Removal of V(V) from aqueous Cr(VI)-bearing solution using anion exchange resin: Equilibrium and kinetics in batch studies

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Abstract

Vanadium (V) and chromium (Cr) co-exists in the whole process of V extraction from the vanadium titano-magnetite ore in China. It remains a challenge to remove trace V(V) from Cr(VI) in a simple way. Based on facile pretreatment of transforming Cr(VI) selectively, a novel method to remove V(V) from Cr(VI) by anion exchange resin Dex-V has been established. The influence of operation parameters including pH, contact time and temperature on adsorption ratio has been investigated. The Langmuir model and Henry model were successfully applied to describe the adsorption behavior of V by the Dex-V resin. It is shown that V is adsorbed chemically in monolayer and the Dex-V resin presents a homogeneous nature. Kinetics of V adsorption was analyzed with the pseudo-second order model, the Richenberg model and the Weber–Morris model. Results show that the rate of V adsorption is controlled by film diffusion in initial 70 min and the intra-particle diffusion contributes to the rate-controlling after 70 min. The proposed method was applied to remove V from real waste water and the removal ratio as high as 96% was obtained, with Cr recovery of 95%, which validates the effectiveness and efficiency of the novel method. This work has thus provided new insights into separation and recovery of analogue metals in aqueous.

Keywords

Vanadium; Chromium; Anion exchange resin; Adsorption; Separation

1. Introduction

Vanadium (V) is an important nonferrous metal element which is widely applied in metallurgical, material and chemical industries. About 88% of vanadium is extracted from vanadium titano-magnetite ore (Moskalyk et al., 2003; Tavakoli and Dreisinger, 2014a). During processing of vanadium titano-magnetite ore in the steelmaking industry, vanadium is reduced into hot metal and then oxidized and enriched into solid slag which is usually called *vanadium slag* (Fang et al., 2015). To extract V, the vanadium slag is roasted oxidatively with sodium or calcium salts and the roasted slag is leached with water, acidic or alkaline solution to obtain the V-containing liquor (Li et al., 2012a; Li et al., 2012b; Zhang et al., 2011). In the liquor, V is pentavalent (denoted as V(V)) and exists in form of vanadate ions, which is recovered through precipitation of ammonium polyvanadate (APV), leading to the production of APV-precipitated waste water.

The APV-precipitated waste water is highly toxic not only due to the toxicity of residual V(V) but also due to the existence of toxic Cr(VI) in high concentration. Cr co-exists with V in the vanadium titano-magnetite ore although usually in much lower content (Diao et al., 2009; Liu et al., 2013a). During extraction process of V, Cr transforms in the same route as V due to their similar chemical characters, which leads to the existence of chromate ions (Cr(VI)) in the liquor (Fang et al., 2012; Zhang et al., 2012). Cr(VI) is maintained in the liquor when V(V) is recovered by ammonium precipitation, resulting in the high concentration of Cr(VI) in the APV-precipitated waste water. The concentration of Cr(VI) in the waste water can be as high as 100 g/L due to accumulation caused by cyclic usage of liquor. The waste water is thus a severe threaten to the environment and must be detoxicated, by Cr(VI) and residual V(V) before emission. In addition, in view of resource utilization, Cr in such high concentration should be recovered. However,

valuable Cr products can not be obtained directly from the waste water due to impurity caused by the residual V(V) in waste water, which is resulted from the high similarity in chemical characters of V and Cr. Therefore, it is necessary to remove V(V) from Cr(VI) in the waste water for sake of both environmental safety and resource utilization.

There are several methods which have been introduced to separate and remove V from Cr. The method of precipitation is the most cost-efficient and easiest way to extract V from solution (**Chen et al., 2007**) but it is not suitable for the removal of V in trace amount as in the waste water. The method of capillary electrophoresis has been introduced to separate V and Cr ions (**Yeh et al., 2004**), but its column capacity is too low to remove V in quantity from Cr. The method of solvent extraction has successfully extracted V selectively from Cr-containing solution and even applied in some plant in China (**Ning, et al., 2013a; Ning, et al., 2013b; Ning, et al., 2014**). However, the solvent extraction method usually presents low extraction of V in trace concentration and low efficiency in concentrating V, which is not suitable to removing or recovering trace V from the waste water. The method of ion exchange resin has advantages of high extraction, separation efficiency and concentrating efficiency, which is extremely suitable to removal of trace V from the Cr-containing waste water (**Hu et al., 2009; Zeng et al., 2006; Zeng et al., 2009**). By ion exchange resin, V can be not only removed from Cr but also recovered from the waste water due to the high adsorption capacity of resins. Macroporous weak base resin D314 was used to separate V and Cr and recover them respectively in two resin columns by double-adsorption (**Fan et al, 2013**). However, the double-adsorption increased reagent cost and operation time, which might limit its practical application. Therefore, it remains a big challenge to remove V from Cr in a simple way.

In this work, a facile method based on anion exchange resin has been established to remove

V(V) from Cr(VI) in aqueous solution. As shown in **Schematic 1**, ingenious pretreatment has been proposed to selectively transform Cr(VI) anions into Cr(III) cations which can be separated from V(V) anions by anion exchange resin of Dex-V. The toxicity caused by Cr and V is reduced simultaneously. The adsorption condition of V(V) anions by the Dex-V resin was optimized. Equilibrium isotherm and kinetics of V(V) adsorption by Dex-V resin were investigated in details with modeling. Then the proposed method was applied to remove V from the APV-waste water. Results show that the proposed method can remove V from the waste water effectively and efficiently and is tolerant to wide concentration ranges of V and Cr, which provides new insights to separation and recovery of analogue metals in aqueous.

2. Materials and methods

2.1. Ion-exchange resin

The macroporous weak base anion exchange resin Dex-V (analogue to Amberlite IRA-94, Zhengzhou Qinshi Technology Co., Ltd., China) was used in this work. The properties of the resin Dex-V are given in **Table 1**. The resin was activated with 3% NaOH and transformed with 3% HCl.

2.2. Chemicals

Stock solution of V(V) in concentration of 10 g/L was prepared by dissolving 17.843 g V_2O_5 in 400 mL 50wt% sulfuric acid and adding H_2O to total volume of 1 L in volumetric flask. Adsorption experiments were conducted by diluting the stock solution of V(V) to required concentrations. Solution pH was adjusted with 1 M H_2SO_4 or 1 M NaOH. All reagents used are of analytical grade and deionized water is produced by AQUELIX5 (Millipore Corp., USA).

2.3. Pretreatment of solutions

The solution pH was adjusted to 1.6-1.9. NaHSO₃ was added into the solution in stoichiometric ratio according to concentrations of V and Cr. The mixture solution was heated in water bath at 70°C for 3 hours. The cooled solution was adjusted to pH 3.0, into which 30% H₂O₂ was added in H₂O₂/V molar ratio ≥ 8 , followed by being stirred at 30 rps for 4 h. Then the solution was heated at 100 °C until no gas bubbles escaped in order to oxidize V completely and eliminate redundant H₂O₂.

2.4. Batch experiments

For optimization of adsorption parameters, 8 g resin was added into the V solution diluted to desired concentrations at desired pH and temperatures for desired contact time. The investigated pH range is 2.0-10.0 and temperature range is 25-65°C. The contact time is investigated from 5 min to 290 min.

Adsorption equilibrium experiments was conducted by adding 8 g resin into 150 mL V solution in concentrations of 0.1-7.6 g/L at pH 3.0 and 25°C. After contacting for 250 min, the resin was separated from solution and the V concentration in the rest solution was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 4300DV, Perkin Elmer, USA).

Kinetic experiments was conducted by adding 8 g resin into 150 mL V solution in concentrations of 0.1-1.4 g/L at pH 3.0 at temperatures of 25-65°C. Aliquot of 1 mL was taken out from the contacting solution at different time intervals, in which the V concentration was determined by ICP-AES (Optima 4300DV, Perkin Elmer, USA).

2.5. Adsorption isotherm models

The adsorption capacity at equilibrium q_e (mg·g⁻¹) is defined as follows:

$$q_e = (C_0 - C_e)v/w \quad (1)$$

where C_0 (mg·L⁻¹) is the initial concentration of V; C_e (mg·L⁻¹) is the V concentration in solution at

equilibrium; v (mL) is the volume of solution and w (mg) is the weight of resin used.

The Langmuir model is described in the linear form as

$$C_e / q_e = C_e / q_m + 1 / (q_m \cdot K_L) \quad (2)$$

where q_m (mg/g) is the maximal adsorption capacity; K_L (L/g) is the Langmuir constant related to the affinity between adsorbates and active adsorption sites. The dimensionless separation factor, R_L , is an indicator of adsorption type, which is defined as

$$R_L = 1 / (1 + K_L C_0) \quad (3)$$

The Freundlich model is linearized as

$$\log q_e = \log K_F + (\log C_e) / n \quad (4)$$

where K_F is the binding constant which reflects the affinity of adsorbates towards adsorption sites; n is the Freundlich constant which indicates the favorability and type of the adsorption.

The Henry model is represented as

$$q_e = K_H C_e \quad (5)$$

where K_H is the binding constant indicating the affinity between adsorbates and adsorption sites.

2.6. Adsorption kinetics models

The adsorption kinetic behavior of V was analyzed with the pseudo-first model, the pseudo-second model, the Richenberg model and the Weber–Morris kinetic model.

The linear equation of pseudo-first model is expressed as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_t (mg/g) is the adsorption capacity at the time of t ; k_1 is the rate constant of the first-order adsorption (min^{-1}).

The linear equation of pseudo-second model is represented as

$$t / q_t = 1 / (k_2 q_e^2) + t / q_e \quad (7)$$

where k_2 is the rate constant of the second-order adsorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$).

The Richenberg model was used to explore the adsorption rate of V is controlled by liquid film diffusion or intra-particle diffusion (**Riaz, 2007**).

$$\text{For film diffusion:} \quad Rt = -\ln(1 - F) \quad (8)$$

$$\text{For intra-particle diffusion:} \quad Bt = -\ln(1 - F) - 0.4977 \quad (9)$$

where $F = q_t / q_e$; R is the rate constant for film diffusion; B is the rate constant for intra-particle diffusion.

The Weber–Morris kinetic model was utilized to investigate the intra-particle diffusion. The linear equation is as follows:

$$q_t = K_d t^{1/2} + c \quad (10)$$

where K_d ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5}$) is the intra-particle diffusion constant; c ($\text{mg} \cdot \text{g}^{-1}$) is the intercept related to the thickness of the boundary layer.

Together with correlation coefficient R^2 , the normalized standard deviation $\Delta q(\%)$ was also used to evaluate the validity of these models (**Hameed et al., 2008**).

$$\Delta q(\%) = 100 \times \sqrt{\sum \frac{((q_t^{\text{exp}} - q_t^{\text{cal}}) / q_t^{\text{exp}})^2}{n-1}} \quad (11)$$

where n is the number of data points.

2.7 Removal of V from waste water

The APV-precipitated waste water is obtained from Pan-steel Corp. Ltd. in China, which contains 24-333 mg/L V(V), 2-100 g/L Cr(VI), 20-500 mg/L Si(IV) and 20-100 g/L Na_2SO_4 .

$\text{Al}_2(\text{SO}_4)_3$ was added into waste water in molar ratio of 1:1 (Si/Al) at pH 9.0 to inhibit silicates interference. After pH adjustment to 1.7, 1.9 g/L NaHSO_3 was added into the solution at 70 °C. Then 30wt% H_2O_2 was added in molar ratio of 10 ($\text{H}_2\text{O}_2/\text{V}$) at pH 3.5. The redundant H_2O_2 was eliminated by exposure to sunshine for 3 h, followed by heating in water bath at 100 °C for 1.5h. Then 3 L pretreated waste water was mixed with 2.3 g resin. The solution separated from loaded resin was added with 1 M NaOH to precipitate $\text{Cr}(\text{OH})_3$ which is calcinated to obtain final product of Cr_2O_3 . Saturatedly loaded resin was eluted with 2% NaOH to recover V in final form of V_2O_5 . Purity of products is determined by ICP-AES (Optima 4300DV, Perkin Elmer, USA).

3. Results and discussion

3.1. Fundamental of V removal from Cr

In aqueous solution with pH 3 and above, both vanadate ions ($\text{V}(\text{V})$) and chromate ions ($\text{Cr}(\text{VI})$) are anions and they can adsorb onto anion exchange resins simultaneously, which requires intensive efforts to find a strategy to elute them in chromatographic way. In order to establish a method in the simple ion exchange way to remove vanadate ions from chromate ions, it is essential to focus on the difference between these ions. Although vanadium and chromium are both multivalent elements, vanadium possesses more valent states than chromium and thus more complexity in redox chemistries. Based on this consideration, strategic reduction and oxidation can give birth to differentiable forms of V and Cr in aqueous solution.

Vanadate ions ($\text{V}(\text{V})$) and chromate ions ($\text{Cr}(\text{VI})$) are chemically reduced by NaHSO_3 at pH 1.7 as shown in **Eq. 12 - Eq. 14**. Vanadate ions ($\text{V}(\text{V})$) in each existing form will transform to vanadyl ions VO_2^+ at pH lower than 2.0 (**Baes et al, 1976**). After reduction, the resulted VO_2^+ ions

are selectively oxidized by H_2O_2 to $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ anions at pH 3.5 (**Eq. 15**). Meanwhile, the resulted Cr^{3+} ions can not be oxidized by H_2O_2 at pH 3.5 and thus maintain as cations in the solution. The selective oxidation of VO^{2+} ions other than Cr^{3+} ions is due to that H_2O_2 presents relatively low oxidation ability in acidic condition and can only oxidize stronger reductants, such as VO^{2+} ions in this case, instead of weak reductant Cr^{3+} ions. The oxidation selectivity does not origin from the priority of VO^{2+} in oxidation order but origins from the low thermodynamic possibility of Cr^{3+} oxidation in this condition, according to the thermodynamics calculation based on electrode potentials (data not shown). This is proved by the results of control experiments without vanadate ions: the solution maintains the green color of Cr^{3+} ions, indicating the nonoccurrence of Cr^{3+} oxidation.

In this way, V(V) and Cr (VI) in the original solution are transformed into V anions and Cr cations, respectively, during the pretreatment of reduction - selective oxidation. Therefore, V and Cr can be separated by anion exchange resin in the simple ion exchange way, due to different charge natures, and V can be thus removed and recovered from Cr solution easily.

The solution containing $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ ions and Cr^{3+} ions, obtained after pretreatment, was loaded onto the anion exchange resin Dex-V. The loaded resin particles were taken out for SEM/EDS analysis (FEI Nova 400, Netherland). Results of EDS element mapping shows that only the vanadium element, not including the chromium element, has substituted the chlorine element in the

resin particle after adsorption (**Fig. 1**), indicating that $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ ions have been adsorbed onto the resin while Cr^{3+} ions stay in the solution. This is further confirmed by results of FT-IR characterization (Nicolet 5DXC, USA) of resin particles before and after adsorption (**Fig. 2**). FT-IR spectra of loaded resin particles shows more peaks in the range of $1118\sim 618\text{ cm}^{-1}$ than that of resin particles before adsorption. The peaks at 1118 cm^{-1} and 965 cm^{-1} are related to $\text{V}=\text{O}$ bonds. The peaks at 833 cm^{-1} and 755 cm^{-1} are ascribed to the asymmetric stretching vibration while peak at 618 cm^{-1} is ascribed to symmetric stretching vibration of $\text{V}-\text{O}-\text{V}$, respectively (**Chen et al., 2004; Harreld et al., 1998**). There is not any obvious peak corresponding to coordinate bonds between Cr^{3+} and potential functional groups in the FT-IR spectra after adsorption, indicating the absence of Cr^{3+} in the loaded resin particles. It is thus demonstrated that vanadium has been adsorbed selectively by the Dex-V resin while chromium stays in the solution.

Therefore, with the proposed pretreatment method of reduction-selective oxidation, the charge natures of V-bearing species and Cr-bearing species are differentiated and vanadium can be thus separated and removed from chromium in aqueous solution by anion exchange resin Dex-V. The Dex-V resin, a kind of macroporous anion exchange resin, has strong affinity to vanadate ions due to its special molecular structure and it is utilized in this paper to adsorb and remove vanadium from chromium solution. Since the proposed pretreatment method is a general method compatible to all anion exchange resins, other kinds of anion exchange resin may also adsorb V selectively from Cr but high affinity to vanadate ions is required. Although relatively large amount of reductant NaHSO_3 will be consumed to reduce both vanadium and chromium during the pretreatment, it is essential to reduce chromate ions and transform them into the environmentally safe form of Cr^{3+} which can be precipitated and thus extracted easily, no matter whether it is planned to remove vanadium or not.

In addition, chromates should be reduced into Cr^{3+} ions for consideration of environmental safety.

3.2. Effects of operation parameters on removal of V

According to the fundamental of V removal, V adsorption onto resin leads to removal of V from Cr. In order to remove V as much as possible, the operation parameters for V adsorption, including pH, contact time and temperature, have been optimized systematically.

pH influences the existing form of pentavalent V-bearing ions (denoted as V(V)) in the solution and thus plays a major role in the adsorption of V. As shown in **Fig. 3**, adsorption ratio reaches maximum of 98.87% at pH 3.0. It is believed that at pH 2.0 V(V) anions are prone to precipitate as $5\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ ($\text{H}_2\text{V}_{10}\text{O}_{28}^{4-} + 4\text{H}^+ + 2\text{H}_2\text{O} = 5\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O} \downarrow$) (**Livage et al, 1991**). The precipitation easily blocks free adsorption sites on resin surface and thus restricts V adsorption onto resin, resulting in adsorption ratio of V lower than that at pH 3.0. The situation of $\text{pH} < 2.0$ was not taken into consideration due to the fact that V(V) exists as VO_2^+ in this pH range (**Baes et al, 1976**). When pH increases from 3.0 to 6.0, the adsorption ratio of V decreases gradually; it decreases dramatically from pH 6.0 to pH 8.0, after which it decreases gradually as pH increases from 8.0 to 10.0. This is due to the change in mass/charge ratio (N/Z) of vanadate ions in different existing forms along with solution pH. High N/Z ratio of vanadate ions leads to high adsorption ratio of V since the adsorption lies in electrostatic attraction force between vanadate ions and active sites on resin surface. As shown in **Table 2**, the N/Z ratio of vanadate ions decreases with increasing pH values, which is in accordance with the change trend of V adsorption ratio in **Fig. 3**. The N/Z ratio decreases quickly from pH 6.0 to pH 8.0, which explains well the dramatic decrease in V adsorption ratio in the same pH range. Therefore, it is concluded that V adsorption onto the resin should be operated at pH 3.0

in order to achieve high removal ratio of V from Cr.

The effect of contact time on the adsorption of V by the anion exchange resin Dex-V was studied (**Fig. 4**). At all concentrations investigated, the adsorption ratios of V increase quickly in the initial 30 min and reach a plateau at 135 min, after which the adsorption ratio does not change significantly, nearly representing an equilibrium pattern. The appropriate contact time between resin particle and solution is thus suggested as 135 min when extracting vanadium in the concentration range of 0.2-1.4 g/L. Adsorption kinetics experiments were conducted with wider time range and detailed kinetics is discussed in Section 3.4.

Temperature influences the rate of reaction and diffusion and thus influences the rate of V adsorption onto resin. As shown in **Fig. 5**, higher temperature leads to higher rate of V adsorption and thus V adsorption reaches equilibrium more quickly at higher temperatures. The higher adsorption rate of V also leads to higher adsorption ratio of V at equilibrium, although the increase in adsorption ratio of V is not significant. For sake of reducing energy cost, the adsorption temperature for V by Dex-V resin is still recommended as 25°C.

The interference of co-existing ions in the solution has also been investigated. Since the initial waste water contains high concentration of SO_4^{2-} , Na^+ and Cr(VI) ions, attention should be paid to the interference of SO_4^{2-} anions and potential Cr^{3+} cations to adsorption and removal of V by anion exchange resin. Results show that SO_4^{2-} anions in molar concentration of 15 times higher did not influence the kinetic curve or maximal adsorption capacity of V adsorption. It is shown that Cr^{3+} cations in molar concentration of 5 times higher did not influence the V adsorption either. It is thus demonstrated that vanadate ions can be selectively adsorbed by the Dex-V resin, indicating the robustness of the proposed method of removing V from Cr in aqueous solution.

3.3. Equilibrium adsorption of V

The adsorption ratio of V is highly dependent upon the initial concentration of V and the resin. The initial V concentrations tested are from 0.1 to 7.6 g/L for 8 g Dex-V resin. The experimental data of equilibrium adsorption of vanadate ions by Dex-V at pH 3.0 are presented in **Fig. 6**. The Langmuir model (**Eq. 2**) and the Freundlich model (**Eq. 4**) have been utilized to fit the experimental data. The relative isotherm curves are also drawn in **Fig. 6** and fitted adsorption parameters are shown in **Table 3**. In view of the correlation coefficient (R^2) values, the Langmuir model exhibits a better fit to the experimental data than the Freundlich model. This is further confirmed by the fact that the adsorption capacity at equilibrium predicted by the Langmuir model $q_{\max}^{\text{cal}}$ is much closer to the adsorption capacity at equilibrium determined by experiments $q_{\max}^{\text{exp}}$. It is thus indicated that vanadate ions, with negligible interaction between them, are absorbed onto the Dex-V resin by chemical force in monolayer and the resin possesses a homogeneous nature (**Yu et al., 2001**).

The values of adsorption model constants express the surface properties and affinity of the adsorbent (**Aksu, 2001**). The Langmuir constant, K_L , is an indicator of affinity between adsorbates and active adsorption sites in resin particles. The high value of K_L indicates that the Dex-V resin has strong affinity to the vanadate ions (**Pradhan et al., 1999**). The dimensionless separation factor, R_L , is a reliable indicator for the type of adsorption. The obtained R_L value is lower than 1.0, indicating the adsorption to be favorable (**Gode and Pehlivan, 2006**).

For the range of low initial V concentration concerning to the waste water, from 0.2 to 1.4 g/L, the adsorption isotherm is studied in detail. The equilibrium data in this range of V concentration follow well the Henry isotherm (**Fig. 7**), showing that the adsorption capacity of V in resin varies

linearly with the equilibrium concentration of V in solution. It is indicated that vanadate ions in this concentration range can only occupy less than 10% of active adsorption sites in resin and the adsorption is far away from saturation (Cui et al., 2014). Vanadate ions in concentration even lower than 0.2 g/L can also be adsorbed linearly by the Dex-V resin. The slope of Henry equation, K_H in Eq. 5, stands for the distribution ratio of adsorbates between resin phase and solution phase (Mitchell et al., 2014). The regression slope in Fig. 7 is in magnitude of 10^3 , indicating further the high affinity and selectivity of the Dex-V resin to the vanadate ions, which assures the high removal ratio of V from Cr in aqueous solution.

3.4. Adsorption kinetics of V

The adsorption kinetics of V was analyzed with the pseudo-first order model (Lagergren and Svenska, 1898) and pseudo-second order model (Ho and McKay, 2000) which are extensively used to describe the adsorption kinetics of solutes in liquid (Zhang et al., 2014). The obtained correlation coefficients (R^2) of the pseudo-second order model are larger than those for the pseudo-first order model in all experimental conditions (Fig. 8), indicating that the pseudo-second model fits better to experiment data and can thus better describe the adsorption kinetic behavior of V by Dex-V resin (Fig. 9). The regression results of the pseudo-second model are shown in Table 4. It can be seen from Table 4 that the calculated adsorption capacity at equilibrium q_e^{cal} agrees well with the adsorption capacity at equilibrium determined by experiments q_e^{exp} and the normalized standard deviation (Δq) is always lower than 5%, which indicates the validity of the pseudo-second order model to describe the adsorption kinetics of V by Dex-V resin. The high R^2 values in all cases also indicate the validity of this kinetic model. The obtained rate constant k_2 decreases with increasing

V concentration. This is due to that adsorption sites are more abundant in lower concentrations, which decreases the diffusion path of vanadate ions to available adsorption sites in resin particles and thus increases the adsorption rate of V. The rate constant k_2 also varies with adsorption temperature T when the initial concentration of V is maintained constant (data not shown), following the Arrhenius equation (**Lyubchik et al., 2004**). Plot of $\ln k_2$ versus $1/T$ displayed the straight line of $\ln k_2 = -4301.114/T + 9.573$ with $R^2 = 0.999$. The activation energy E_a was calculated to be $35.76 \text{ kJ}\cdot\text{mol}^{-1}$, suggesting that V adsorption by Dex-V resin is activated chemi-adsorption. This is in accordance with results of adsorption isotherm studies. The low E_a value ($< 42 \text{ kJ}\cdot\text{mol}^{-1}$) indicates that the adsorption process of V by the Dex-V resin is controlled by diffusion mechanism (**Al-Ghouti et al., 2005; Scheckel and Sparks, 2001; Zhang et al., 2014**).

In order to investigate further the diffusion mechanism during V adsorption, the Richenberg model was utilized to explore that the rate-controlling step is liquid film diffusion or intra-particle diffusion (**Riaz, 2007; Shaukat et al., 2005**). Results in **Table 5** show that there are two regions in the time range investigated (**Erosa et al., 2001**). In the initial 70 min, the experiment data follows excellent linearity as represented in **Eq. 8**. The obtained straight lines pass the origin, indicating that film diffusion is the rate-controlling step of the adsorption process in this time range (**Riaz, 2007**). The experiment data after 70 min was regressed with **Eq. 8** and **Eq. 9** but the obtained straight lines did not pass the origin. It is thus indicated that film neither diffusion nor intra-particle diffusion is the unique rate-controlling step of the overall adsorption process and the adsorption rate of V by Dex-V resin is controlled by both after adsorption for 70 min.

To confirm further the diffusion mechanism of V adsorption by Dex-V resin, the Weber-Morris equation has been adopted to assess the contribution of intra-particle diffusion to the adsorption

kinetics. Adsorption capacities at time intervals q_t were plotted versus $t^{1/2}$ as shown in **Fig. 10**, in which two distinct regions are observed. The regression results of the two regions for each initial concentration of V are listed in **Table 6**. In the first region ($t < 70$ min), the regressed equations did not pass the origin, indicating that the rate of adsorption process is not controlled by intra-particle diffusion (**Zhang et al., 2012**), which agrees with results of the Richenberg modeling. The small intercepts indicate thin boundary layer and thus low diffusion resistance, leading to fast intra-particle diffusion (**Venkat et al., 2007**). The slope of regressed equation, which is the intra-particle diffusion constant K_d , increases with increasing V concentration, indicating the increase in diffusion rate. This is due to that higher V concentration gives rise to higher concentration gradient in the boundary layer, leading to faster intra-particle diffusion. In the second region ($70 \text{ min} < t < 250 \text{ min}$), the intercepts become greater, which indicates the increase in thickness of boundary layer. Thicker boundary layer gives rise to greater diffusion resistance, resulting in lower intra-particle diffusion rate. The intra-particle diffusion becomes one of the main rate-controlling steps after adsorption for 70 min, which is in accordance with results of the Richenberg modeling. It can be seen in Table 6 that the intra-particle diffusion constants K_d for all concentrations are almost the same, which indicates that after 70 min the intra-particle diffusion is steady and the diffusion rates in cases of all initial concentrations reach the same low level. It is thus indicated that intra-particle diffusion proceeds fast in initial 70 min and contributes to the rate-controlling of V adsorption after 70 min during removal of V by Dex-V resin.

3.5. Removal of V from APV-precipitated waste water

The proposed removal method has been applied to remove V from the APV-precipitated waste

water. After removal of silicate ions Si(IV) by aluminum sulfate, the waste water was pretreated with NaHSO_3 reduction and H_2O_2 oxidation, followed by being loaded onto the Dex-V resin in optimal conditions. After adsorption of V, the residual solution was separated from resin. The chemical composition of the residual solution is shown in **Table 7**, together with those of APV-precipitated waste water and desiliconized waste water. The achieved removal ratio of V is as high as 96%. From the residual solution, Cr(III) precipitated as Cr(OH)_3 which were calcinated subsequently. Final product of Cr_2O_3 was obtained in purity of 93.10% (V less than 1.00%) with Cr recovery of 95%. Major loss of Cr lies in the calcination procedure. The resin loaded with V was used repeatedly until saturation of adsorption, from which final product V_2O_5 was obtained in purity of 96.20% with Cr less than 0.03%. It is demonstrated that the proposed method of removing V from Cr is effective, which can be extended to removal of other metals from their analogues.

4. Conclusion

In this work, a novel approach has been proposed to remove V(V) from Cr(VI) in aqueous solution by anion exchange resin. Facile pretreatment method is introduced based on reduction and selective oxidation to transform V(V) and Cr(VI) anions to differentiable forms which can be differentiated by the Dex-V resin. V(V) anions were absorbed by Dex-V resin while Cr(III) cations were maintained in solution and ready for recovery. Maximal adsorption ratio was obtained at pH 3.0. The Langmuir model can describe the adsorption behavior in overall concentration range while the Henry model can represent the adsorption behavior in low concentration range, which indicates that V is adsorbed chemically in monolayer and the Dex-V resin presents a homogeneous nature. Kinetics of V adsorption by Dex-V was investigated in detail, which shows that the rate of V

adsorption is controlled by film diffusion in initial 70 min and after 70 min the intra-particle diffusion makes obvious contribution to the rate-controlling of V adsorption. The proposed method was applied to removing V from APV-precipitated waste water. The obtained removal ratio of V from Cr was as high as 96% with Cr recovery of 95%. It is demonstrated that the proposed method is an effective and efficient method to remove V from Cr in aqueous solution, which provides new insights to separation and recovery of analogue metals.

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Figure Captions

Schematic 1. The flowsheet of proposed method to remove V from Cr-bearing solution

Fig. 1. (a) SEM image and EDS element mappings (b) C, (c) O, (d) Cl of a resin particle before adsorption; (e) SEM image and EDS element mappings (f) C; (g) O; (h) V of a resin particle after adsorption

Fig. 2. FT-IR spectra of the resin before and after adsorption

Fig.3. Effect of pH on the adsorption ratio of V onto resin

(T =25 °C, initial V concentration = 1.3 g/L, contact time = 250 min, resin dosage = 53.3 g/L)

Fig. 4. Effect of contact time on the adsorption of V by Dex-V resin (T =25 °C, pH = 3.0, resin dosage = 53.3 g/L).

Fig. 5. Effect of temperature on the adsorption of V by Dex-V resin (pH = 3.0, resin dosage = 53.3 g/L).

Fig. 6. Equilibrium adsorption of V by Dex-V at pH 3.0 and 25 °C.

The points are experimental data and the lines are simulated with Langmuir (red solid line) and Freundlich (blue dash line) models.

Fig. 7. Equilibrium adsorption of V in concentration of 0.2-1.4 g/L by Dex-V at pH 3.0 and 25 °C.

Fig. 8. Linear plots of the pseudo-second order model for the adsorption kinetics of V (a) in different initial concentrations and (b) at different temperatures

Fig. 9. Experiment data simulated with the Pseudo-second order model (pH 3.0, 25°C)

Fig. 10. Plots of the Weber-Morris model for adsorption kinetics of V by Dex-V resin at pH 3.0 and 25°C

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Fig. 6. Equilibrium adsorption of V by Dex-V at pH 3.0 and 25 °C.

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Fig. 7. Equilibrium adsorption of V in concentration of 0.2-1.4 g/L by Dex-V at pH 3.0 and 25 °C.

Fig. 8a. Linear plots of the pseudo-second order model for the adsorption kinetics of V in different initial concentrations

Fig. 8b. Linear plots of the pseudo-second order model for the adsorption kinetics of V at different temperatures

Fig. 9. Experiment data simulated with the Pseudo-second order model (pH 3.0, 25°C)

Fig. 10. Plots of the Weber-Morris model for adsorption kinetics of V by Dex-V resin at pH 3.0 and 25°C

Table 1 Physical and chemical properties of the resin used in this study

Properties	Dex-V
Structure	Macroporous styrene-based chain-like copolymers
Functional groups	- N(CH ₃) ₂
Physical form	White or light yellow; spherical grain
Ionic form	Cl ⁻
Particle size (mm, wet)	0.50 - 0.60*
Water retention capacity (%)	48 - 58
Mass total capacity (mmol/g dry resin)	≥ 4.8
Bulk density (g/ml)	0.65 - 0.75
Operating pH range	1 - 10
Maximum operating temperature (°C)	80

* Resin particles were sieved; other properties are obtained from manufacturer.

Table 2 Mass-to-charge ratios (N/Z) of V(V)-bearing ions at different pH values

pH	Major existing form of V(V)-bearing ions	N/Z ratio values
2	$V_2O_5 \cdot H_2O$	—
3	$H_2V_{10}O_{28}^{4-}$	2.5
4-5	$HV_{10}O_{28}^{5-}$	2.0
6	$V_{10}O_{28}^{6-}$	1.7
7	$V_4O_{12}^{4-}$	1.0
8-10	$V_2O_7^{4-}$	0.5

Table 3

Regressed adsorption parameters of Langmuir and Freundlich isotherm curves for V adsorption.

Isotherm models	Parameters			
	R^2	$q_{\max}^{\text{cal}}$ (mg/g)	$q_{\max}^{\text{exp}}$ (mg/g)	Constants
Langmuir	0.924	128	133	$K_L=25.840$; $R_L:0.202-0.962$
Freundlich	0.793	192	133	$n=1.733$; $K_F=274.789$

Table 4

Kinetic model constants for the adsorption of V in initial concentration of 0.2 - 1.4 g/L

T (°C)	C_0 (g/L)	q_e^{exp} (mg/g)	Pseudo-second order model			
			q_e^{cal} (mg/g)	k_2 (g/mg min)	R^2	Δq (%)
25	0.2	3.607	3.926	1.29E-02	0.998	3.638
25	0.5	9.104	9.718	6.21E-03	0.999	4.803
25	0.8	14.491	15.480	3.81E-03	0.999	4.597
25	1.1	19.775	21.097	2.88E-03	0.999	4.962
25	1.4	25.421	27.027	2.19E-03	0.998	3.494
25	0.24	4.210	4.043	1.05E-02	0.998	4.327
35	0.24	4.353	4.015	1.84E-02	0.998	4.652
45	0.24	4.491	4.108	3.74E-02	0.994	3.574
55	0.24	4.543	4.246	4.25E-02	0.995	3.126
65	0.24	4.558	4.392	1.48E-01	0.993	2.265

Table 5

Regression results of the Richenberg model for adsorption kinetics of V by Dex-V resin

Model Rt-t/Bt- t	T (°C)	First region: $t < 70$ min		Second region: $70 \text{ min} < t < 250$ min	
		Regression equation	R^2	Regression equation	R^2
Rt-t	25	$Rt = 5.970 \times 10^{-3}t$	0.997	$Rt = 1.279 \times 10^{-2}t - 0.713$	0.952
	35	$Rt = 6.370 \times 10^{-3}t$	0.997	$Rt = 1.297 \times 10^{-2}t - 0.694$	0.955
	45	$Rt = 6.500 \times 10^{-3}t$	0.997	$Rt = 1.313 \times 10^{-2}t - 0.689$	0.957
	55	$Rt = 6.730 \times 10^{-3}t$	0.998	$Rt = 1.317 \times 10^{-2}t - 0.669$	0.958
	65	$Rt = 6.950 \times 10^{-3}t$	0.998	$Rt = 1.319 \times 10^{-2}t - 0.653$	0.958
Bt-t	25	$Bt = 5.730 \times 10^{-3}t - 0.486$	0.991	$Bt = 1.279 \times 10^{-2}t - 1.211$	0.952
	35	$Bt = 6.120 \times 10^{-3}t - 0.485$	0.989	$Bt = 1.297 \times 10^{-2}t - 1.192$	0.955
	45	$Bt = 6.290 \times 10^{-3}t - 0.487$	0.991	$Bt = 1.313 \times 10^{-2}t - 1.187$	0.957
	55	$Bt = 6.560 \times 10^{-3}t - 0.489$	0.992	$Bt = 1.317 \times 10^{-2}t - 1.166$	0.958
	65	$Bt = 6.780 \times 10^{-3}t - 0.489$	0.992	$Bt = 1.319 \times 10^{-2}t - 1.150$	0.958

Table 6

Regression results of the Weber-Morris model for adsorption kinetics of V by Dex-V resin

C_0 (g/L)	First region: $t < 70$ min		Second region: $70 \text{ min} < t < 250$ min	
	Regression equation	R^2	Regression equation	R^2
0.2	$q_t = 3.752t^{1/2} + 3.211$	0.959	$q_t = 1.091t^{1/2} + 25.813$	0.986
0.5	$q_t = 4.542t^{1/2} + 3.361$	0.989	$q_t = 1.631t^{1/2} + 27.563$	0.977
0.8	$q_t = 6.272t^{1/2} + 1.666$	0.990	$q_t = 1.553t^{1/2} + 42.054$	0.976
1.1	$q_t = 7.019t^{1/2} - 1.136$	0.978	$q_t = 2.315t^{1/2} + 40.393$	0.959
1.4	$q_t = 8.571t^{1/2} + 8.961$	0.966	$q_t = 2.276t^{1/2} + 63.684$	0.959

Table 7

Chemical compositions of the waste water and the residue solution after resin loading

	V mg/L	Cr g/L	P mg/L	Si mg/L	Ca mg/L	Al mg/L
APV-precipitated Waste Water	91.58	1.18	2.28	411.24	134.92	2.14
Desiliconized Waste Water	82.94	1.17	0.82	4.03	62.51	9.05
Residue solution	3.63	1.16	*	*	*	*

*The concentrations of these elements were not determined.

Table captions

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Graphical Abstract