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ORIGINAL ARTICLE

Removal of vanadium from vanadium-containing wastewater by amino modified municipal sludge derived ceramic

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Abstract In this work, an amino modified porous ceramic derived from municipal sludge was synthesized for the adsorption of vanadium (V) from wastewater. In this approach, a maximum vanadium (V) removal of 99.8% can be achieved by using 800 g adsorbent with a height of 800 mm when the initial concentration of vanadium (V) was 50 mg/L, pH was 4, flow rate was 5 L/h.

1. Introduction

Vanadium is one of the rare metals, and it is also a kind of strategic source. Right now, vanadium is mainly extracted from stone coal and vanadium slag by adding sodium chloride and calcium oxide. Likewise, elements such as chromium, arsenic, mercury, lead, and cadmium, were associated with the extraction process. Without discharging treatment, these toxic substances can enter wastewater easily, resulting in an acute threat to the watery environment (Zhang et al., 2011; Zhu et al., 2010). Meantime, the vanadium exists as V (V), which is the most hazardous product, and if lack of control, it can cause water pollution due to its high solubility and toxicity. Not only respiratory, metabolic system, digestive system and the nervous system but also skin, heart and kidney will be affected by vanadium through the food chain. Therefore, it is urgent to seek harmless and resourceful process to treat vanadium-containing wastewater.

Traditional methods to vanadium-containing wastewater can be divided into four categories: physical, chemical, physic–chemical and biological methods. However, the removal efficiency of these methods is limited due to the high salinity and low biodegradability of (V-containing) wastewater. In addition, traditional methods are difficult to meet the requirements of harmless and resourceful treatment (Minelli et al., 2000; Zhang et al., 2012, 2009).

Novel adsorption and ion exchange technique have become the focus in the field of harmless and resourceful treatment for heavy metals due to their recycle ability, high selectivity, large absorption capacity, low cost, high efficiency and

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environmental-friendliness. Many works on vanadium removal have been reported on the adsorption (Keränen et al., 2015; Kaczala et al., 2009; Sharififard and Soleimani, 2015; Anirudhan et al., 2009; Doğan and Aydın, 2014; Zhang et al., 2014; Sirviö et al., 2015; Bhatnagar et al., 2008; Naeem et al., 2007; Xie et al., 2013) and ion exchange (Hu et al., 2009; Fan et al., 2013) processes and materials.

In this study, ceramic derived from municipal sludge was selected as a support, and it was modified by amino to remove vanadium. Ceramic derived from municipal sludge can achieve resource utilization and there is a lot of research on ceramic preparation. Basegio et al. (2002) studied the environmental and technical aspects of the utilization of tannery sludge as a raw material for clay products. Qin et al. (2012) studied the preparation and properties of sewage sludge ceramic pellets, showing that it is feasible to prepare sewage sludge ceramic pellets (SSCP) as filter material by sintering sludge with added coal fly ash and farmland clay. Nan et al. (2010)developed a new medium, granular ceramic for fluoride removal from water, results suggested that the granular ceramic was advantageous as an adsorbent due to its granular structure, high surface area, and low cost. Amino modification was demonstrated to be an effective way to adsorb a wide range of heavy metals. Ulla et al. (2005) studied the adsorption of Pb and Cd by amine-modified zeolite, only partial exchange of cysteamine and propylamine into the zeolite structure was observed and isomerization of cysteamine may have led to higher sorption of this compound onto zeolite.

The aim of this study was to synthesize an amino modified ceramic for extraction and recycle of vanadium. The mechanism of adsorption of vanadium and other heavy metals on the amino modified ceramic was elaborated and the adsorption parameters, such as pH, initial concentration and flow rate were optimized to enhance the removal efficiency.

2. Experimental

2.1. Material synthesis

2.1.1. Preparation of ceramic

Deeply dehydration urban sewage sludge was crushed and mixed with kaolin clay, coal ash and water glass in addition of 38% ± 2% moisture by a mixer. The mixture was squeezed into columnar blank of φ3 mm by granulator, dried for 4 h at 105 °C continuously/constantly. Then, it was cut off to short columnar dry blank. Dry blank was then sintered in an electric muffle in air atmosphere, and charged at temperature of 500 °C by 10 °C/min, then maintained at this temperature for 40 min, and charged at temperatures of 1000–1200 °C by 10 °C/min, then maintained at this temperature for 30 min and left them to cool naturally to get ceramic (with a density of 1.23 g/cm^3).

2.1.2. Functionalization of ceramic with amino modification

Ceramic was modified by silane coupling agent-γ-aminopropyl triethylsilane: $H_2NCH_2CH_2CH_2Si(OC_2H_5)_3$ (WS-50, GR, Hubei WD silicone Co., Ltd) to strengthen its adsorption performance.

The modification step was as follows: a silane coupling agent was added to the solvent (75% ethanol) with a final concentration of 2%.Subsequently, 20 g ceramic was mixed with 200 mL silane coupling agent solution, and the mixture was added into a three-necked flask, adding glacial acetic acid to adjust the pH to 3–5. Refluxed sample was collected in a water bath at 80 °C. Afterward, the sample was filtered and elution by ethanol for three times. Amino modified ceramic was obtained after drying at 80 °C for 2 h.

2.1.3. Characterization of the material

Surface and section morphologies were determined by SEM (Helios Nanolab 600i, FEI Co., Ltd). Phase identification of ceramic and modified ceramic was determined by XRD (IMENS D500, Bruker Co., Switzerland). Amino group was characterized by Fourier Infrared Spectrometer (Nicolet 6700, Thermo Electron Scientific Instruments, U.S.A).

2.2. Procedures

2.2.1. Experimental subjects

Vanadium-containing wastewater was taken from an enterprise in Huaihua, Hunan province. The pH of the wastewater was detected to be 2.0. The main components of the wastewater are shown in Table 1.

2.2.2. Sorption and desorption experiments

In adsorption and desorption experiments, initial pH of the wastewater was adjusted to a design value with 5% lye and 0.1 M H_2SO_4. Municipal sludge derived ceramic, which was modified by amino, was used as adsorbent. $NaHSO_3$ was used as reducing agent and 30% H_2O_2 was used as oxidizing agent.

At first, pH values were adjusted to 1.8 after we collected 50 L wastewater and the wastewater was pre-processed by selective reduction and oxidation reactions. After selective reduction, V(V) and Cr(VI) were reduced to V(IV) and Cr (III) by $NaHSO_3$ and after oxidation, V(IV) was oxidized to V(V) by H_2O_2. To avoid the interference of remaining H_2O_2, the treated water was heated and stirred to remove the remaining H_2O_2.

Dynamic experiments of resin adsorption were conducted. pH values were adjusted to 4.5 after preparation. Amino modified ceramic was filled into an adsorption column with a width of 5 cm and height of 100 cm. The schematic diagram of experimental set-up is illustrated in Fig. 1. The packing height was 80 cm and flow rate was controlled at 2–10 L/h. 10–15 mL of samples was collected per 1000 mL effluent by measuring cylinder, and measurements of heavy metals were conducted.

The treatments mentioned above were performed at room temperature and under atmospheric pressure.

3. Results and discussion

3.1. Properties of the material

Fig. 2 shows the surface (a) and section (b) morphology of the sludge derived ceramic. As can be seen, the surface of ceramic was rough with high porosity, which suggests that the ceramic would possess a good adsorption capacity and exchange capacity since the pores are nano-sized.

To demonstrate the existence of amino group on ceramic after modification, Fourier infrared absorptions of the derived and modified ceramic were compared and results are shown in

Table 1 Vanadium-containing acid wastewater (mg/L).

V	Cr	Ni	Cd	Mg	Zn	NH_4^+	Na^+	SO_4^{2-}
30–100	30–40	30–35	25–30	30–50	20–30	3000–5000	3000–8000	10,000–12,000

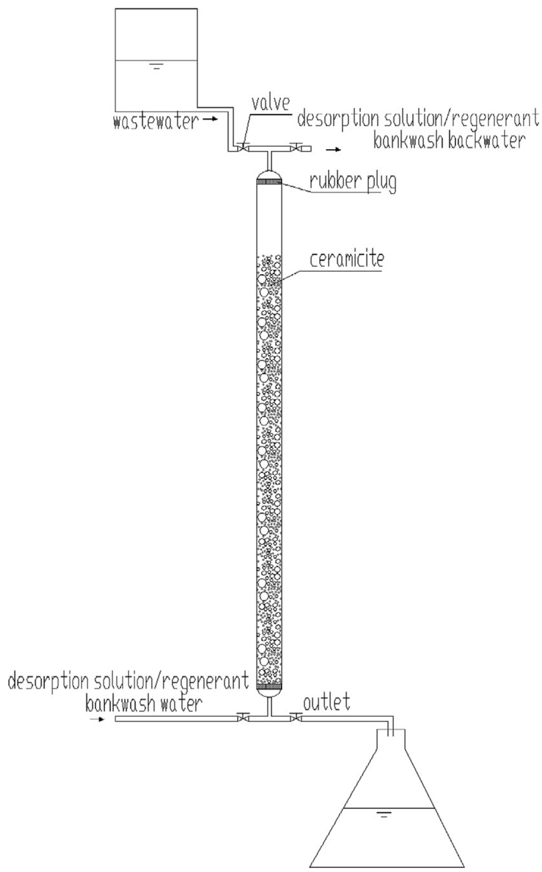

Figure 1 Schematic diagram of dynamic equipment of resin adsorption.

Fig. 3. It can be observed that $–NH_2$ had been successfully attached/bonded/grafted to the sludge derived porous ceramic matrix material. There are two peaks, 1570 cm^{-1} and

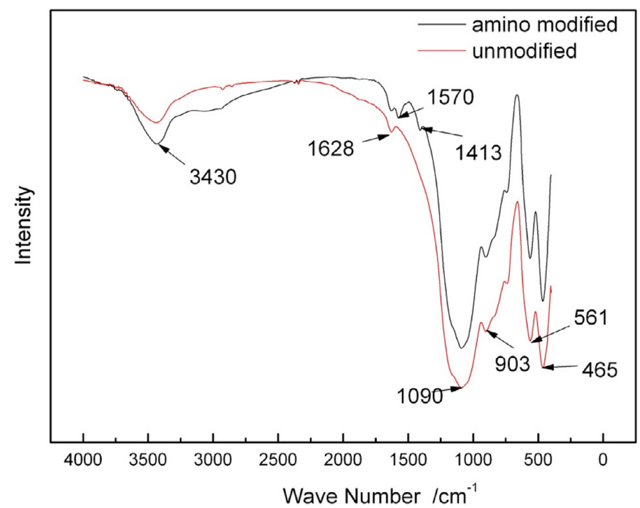

Figure 3 Fourier infrared absorption of before and after modification by amino modified.

1413 cm^{-1}, after WD-50 modified from the infrared absorption spectrum. The peak at 1570 cm^{-1} was attributed to the distortion shaking of $–NH_2$ and the peak at 1413 cm^{-1} was attributed to the distortion shaking of $–CH_2$. The graft was $H_2N–CH_2CH_2CH_2–Si–(OCH_2CH_3)_3$ and the group was $H_2N–CH_2CH_2CH_2–Si–O–R$, in which R represents ceramic.

3.2. Dynamic adsorption by amino modified ceramic

3.2.1. Effect of pH

The effect of pH on the adsorption of vanadium by amino modified ceramic is shown in Fig. 4. In each set of experiment, the influent concentration of V was 50 mg/L and the dosage of ceramic was 800 g with the flow rate of 5 L/h. Initial pH values were adjusted to 3.0, 4.0, 4.5, 5.0, 6.0, 7.0, respectively. The

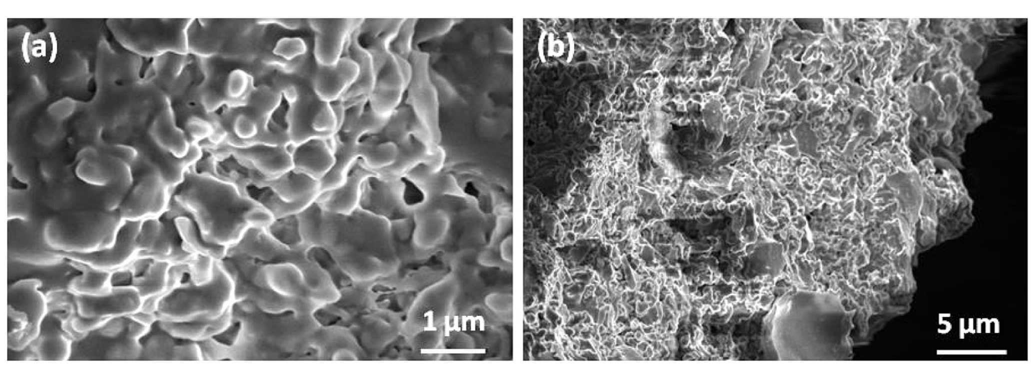

Figure 2 SEM images of the surface (a) and section (b) of the municipal sludge derived ceramic.

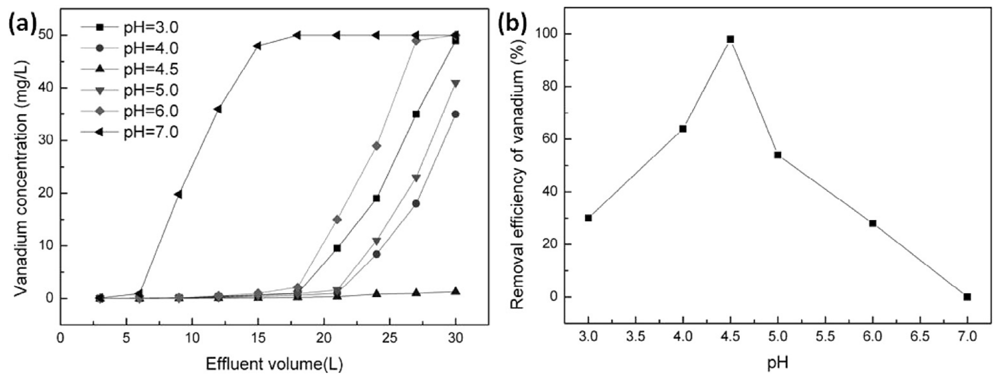

Figure 4 Effect of pH. (a) The effluent V concentration at different initial pH values. (b) Removal efficiency of V at different initial pH values.

amount of influent volume was 40 times (about 30 L) than ceramic. The effluent concentration was detected per 5 L waters and the end point of the experiment was from V leakage (effluent concentrations > 1 mg/L) to total leakage (close to background).

The effluent concentration at different initial pH values and same flow rate and influent concentration is shown in Fig. 4(a). The leakage of vanadium occurred when effluent volume was 8 L at pH 3 and effluent concentration increased to total leakage on the undergoing experiments, illustrating the effect was actually modest. The effect increased with the increase in pH value and the leakage point was 22 L and 28 L when pH 4.0 and 4.5, respectively. However, the absorption effect decreased when effluent volume was 18 L at pH 5.0. The absorption effect obviously reduced and leakage point was about 6 L when pH 6.0 and 7.0. Thus, pH 4.5 was chosen as the conducting pH because of the highest efficiency.

Besides, from Fig. 4(b), we can find that the highest adsorption rate was achieved at pH 4.5. Vanadium existed in the form of pentavalent cations (VO^{2+}) when pH is lower than 4.5, especially pH $\leqslant$ 3.0.

The amino modified ceramic has anion multi-amidocyanogen functional groups, which are unfavorable for adsorption reaction. Vanadium changes to pentavalent anions (VO_3^-) when 3.0 < pH < 4.5, which is the most conductive to the adsorption of vanadium by amino modified ceramic. Adsorption efficiency decreased with the increase in pH and OH^- because the increasing OH^- suffered competitive adsorption with vanadium anions. Thus pH 4.5 was chosen as the conducting pH for further experiment.

3.2.2. Effect of flow rate

Adsorption of V at different flow rates was conducted. Flow rates were adjusted to 3, 4, 5, 6, 7 L/h respectively, and the results are compared in Fig. 5. Based on the experimental results above, initial pH values were adjusted to 4.5, with influent concentration of V 50 mg/L and 800 g ceramic (height of adsorbent: 800 mm). The highest flow rate of leakage was measured by analyzing the concentration of vanadium per 2 L samples of effluent.

The optimal flow rate was 5 L/h when other things being equal, as shown in Fig. 5.The initial stage of adsorption of vanadium was ideal at different flow rates, but the period of initial stage became shorter as the flow rate increased. The leakage occurred after 5.5 h when the flow rate was 5 L/h, so the highest flow rate of leakage at last was 5 L/h. The adsorption process can be divided into two phases: pre-adsorption and post-adsorption. Pre-adsorption showed a complete adsorption completely, with the feature that the removal of the adsorption flow rate is approximately linear decreasing relationship. Post-adsorption will approach the adsorption equilibrium and the removal rate will drop significantly as the adsorption rate increasing. As a result, the leakage rate accelerates. Thus 5 L/h was chosen as the conducting flow rate for further experiments.

3.2.3. Effect of initial concentration

To determine the effect of initial concentration on the adsorption, the vanadium solution with initial concentrations of 30 mg/L, 50 mg/L, 70 mg/L, 90 mg/L were adjusted at pH 4.5 and flow rate 5 L/h. The concentration of vanadium was analyzed per 0.5 h and results were as shown in the Fig. 6(a).

It was demonstrated that the initial concentration directly affects the effluent concentration at the same pH value and flow rate. The effluent concentration rises as the increase in influent concentration of vanadium and accelerated the leakage rate of adsorption. So the optimal concentration of vanadium was 50 mg/L with 800 g adsorbent and 800 mm high. The increase in the equilibrium adsorption capacity is not so obvious due to the limited active sites on the resin surface. Thus, the adsorption rate will decrease with reducing the absorption rate when the initial concentration reaches a certain value.

3.2.4. Mechanism for the adsorption of vanadium

The ceramic possesses high specific surface areas (> 1400 m^2/g) and microstructures. Amine-terminated groups were introduced (–RNHCl) by grafting, resulting reusable, efficient and easily manipulated microstructure absorbing materials that can absorb metal anion in gas and liquid.

Seen from Fig. 7, (Yang, 2010) in weak acid condition, vanadium existed in the form of anions (VO_3^-, $HV_{10}O_{28}^{4-}$, $V_{10}O_{28}^{6-}$) after selective oxidation in low concentration solution, while Cr^{3+}, Ni^{2+}, Fe^{3+}, Al^{3+}, Cd^{2+}, Mg^{2+}, Zn^{2+} and NH_4^+ existed in free or binding forms, all of which enable selective vanadium adsorption and separation by amine-terminated anion special properties.

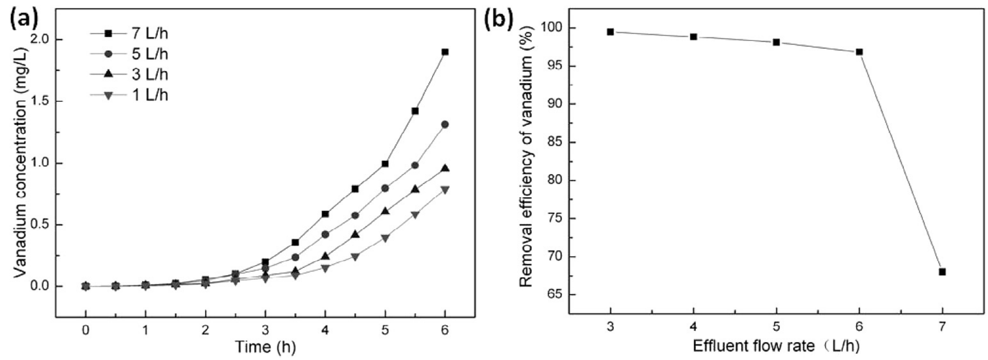

Figure 5 Effect of flow rate. (a) Absorption of V over time at different initial flow rate. (b) Removal efficiency of V at different initial flow rate.

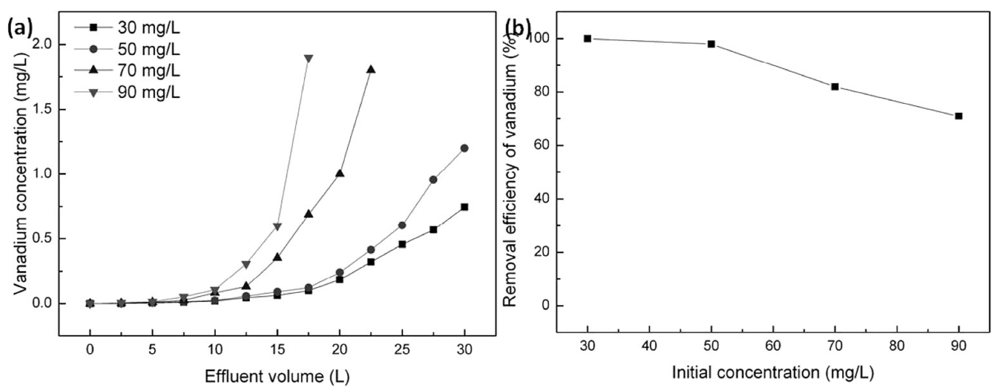

Figure 6 Effect of initial concentration. (a) Absorption of V over time at different initial concentration. (b) Removal efficiency of V at different initial concentration.

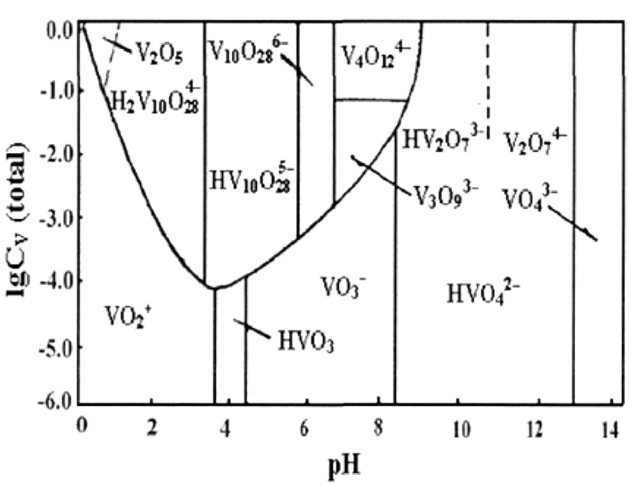

Figure 7 The form of vanadium in aqueous phase.(Yang, 2010)

The mechanism of selective adsorption and separation of vanadium can be described in three steps as following: adsorption, desorption and regeneration.

$$\text{Adsorption}: VO_3^- + RNHCl \rightarrow RNHVO_3 + Cl^-$$

$$\text{Desorption}: RNHVO_3 + OH^- \rightarrow VO_3^- + RNHOH$$

$$\text{Regeneration}: RNHOH + HCl \rightarrow RNHCl + H_2O$$

4. Conclusion

A type of ceramic, derived from municipal, possessing high specific surface areas (> 1400 m^2/g) was adopted to treat vanadium containing wastewater. An amine-terminated groups were introduced (–RNHCl) by grafting to synthesize reusable, efficient and easily manipulated microstructure absorbing materials that can absorb metal anion in gas and liquid.

The initial pH, initial flow rate and flow rate are the main influence of adsorption performance on amino modified ceramic. Maximum vanadium (V) removal of 99.8% can be achieved when the initial concentration of vanadium (V) was 50 mg/L at pH 4 with 800 g adsorbent (height of adsorbent: 800 mm), and the optimal flow rate was 5 L/h.

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