai, China) and used in the study without further purification. Humic acid sodium salt (technical grade, CAS No. 68131-04-4) was obtained from Aldrich. The stock solution of humic acid was prepared by dissolving a predetermined amount of humic acid sodium salt into ultrapure water followed by filtering through a 0.45-μm cellulose acetate membrane filter [37]. Humic acid concentration was expressed as dissolved organic carbon (DOC).

2.2. Ligand exchanger preparation

Copper (II)-bound polymeric ligand exchanger was prepared as shown in Scheme 1. In brief, the poly (4-vinylpyridine) resin was prepared by suspension copolymerization of 4-vinylpyridine and divinylbenzene. The synthetic process had been described in detail in previous papers [38,39]. The attained poly (4-vinylpyridine) resin was then saturated with CuSO₄ solution (containing 500 mg L⁻¹ Cu²⁺, pH=4.2) using column adsorption. Finally, the copper loaded poly (4-vinylpyridine) resin were thoroughly rinsed with double distilled water and dried for use. For typographical convenience, the poly (4-vinylpyridine) resin and copper-loaded poly (4-vinylpyridine) complex would be referred



Scheme 1. Preparation procedure of WH-425-Cu.

Table 1
Salient properties of WH-425 and WH-425-Cu.

Property	WH-425	WH-425-Cu
BET surface area (m ² g ⁻¹)	45.5	40.6
Micropore area (m ² g ⁻¹)	8.6	7.2
Pore volume (cm ³ g ⁻¹)	0.1325	0.1269
Micropore volume (cm ³ g ⁻¹)	0.0036	0.0029
Average pore diameter (nm)	11.6	12.4
Cu content (%)	0	6.2
Color	White	Blue

to as WH-425 and WH-425-Cu, respectively. The salient properties of the copolymer WH-425 and WH-425-Cu were shown in Table 1.

2.3. Adsorption assay

A mass of 0.1 g of WH-425-Cu was mixed with 100 mL arsenate solution with various concentrations As (V) in a series of 150 mL conical flasks. The flasks were then completely sealed and placed in a model G25 incubator shaker (New Brunswick Scientific Co. Inc.) at a pre-set temperature with shaking speed of 150 rpm for 36 h at a desired temperature to ensure adsorption equilibrium (preliminary tests indicated that adsorption equilibrium was achieved within about 7 h). If necessary, the pH of solution could be adjusted by hydrochloride acid and/or sodium hydroxide. The As (V) uptake on WH-425-Cu and the percentage removal (R%) of As (V) were calculated according to Eqs. (1) and (2), respectively, as shown below:

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

$$R\% = \frac{100(C_0 - C_e)}{C_0} \quad (2)$$

where V is the volume of solution (L); W is the mass of adsorbent (g); C_0 and C_e are the initial As (V) concentration and equilibrium As (V) concentration ($\mu\text{g L}^{-1}$), respectively; and q_e is the equilibrium adsorption capacity ($\mu\text{g g}^{-1}$).

As (V) concentration in aqueous solution was determined by using an atomic fluorescence (AF) spectrometer with an online hydride generation unit (AF-610A, Rayleigh Instrument Co., Beijing, China), following the reduction of As (V) to As (III). The copper content loaded in the resin was analyzed through HClO_4 solution and measured by using an atomic absorption spectrophotometer (Hitachi Z-8100, Japan). The values of pH were measured with a pH meter (PHS-3C, Shanghai, China). Each experiment was run in triplicate and mean values were reported.

2.4. Effect of coexisting ions and humic acid

The effect of coexisting anions (chloride, sulfate, silicate, phosphate) and humic acid (HA) on the adsorption of arsenate onto WH-425-Cu was investigated by using the following experiment. 0.1 g of WH-425-Cu was introduced to conical flasks containing 100 ml of 250 $\mu\text{g L}^{-1}$ As (V) and coexisting ions or humic acid. The pH of solution was adjusted to 8.0. The mixtures were equilibrated at 298 K for 36 h with mild agitation, and then the concentration of residual As (V) was analyzed.

2.5. Column adsorption and desorption test

Column sorption runs were carried out with a glass column (11 mm diameter and 200 mm length) equipped with a water bath to maintain a constant temperature. 5 ml WH-425-Cu was packed in the column for test use. A peristaltic pump (Lange BT100-2], China) was employed to assure a constant flow rate. The exhausted WH-425-Cu was regenerated using 6% NaCl solution at pH 9.0.

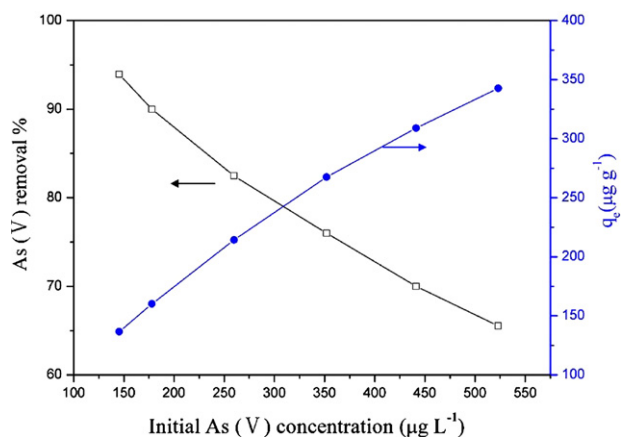


Fig. 1. Effect of the initial As (V) concentration on As (V) removal and the equilibrium adsorption capacity (0.1 g WH-425-Cu was added into 100 mL solution at 288 K, pH = 8.0).

3. Results and discussion

3.1. Influence of initial As (V) concentration and adsorption model

Experimental runs were carried out to assess the effect of initial As (V) concentration on adsorption performance by WH-425-Cu. Curves in Fig. 1 showed the effect of the initial As (V) concentrations on the corresponding removal percentage and the equilibrium adsorption capacity, respectively. It could be found that the As (V) adsorbed onto WH-425-Cu increased with the increase of the initial As (V) concentration. However, the removal percentage of As (V) exhibited a descending trend as the initial As (V) concentration increased. When the initial As (V) concentration was lower than about 180 $\mu\text{g L}^{-1}$, the As (V) removal was more than 90%. For the system with 150 $\mu\text{g L}^{-1}$ of the initial As (V) concentration, the residual As (V) in the solution was measured to be as low as 8 $\mu\text{g L}^{-1}$. This was lower than the current USEPA maximum contaminant level (MCL) of 10 $\mu\text{g L}^{-1}$ for drinking water.

The equilibrium data were plotted with the Langmuir and Freundlich isotherm models over the entire concentration range (figure omitted for the sake of brevity). The Langmuir and the Freundlich equations are expressed as follows:

Langmuir:

$$\frac{c_e}{q_e} = \frac{1}{K_L} + \frac{c_e}{q_m} \quad (3)$$

Freundlich:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (4)$$

where c_e is the equilibrium concentration of As (V) ($\mu\text{g L}^{-1}$), q_e is the amount adsorbed under equilibrium ($\mu\text{g g}^{-1}$), q_m ($\mu\text{g g}^{-1}$) is the theoretical maximum adsorption capacity of the adsorbent for As (V), and K_L (L g^{-1}) is the a Langmuir binding constant related to the energy of adsorption, K_F and n are the Freundlich characteristic constants. The fitting constants for the Langmuir and Freundlich isotherm models along with correlation coefficient value (R^2) were summarized in Table 2. It was found that the adsorption isotherm data were described well by Freundlich model. The calculated n was larger than 1, indicating favorable sorption of As (V) onto WH-425-Cu.

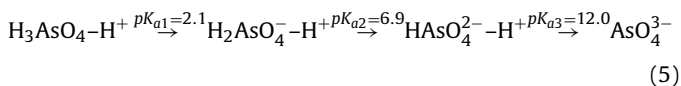
3.2. Effect of pH on adsorption

Fig. 2 depicted that the As (V) uptake data as a function of the equilibrium solution pH. It could be found that the solution pH had

Table 2
Isotherm parameters for As (V) sorption onto WH-425-Cu.

Isotherm/parameters	Value
<i>Langmuir isotherm</i>	
$q_m, \mu\text{g g}^{-1}$	355.72
$K_L, \text{L g}^{-1}$	16.73
R^2	0.9192
<i>Freundlich isotherm</i>	
K_F	64.89
n	3.1323
R^2	0.9976

an important effect on As (V) sorption onto WH-425-Cu, and the optimal As (V) uptake occurred in the pH range of 6.0–8.0. The effects of solution pH on As (V) adsorption are general based on two factors: (i) distribution of As (V) species in solution, and (ii) competition from OH^- in aqueous solution. Distribution of As (V) species based on the corresponding pK_a values is given in Eq. (5):



Based on both ligand strength and ionic charge, the adsorbability of various As (V) species follows the sequence of $\text{H}_3\text{AsO}_4 < \text{H}_2\text{AsO}_4^- < \text{HAsO}_4^{2-} < \text{AsO}_4^{3-}$. When the solution pH value was from 2.0 to 4.0, H_2AsO_4^- and H_3AsO_4 , which were the predominant As (V) species, could not be more adsorbed onto WH-425-Cu. In the pH range of 4.0–6.0, the formation of more adsorbable HAsO_4^{2-} species increased with the increase of pH value, leading to the increase of As (V) removal. However, when pH value was above 8.0, even though the more adsorbable HAsO_4^{2-} ions were predominant species, the competition from OH^- increased significantly, resulting in the reduction of As (V) uptake by WH-425-Cu. Since the pH value for the most natural waters falls in the range 6.0–8.0 [40], there is no need to adjust source water pH to achieve the maximum sorption capacity of WH-425-Cu for As (V).

In addition, it could be found from Figs. 1 and 2 that the temperature had a negative effect on the removal percentage of As (V) at the same pH value. The removal percentage (90%) of As (V) at 298 K was lower than that (94%) at 288 K when pH value of As (V) solution was 8.0. This result was attributed to the formation of inner-sphere complexations between As (V) and the fixed copper (V) of polymer, which was coupled with the negative enthalpy change [41].

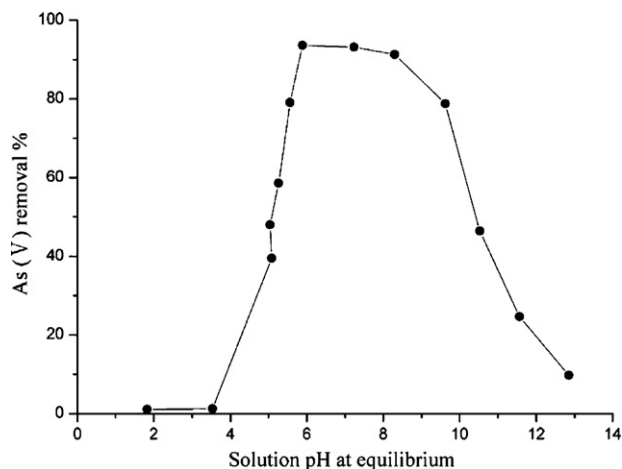


Fig. 2. Effect of solution pH on As (V) removal by WH-425-Cu at 298 K (0.1 g WH-425-Cu was added into 100 mL solution containing $150 \mu\text{g L}^{-1}$ As (V)).

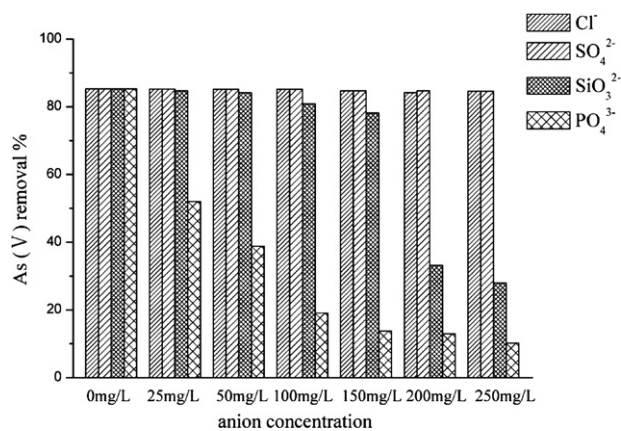


Fig. 3. Effect of coexisting anions on As (V) removal at fixed initial As (V) concentration (0.1 g WH-425-Cu was added into 100 mL solution containing $250 \mu\text{g L}^{-1}$ As (V) at 298 K).

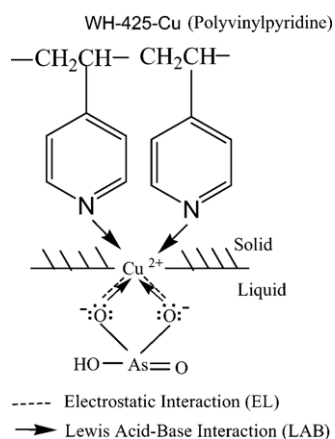
So the lower temperature was more favorable for As (V) removal by WH-425-Cu.

3.3. Effect of coexisting ions on adsorption

Considering some anions such as chloride, sulfate, silicate and phosphate commonly exist in groundwater [42–44], their effects on the sorption of As (V) by WH-425-Cu were studied. As shown in Fig. 3, chloride and sulfate ions displayed little interference in the As (V) removal efficiency in the range of concentration investigated. According to the concept of ligand exchange, the adsorbent WH-425-Cu would selectively adsorb strong ligand ions [33].

The polymeric ligand exchanger (WH-425-Cu) in this study was prepared by loading Cu^{2+} onto poly (4-vinylpyridine) resin. Since Cu^{2+} is firmly immobilized on the polymer surface by covalently bonding with the N donor atoms, the positive charges of loaded Cu^{2+} ions remain available to interact with anions in the aqueous phase. Under the experimental conditions, HAsO_4^{2-} was the predominant As (V) species (see Section 3.2 for details). Therefore, the remaining two coordination numbers and the two residual positive charges of the polymer-phase copper (V) ion were satisfied simultaneously by the divalent arsenate anion (HAsO_4^{2-}). That is to say, the sorption of arsenate (the target adsorbate) onto WH-425-Cu involved electrostatic interaction due to fixed positive charges of the polymer phase, accompanying Lewis acid–base interaction with immobilized copper ions (electron acceptors) [24,33]. Because HAsO_4^{2-} was much stronger ligand than Cl^- and SO_4^{2-} , the improved As (V) selectivity of WH-425-Cu was attributed to much stronger Lewis acid–base interactions between As (V) and the immobilized Cu^{2+} . Scheme 2 provided a presentation of the functional group of toward HAsO_4^{2-} .

However, as to the two co-existing anions, phosphate and silicate, the case was quite different. For anion phosphate, even the low concentration of 25 mg L^{-1} could lead to adverse effect on As (V) removal, and in the case of silicate, on the other hand, its high concentration ($\geq 150 \text{ mg L}^{-1}$) would lay a moderate influence on As (V) removal efficiency. Since concentration of both phosphate and silicate in groundwater is normally low [45,46], their effect on As (V) sorption could be neglected. This result was in agreement with a number of other results [46–48]. This interfering effect of phosphate and silicate on the As (V) removal could be explained by the similar structure to that of arsenate. In addition, phosphate and silicate were much stronger ligand than Cl^- and SO_4^{2-} . A ligand exchange would selectively take up those ligands that had stronger affinity to itself even in the presence of competing co-existing ions [33,49].



Scheme 2. Illustration of adsorbing HAsO_4^{2-} onto WH-425-Cu from aqueous solution.

For comparison, a commercial strong base anion exchanger (D201) with quaternary ammonium functional groups was tested as reference in this study, which has been demonstrated for effective removal of arsenate from aqueous media through ion exchange [50–52]. Here, sulfate was introduced as a representative foreign ion, and the results (in Fig. 4) indicated that high removal efficiency of As (V) was easily achieved by D201 when sulfate was absent in solution. However, when sulfate was added in the solution, the removal efficiency was markedly decreased and even approached to zero in the presence of sulfate at concentration of 150 mg L^{-1} . Such different sorption performance between D201 and WH-425-Cu was attributed to their different sorption mechanisms for As (V). For As (V) sorption by D201, only electrostatic interaction (ion-pair formation) was formed between the positively charged quaternary ammonium group (R_4N^+) and the anion (HAsO_4^{2-}), because R_4N^+ did not have any electron-acceptor characteristic.

3.4. Effect of humic acid

Humic acid (HA) consists of hydrophobic parts and hydrophilic functional groups such as phenolic, carboxylic, ester and quinone in aqueous system, the majority of which are negatively charged at neutral and alkaline pH [37]. In order to find out the effect of HA on adsorption arsenate, As (V) concentration was set at $250 \mu\text{g L}^{-1}$. When the concentration of HA ranged from 3.7 to 14.9 mg L^{-1} , the

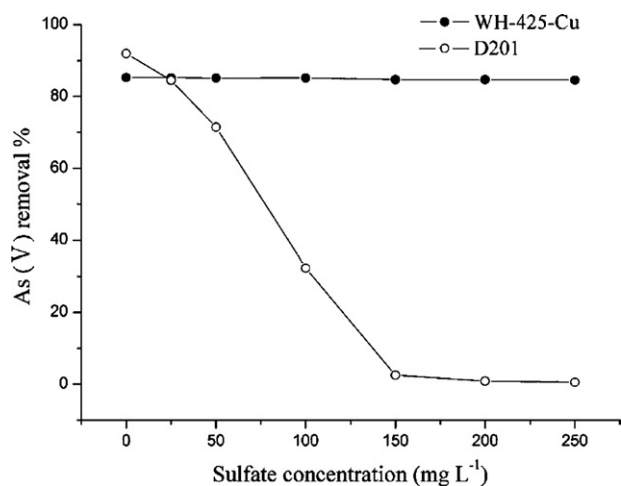


Fig. 4. Effect of sulfate anion on As (V) removal by WH-425-Cu and D201 at 298 K (0.1 g WH-425-Cu or D201 beads were added into 100 mL solution containing $250 \mu\text{g L}^{-1}$ As (V)).

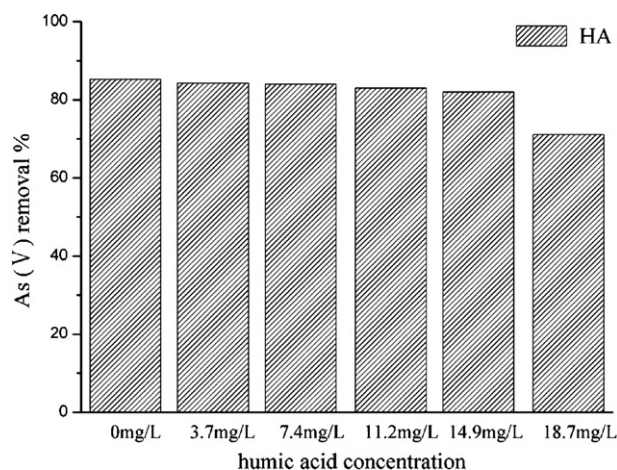


Fig. 5. Effect of humic acid on As (V) removal by WH-425-Cu at fixed initial As (V) concentration ($250 \mu\text{g L}^{-1}$) at 298 K.

As (V) removal efficiency was slightly affected as shown in Fig. 5. As (V) sorption was only decreased by about 16% even at high concentration of HA (18.7 mg L^{-1}). The decrease in As (V) sorption could be owing to the large HA molecules, which occupied a large fraction of sorption sites on WH-425-Cu. This phenomenon caused steric congestion on the Cu^{2+} sites and formation of physical barrier to mass transfer of arsenate to the Cu^{2+} sites [37]. In addition, the metal-bridge combination occurring between HA and the arsenate compound might inhibit As (V) removal at the high concentration (18.7 mg L^{-1}) [53]. Competition between arsenate anions and electronegative humate was also likely to contribute the reduction to the removal efficiency of As (V) [54].

3.5. Column sorption run

To further examine the performance of WH-425-Cu, the column sorption (packed with 5 mL wet resin) runs were conducted with a simulate groundwater as the influent. The simulate water consists of $400 \mu\text{g L}^{-1}$ As (V) and competing $80 \text{ mg L}^{-1} \text{SO}_4^{2-}$, $60 \text{ mg L}^{-1} \text{Cl}^-$, $25 \text{ mg L}^{-1} \text{SiO}_3^{2-}$, $1 \text{ mg L}^{-1} \text{PO}_4^{3-}$ and 2 mg L^{-1} humic acid at pH 8.0. A constant flowrate of 3 BV/h (BV represented the total volume of resin bed) was maintained. The breakthrough point was set as $10 \mu\text{g L}^{-1}$ (the horizontal dashed line in Fig. 6), which is the maximum contaminant level for arsenic in drinking water promulgated by U.S. Environmental Protection Agency (U.S. EPA) and World Health Organization (WHO). Based on the As USEPA MCL,

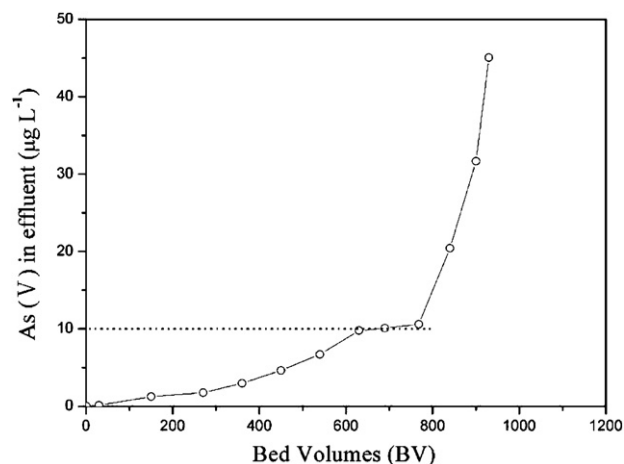


Fig. 6. Breakthrough curves of As (V) onto WH-425-Cu at 298 K.

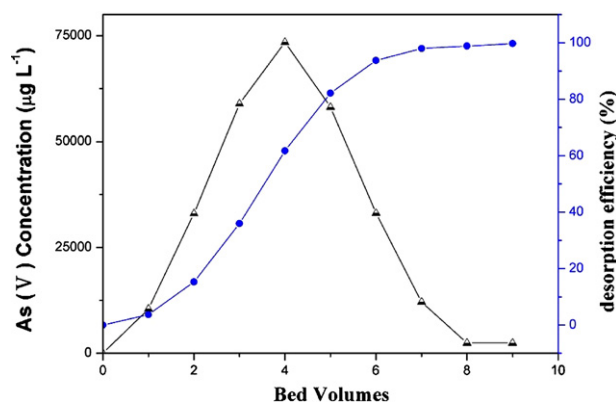


Fig. 7. Column dynamic desorption and desorption efficiency curve of As (V) on WH-425-Cu using 6% NaCl at pH=9.0 as the regeneration reagent by continuous flow column method at a rate of 1 BV h⁻¹.

about 700 bed volumes of water could be treated in each operation cycle before the breakthrough occurred.

Effectively regenerating the As (V) saturated WH-425-Cu to reuse the ligand exchanger was quite important for field applications. Fig. 7 showed one of the As (V) desorption profiles during regeneration with 6% NaCl at 9.0 of pH value. The As (V) loaded on WH-425-Cu could be completely rinsed within seven bed volumes of regenerant.

4. Conclusions

In this study, the copper-loaded PLE, was prepared by binding Cu (II) onto synthesized WH-425 and its performance for arsenate removal from aqueous solution was investigated by batch adsorption experiments. The PLE exhibited unusually high selectivity for As (V) even in the presence of high concentrations of chloride and sulfate except for silicate (at concentration value > 200 mg L⁻¹) and phosphate (at concentration value > 25 mg L⁻¹), and As (V) sorption was only decreased by about 16% even at high concentration of humic acid (18.7 mg L⁻¹). The exhausted sorbent was amenable to be regenerated by using NaCl solution. Column sorption and regeneration tests suggested that sorption onto WH-425-Cu would be a potential alternative for selective removal As (V) from water.

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