An Ion-Imprinted Imidazole-Functionalized Ordered Mesoporous Silica For Selective Removal of Chromium(VI) From Electroplating Effluents

Shuibin Cen

Guangdong Industry Polytechnic

Lan Yang

Guangdong Industry Polytechnic

Ruimin Li

Guangdong Industry Polytechnic

Shengzhao Gong

Guangdong Industry Polytechnic

Jiean Tan (✉ tjafsy@126.com)

Foshan University <https://orcid.org/0000-0001-6096-3202>

Lixi Zeng

Jinan University

Research Article

Keywords: Hexavalent chromium, Mesoporous silica, Ion imprinted polymers, Imidazole-functionalized, Adsorbent, Removal

Posted Date: September 14th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-741648/v1>

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Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on February 19th, 2022. See the published version at <https://doi.org/10.1007/s11356-022-19209-8>.

Abstract

In this work, ion imprinted technology incorporated with mesoporous silica materials (MCM-41) to obtain the novel specific adsorbent, ion imprinted mesoporous silica. Cr(VI) imprinted mesoporous silica (Cr(VI)IMS) was synthesized and used for adsorption studies and waste water application. A synthesized imidazolyl silane agent act as the functional monomer in the imprinted process to build up highly ordered functionalized imprinted materials. The chemical composition, thermal stability, porosity and highly ordered morphology were characterized by Fourier transform infrared spectroscopy (FTIR), solid state nuclear magnetic resonance (NMR), Brunauer-Emmett-Teller (BET) method, X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) respectively. The Brunauer-Emmett-Teller (BET) surface area was $1054.51 \text{ m}^2 \text{ g}^{-1}$ in this study. The Cr(VI)IMS showed great adsorption capacity to hexavalent chromium ions in acidic solution up to 45.6 mg g^{-1} . Cr(VI)IMS displayed much higher adsorption capacity to Cr(VI) ions than other negative ions. The relative selectivity coefficient was 2.56, higher than those of other anions (below 1.5). After eight adsorption-regeneration cycles, the adsorption efficiency of Cr(VI)IMS still reached 92.5%. The Cr(VI)IMS was found to exhibit equivalent property after multiple cycles of experiments, indicating good repeatability and reproducibility.

Introduction

Chromium is widely used in various industries, such as plating, tanning, paint and pigment production and metallurgy, which could possibly contaminate the environmental waters if it is not treated standardly (Gómez and Callao 2006). It is well known that the toxicological and biological properties of most elements depend upon their chemical forms. Chromium element in waste water is mainly existed as Cr(III) and Cr(VI). Cr(III) is an essential component having an important role in the glucose, lipid and protein metabolism, whereas Cr(VI) poses a definite adverse impact on living organisms (Lin and Huang 2001; Saikia et al. 2011). Strong oxidizing Cr(VI) can easily penetrate biological membrane and cause cancer or other diseases. Cr(III) can be precipitated at high pH (Petruzzelli et al. 1995), while Cr(VI) ions are highly soluble at different pHs (Li et al. 2013) and can be transported over a great distance existing in a variety of oxo-species, namely, dichromate ($\text{Cr}_2\text{O}_7^{2-}$), hydrochromate (HCrO_4^-) or chromate (CrO_4^{2-}), which threatens environment and creature health. Above all, it is indispensable to develop efficient method to cope this problem.

Among many of treatment methods to heavy metal ions, adsorption method is regarded as one of most promising techniques because of the convenience and high efficiency, which has attracted continuous attention in recent decades (Fu et al. 2019; Li et al. 2020). Activated carbon (Mohan and Pittman Jr 2006) and functional chitosan (Boddu et al. 2003) have been utilized to adsorb Cr(VI). Common adsorbents are seldom designed and synthesized according to the chemical structure of targets and show broad spectrum adsorption. Molecular imprinting technology refers to the technique of cross-linking functional monomers in the presence of template molecules to obtain polymers (Haupt 2001). The imprinting cavities structurally and chemically complementary to templates in resultant polymers display specific

binding ability to templates. Benefit from the imprinting process, imprinted polymers can act as specific adsorbents for given targets.

Ionic imprinting is similar to molecular imprinting and the imprinted ions are accessible to the recognition sites and captured in the imprinted polymers. Based on coordination between metal ions and with lone-pair electrons, the study of cation imprinting has been developed in the past decades like Pb(II) ions (He et al. 2015; Shafizadeh et al. 2019), Hg(II) ions (Velempini et al. 2019) and etc.. The studies on anion imprinting are rarely reported, which is possibly due to the lack of recognition sites to form a strong interaction. Generally, electrostatic interaction between functional monomers and anions is a usual principle in anion imprinting (Wu 2012). Tavengwa et al. (Tavengwa et al. 2013) used 4-vinyl pyridine as a functional monomer to prepare magnetic hexavalent chromium imprinted polymer, which was able to selectively adsorb hexavalent chromium ion. In the study of Liu et al. (Liu et al. 2013), chitosan was adopted as matrix material to prepare ion imprinted chitosan composite for the adsorption of hexavalent chromium in polluted water. Resorting to large specific surface area of nano materials, like nano particles and nanotubes, surface imprinted layers are thin and remarkably improve the performance of imprinted polymer, compared with the traditional micron-sized polymers. However, the polymerization process is difficult to control and the nano materials were easy to adhere with each other, which decreases the surface area.

Ordered mesoporous materials possess regular mesoscopic structure and tunnels, which means that the combination of ion-imprinting technology and mesoporous materials is expected to avoid the deep embedment of imprinted sites and the long adsorption time. Imprinted ordered mesoporous materials possess high adsorption capacity, high selectivity and high adsorption rate. Grafting imprinted polymers on the mesoporous materials can lead to decrease of surface area, pore blocking, and heterogeneous distribution of binding sites (Hoffmann et al. 2006). Imprinted mesoporous silica prepared by one-step co-condensation can solve the problems mentioned above. Recently, several imprinted functionalized mesoporous materials have synthesized by this method, focusing on the targets of Pb(II) ions (He et al. 2015), Dy(III) ions (Zheng et al. 2016), phosphopeptides (Chen et al. 2016), U(VI) and Cs(I) ions (Zhou et al. 2021), Ni(II) ions (He et al. 2018) and Pt(II) ions (Dobrzyńska et al. 2021).

Imprinted mesoporous silica prepared by the co-condensation (one-step method) simplifies the synthesis process and effectively avoid the blockage of mesoporous channels. The imprinting sites were uniformly distributed in the pore wall of mesoporous materials. Hexavalent-chromium-anion imprinted mesoporous silica (Cr(VI)IMS) by using co-condensation method has not been reported yet. N-containing functional groups such as amino, imidazole, pyridine etc. can positively charge via a protonation process, so that polymer monomers containing such groups are often used as functional monomers for anion imprinted polymers. In this work, the functional monomer with imidazole group was used to prepared hexavalent chromium imprinted mesoporous silica via a co-condensation method. Chemical groups, porosity and micromorphology of the imprinted mesoporous silica was characterized. The adsorption performance of materials to Cr(VI) ions was investigated by different adsorption experiments. Cr(VI)IMS was utilized to remove Cr(VI) ions from the waste water.

Materials And Methods

Reagents and chemicals

Hexadecyl trimethyl ammonium bromide (CTAB, 95%) were purchased from Shanghai Macklin Biochemical Co., Ltd. (3-Chloropropyl)trimethoxysilane (CPTES 98%) was obtained from Shanghai Energy Chemical technology Co., Ltd. Tetraethyl orthosilicate (TEOS 98%) was acquired from Aladdin Reagent Co., Ltd, and imidazole (ImiAR) was from Tianjin Kemiou Tianjin Kemiou Chemical Reagent Co., Ltd. All other chemicals, namely HCl, NaOH, HNO₃, C₂H₅OH, K₂Cr₂O₇, KH₂PO₄ and KNO₃ were of analytical grade. No additional purification was needed. Experimental water was deionized water.

Instruments

Fourier transform infrared spectroscopy (4000-400 cm⁻¹) was conducted by a PerkinElmer Spectrum Two fourier transform spectrophotometer. ¹³C NMR spectra were collected on a Bruker AVANCE III HD 400 superconducting NMR spectrometer. Small angle X-ray diffraction (XRD) inspections were recorded on a Bruker D8 Advance Scattering system using Cu K_α (λ = 1.5405 Å). Transmission electron microscopy images and scanning electron microscopy images were conducted on a HITACHI H-7650 transmission electron microscope and a HITACHI SU8010 field emission scanning electron microscope respectively. N₂ adsorption–desorption measurements were carried out by using Micromeritics ASAP-2020 surface area and porosimetry analyzer. All anions concentrations were inspected by Shimadzu UV-1750 spectrophotometer.

Preparation of mesoporous silica MCM-41

As the method published(Chen et al. 2016), 200 mg CTAB and 58 mg NaOH were dissolved in 100 mL deionized water and stirred for 20 min at 80 °C. Then 5 mmol TEOS was added into the mixture sequentially and continued stirred for 5 h. The mixture was then filtered, washed with deionized water and ethanol to remove the unreacted chemicals. Surfactant CTAB was eluted by HCl-ethanol solution (1:9, v/v).

Preparation of CPTES-Imi

The synthesis method of CPTES-Imi was referred to Adam's method(Adam et al. 2013). 0.4 mmol CPTES and 0.4 mmol Imi were mixed and stirred in nitrogen atmosphere for 48 h at 90 °C.

Preparation of Cr(VI)IMS

Cr(VI) imprinted mesoporous silica (Cr(VI)IMS) was synthesized by hydrolysis of CPTES-Imi (functional monomer) and TEOS(Fig. 1). Firstly, 115 mg K₂Cr₂O₇ was added into 5 mL deionized water, followed by adding 0.4 mmol functional monomer. After pre-reacting for 2 h, 200 mg CTAB and 58 mg NaOH were dissolved in 100 mL deionized water by stirring for 30 min at 80 °C. 5 mmol TEOS was added into the mixture dropwise. After stirring for 4 h, the solid product was filtered and washed by deionized water,

ethanol and HCl-ethanol solution (1:9, v/v) separately numerous times to extract chromium (VI) ion and the surfactant. The non-imprinted mesoporous silica (NIMS) was prepared with the same procedure except that no $\text{K}_2\text{Cr}_2\text{O}_7$ was added into the initial mixture.

Adsorption experiments

Adsorption experiments were conducted by adding 10 mg Cr(VI)IMS or NIMS into 10 mL solution at 25 °C. All experiments were carried out in triplicate. The concentration of Cr(VI) was measured by spectrophotometric method after reacted with diphenylcarbazide. To investigate the effect of pH of solution on adsorption ability of Cr(VI)IMS or NIMS to Cr(VI) ions, Cr(VI)IMS or NIMS was added into Cr(VI) solutions (200 mg L^{-1}) at different pH (2.0-10.0) with 3 h shaking. The respective solution pH was adjusted using 0.5 mol L^{-1} HCl/NaOH solutions.

The equilibrium adsorption experiments were conducted in a Cr (VI) solution ($5\text{-}400 \text{ mg L}^{-1}$) at pH 3.0 with 3 h shaking. The binding capacity Q was calculated by $Q = (C_0 - C_e)V/m$, where C_0 and C_e represented the initial concentration and equilibrium concentration of Cr(VI), while V and m were the volume of solutions and the mass of adsorbents. Imprinting factor (IF) is defined as $IF = Q_I/Q_N$, where Q_I and Q_N represent the binding capacity of Cr(VI)IMS and NIMS.

In the adsorption kinetics study of Cr(VI)IMS, we selected Cr(VI) solutions of two levels concentration (50 mg L^{-1} and 200 mg L^{-1}) at pH 3.0 and measured the concentration of Cr(VI) ions at different adsorption time.

Dihydrogen phosphate and nitrate were chosen for comparison to study the adsorption selectivity of Cr(VI)IMS. Cr(VI)IMS was dispersed in the solution containing 1 mmol L^{-1} Cr(VI), H_2PO_4^- or NO_3^- at pH 3.0. The concentration of dihydrogen phosphate and nitrate were measured by phospho-molybdenum blue photometry and phenoldisulfonic acid method, respectively.

Reusability and reproducibility

For the reusability test of Cr(VI)IMS, Cr(VI)IMS adsorbed Cr(VI) in the solution of 200 mg L^{-1} . Then, Cr(VI)IMS was eluted by 2 mol L^{-1} HCl and dried at 85°C for regeneration. The Cr(VI)IMS endured 8 adsorption-regeneration cycles. Five batches of Cr(VI)IMS synthesized with the same method were utilized for reproducibility study.

Removal of Cr(VI) in actual samples

The wastewater sample was collected from Zhaoqing Dawang Electroplate Industrial Park (Guangdong, China) with clean polyethylene bottles. The untreated sample of pH 4.0 contained 22 mg L^{-1} Cr(VI). It was then filtered by $0.45 \mu\text{m}$ membrane. Different amounts of Cr(VI)IMS were added into 500 mL wastewater with 2 h shaking.

Results And Discussion

Characterization

We utilized FT-IR and solid-state ^{13}C NMR to confirm the functional chemical groups in Cr(VI)IMS. Figure 2a is the IR spectra of Cr(VI)IMS. Curve 1 and 2 represented the IR absorption signals of MCM-41 and Cr(VI)IMS, respectively. Three peaks at 1078 cm^{-1} , 941 cm^{-1} and 795 cm^{-1} indicated the silica matrix. The bending vibration of O-H of silica materials was displayed at 1632 cm^{-1} (Wang et al. 2014). The broad band at 3454 cm^{-1} of curve 1 might attributed to the existence of Si-OH. The weak adsorption peak of curve 2 at 1577 cm^{-1} was ascribed from the vibration of imidazole C-N bond (Kryszak et al. 2017). The solid-state ^{13}C NMR spectra of Cr(VI)IMS were exhibited in Fig. 2b. The peaks at 8 ppm, 24 ppm and 50 ppm of Cr(VI)IMS corresponded to C1, C2 and C3, while signals at 121 ppm and 134 ppm were assigned to the C atoms in imidazole ring (Li et al. 2007). The FT-IR and NMR spectra demonstrated that the functional monomers have poly-condensed into Cr(VI)IMS.

Small angle XRD patterns of MCM-41 and Cr(VI)IMS were depicted in Fig. 2c. Two materials showed three diffraction peaks of (100) ($2\theta = 2.0^\circ$), (110) ($2\theta = 3.8^\circ$) and (200) ($2\theta = 4.4^\circ$) lattice plane. This results indicated that Cr(VI)IMS still possessed the typical mesoporous structure of mesoporous silica MCM-41.

The mesoporous features of Cr(VI)IMS were investigated with N_2 adsorption-desorption experiment. The isotherm of Cr(VI)IMS was of the type IV (Fig. 2d), suggesting that the pores of Cr(VI)IMS were in the mesoporous range. The specific surface area ($1054.51\text{ m}^2\text{ g}^{-1}$) and pore volume ($1.16\text{ m}^3\text{ g}^{-1}$) were calculated with Bnmauer-Enunett-Teller (BET) method. The BJH-determined average pore size distribution was 3.45 nm, with pore sizes largely in 2.44–3.63 nm range. The test results corresponded to the characteristics of mesoporous silica MCM-41.

The morphology and microstructure of Cr(VI)IMS was further observed by SEM and TEM. Cr(VI)IMS mainly existed as dispersed microspheres with particle diameter of 100–400 nm in SEM images (Fig. 3a). TEM images (Fig. 3b) demonstrated the ordered 2D hexagonal symmetrical structure of mesoporous channels with pore diameter of 2–3 nm inside Cr(VI)IMS, which basely corresponded with the result of N_2 adsorption-desorption experiment.

Effect of pH on adsorption capacity of Cr(VI)IMS

The acidity of solution poses obvious effects to the absorption performance of Cr(VI)IMS. As displayed in Fig. 4a, at low pH, Cr(VI)IMS showed high absorption ability. Cr(VI)IMS achieved the largest binding capacity (45.6 mg g^{-1}). The protonation of imidazole groups of Cr(VI)IMS were positively charged at low pH. With the increase of pH values, deprotonation increased simultaneously, which can lead to intense decrease of adsorption capacity (Amara and Kerdjoudj 2003). While the pH value of the solution was higher than 7, OH^- was able to neutralize the positive charge of adsorbents, which caused the binding capacities of Cr(VI)IMS obviously decreased. We used imprint factor (IF) value to estimate the specific

adsorption ability of Cr(VI)IMS. The calculation formula of IF value is $IF = Q_I / Q_N$, where Q_I and Q_N represent adsorption capacity of Cr(VI)IMS and NIMS, respectively. Above all, the adsorption abilities of Cr(VI)IMS was mainly determined by the extent of protonation of imidazole groups. The imprinted sites of Cr(VI)IMS exhibited higher affinity to Cr(VI) ions at higher pH, while Cr(VI)IMS showed higher adsorption capacity to Cr(VI) at acidic solution.

Adsorption isotherm study

The adsorption isotherm experiments were carried out at the optimized pH condition (pH = 3), as the initial concentration of Cr(VI) ions increased, the adsorbing capacity increased gradually(Fig. 4b). When the initial concentration of Cr(VI) ions was 200 mg L⁻¹, Cr(VI)IMS reached saturated adsorption (45.6 mg g⁻¹), which was much higher than that of NIMS. The IF value was 2.36, which indicated that imprinted functionalized mesoporous exhibited high affinity to given targets.

We used Scatchard model to analyze the results of adsorption isotherm experiments(Gao et al. 2011). The Scatchard equation is $Q_e/C_e=(Q_{max}-Q_e)/K_D$, where C_e , Q_{max} and Q_e represent equilibrium concentration of Cr(VI) ions, apparent maximum adsorption capacity and equilibrium adsorption capacity. K_D is the equilibrium dissociation constant. The results of the linear regression Scatchard scatter plots of Cr(VI)IMS displayed two separate straight lines with different slopes, suggesting two types of recognition sites (specific binding and nonspecific binding) existed in the Cr(VI)IMS(Li et al. 2014). On the other hand, the scatter plots could be modelled as one straight line, indicating that there was one kind of binding sites NIMS. (Fig. 5 and Table 1)

Table 1
Results of Scatchard analysis

Adsorbent	linear equation	apparent maximum adsorption capacity $Q_{max}(\text{mg g}^{-1})$	equilibrium dissociation constant $K_D(\text{mg L}^{-1})$	R^2
Cr(VI)IMS	1: $Q_e/C_e=-0.05072Q_e + 1.2029$	23.72	19.72	0.9908
	2: $Q_e/C_e=-0.00479Q_e + 0.5100$	106.47	208.77	0.9907
NIMS	3: $Q_e/C_e=-0.00548Q_e + 0.2132$	38.91	182.48	0.9909

The Langmuir adsorption model was also used to assess the adsorption thermodynamic properties(Fig. 6). The expression is $C_e / Q_e = C_e / Q_{max} + 1/ (Q_{max}b)$, where C_e , Q_{max} and Q_e represent equilibrium concentration of Cr(VI) ions, the maximum amount of adsorption and equilibrium adsorption capacity. And b is the constant in the Langmuir adsorption model. The adsorption behavior basically conformed to the Langmuir adsorption model (correlation coefficient $R^2 = 0.9878$), indicating that surface adsorption was rather uniform. The maximum amount of adsorption Q_{max} and the experimental amount Q_{Exp} are 55.9 mg g⁻¹ and 45.6 mg g⁻¹, respectively.

Adsorption kinetic

We studied the adsorption kinetic to Cr(VI) ions of Cr(VI)IMS at the concentration of 50 mg g⁻¹ and 200 mg g⁻¹(Fig. 7). At low concentration, it took Cr(VI)IMS 7 min to achieve equilibrium. For 200 mg g⁻¹, the adsorption equilibrium time of Cr(VI)IMS was 10 min. The results suggested that higher concentration led to longer absorption time for more Cr(VI) ions to enter the imprinted cavities. The recognition sites in nanoscale pore walls of large surface area accelerate the mass transportation. Compared with the ion imprinted polymers of classic structure, the functionalized mesoporous micromorphology remarkably shorten the adsorption time of Cr(VI)IMS to Cr(VI) ions(Bayramoglu and Arica 2011).

Kinetic studies were explored by two equations including the pseudo first order and the pseudo second order model. The fitting plots of kinetic equations are shown in Fig. 8a and 8b. The pseudo first order kinetic equation is $q_t = q_e [1-\exp(-k_1t)]$ and the pseudo second order kinetic equation is $q_t = k_2q_e^2t/(1 + k_2q_e t)$, where t, q_t and q_e represents adsorption time, the amount of adsorption and equilibrium adsorption capacity. k₁ and k₂ are adsorption rate constants of the pseudo first order and the pseudo second kinetic, respectively. The related parameters are presented in Table 2 and Table 3. It is obvious that the pseudo-first-order model was better than the pseudo-second-order model to describe adsorption kinetics as shown by the responding regression coefficient (R²).

Table 2
Calculated kinetic parameters of pseudo-first orders

Adsorbent	concentration (mg L ⁻¹)	R ²	k ₁ (min ⁻¹)	q _e (mg g ⁻¹)
Cr(VI)IMS	50	0.9934	0.3784	15.74
Cr(VI)IMS	200	0.9888	0.2970	46.52

Table 3
Calculated kinetic parameters of pseudo-second orders

Adsorbent	concentration (mg L ⁻¹)	R ²	k ₂ (g mg ⁻¹ min ⁻¹)	q _e (mg g ⁻¹)
Cr(VI)IMS	50	0.9668	0.0274	17.79
Cr(VI)IMS	200	0.9587	0.0065	54.02

Selective experiment

Figure 9 was the results of selective experiments. The functional chemical groups of Cr(VI)IMS were organized during the imprinting process and fixed in the imprinted silica. Because of the existence of complementary imprinted cavities for Cr(VI) ions, the Cr(VI)IMS exhibited obviously selective binding ability to Cr(VI) ions. H₂PO₄⁻ and NO₃⁻ are common anions. And they were adsorbed by positive charged Cr(VI)IMS and NIMS via electric attraction. Distribution coefficient $K = Q/C_e$, where Q and C_e were the adsorption capacity of adsorbents and the concentration of residual ions. We used selective coefficients

$R_{SF} = K_I/K_N$ to estimate the selectivity of three Cr(VI)IMS, where K_I and K_N represented distribution coefficient of Cr(VI)IMS and NIMS. The R_{SF} values of Cr(VI)IMS (2.56) were much higher than other two anions (Table 4), which could signified $H_2PO_4^-$ and NO_3^- were hard to be captured by the recognition sites due to their differences with Cr(VI) ions. On the other hand, functional monomers were distributed randomly in the materials and showed nonspecific adsorption to anions.

Table 4
Results of selective adsorption experiment of Cr(VI)IMS and NIMS

Adsorbent	Ions	$Q_I(\text{mmol g}^{-1})$	$Q_N(\text{mmol g}^{-1})$	$K_I(\text{L g}^{-1})$	$K_N (\text{L g}^{-1})$	R_{SF}
	$Cr_2O_7^{2-}$	0.294	0.140	416.4	162.8	2.56
Cr(VI)IMS	$H_2PO_4^-$	0.168	0.132	201.9	152.1	1.33
	NO_3^-	0.134	0.113	154.7	127.4	1.21

Reusability and reproducibility

Reusability plays a significant role in the application of adsorbents. To estimate the reusability of Cr(VI)IMS, adsorption-regeneration cycling experiments were conducted on the same batch of Cr(VI)IMS. After 8 cycles, the adsorption efficiency of Cr(VI)IMS still reached 92.5%, showing their excellent stability and reusability(Fig. 10a). Reproducibility is another important property of adsorbent. Five batches of Cr(VI)IMS exhibited no obvious difference in adsorption capacities(Fig. 10b).

Application in real water samples

The concentration of Cr(VI) of the filtered waste water was 22.1 mg L^{-1} . The water samples of the same volume were treated by different amount of adsorbent. The adsorption performance to actual waste water was shown in Table 5. Lower residual concentration can be obtained, treated by larger amount of adsorbent. Using 6.0 g L^{-1} of Cr(VI)IMS, the residual concentrations of Cr(VI) ions was 0.2 mg L^{-1} , which was lower than discharge standard of China (GB8978-1996).

Table 5
adsorption performance of different adsorbents to actual waste water

Adsorbent	Initial concentration (mg L ⁻¹)	Amount of adsorbent(g L ⁻¹)	Residual concentration (mg L ⁻¹)
Cr(VI)IMS	22.1	2.0	5.1
Cr(VI)IMS	22.1	3.0	2.9
Cr(VI)IMS	22.1	4.0	1.5
Cr(VI)IMS	22.1	5.0	0.6
Cr(VI)IMS	22.1	6.0	0.2

Comparison of adsorption performance of other adsorbents

To study removal of Cr(VI) ions by adsorption method in the water, several adsorbents have been utilized and their performance were summarized in Table 6. Fe₃O₄ 50%-PANI@GO hybrid composite, imidazole functionalized mesoporous SBA-15 and ion-exchange resin are three kinds of nonspecific anion adsorbents. The adsorption capacities of Cr(VI) ions are higher than that of Cr(VI)IMS. However, the equilibrium time is much longer and they have not shown high selectivity to Cr(VI). After 5 cycles regeneration, the adsorption capacity of Fe₃O₄ 50%-PANI@GO hybrid composite has decreased remarkably while Cr(VI)IMS with relatively robust structure has shown reliable reusability. Cr(VI) imprinted polymers and magnetic Cr(VI) imprinted nano composites mentioned in Table 6 have been applied imprinted technology, so they have performed well in selective adsorption but adsorption time is longer than that of Cr(VI)IMS. According to the comparison of adsorption capacities, adsorption time and selectivity, it can be concluded that ion imprinting technology enhance the selectivity of adsorbents and Cr(VI)IMS prepared by co-condensation method exhibited the advantages of fast adsorption rate, high binding capacity and specific adsorption.

Table 6
Comparison of the reported adsorbents for hexavalent chromium

Adsorbents	Functional groups	Synthesis method	Adsorption capacity (equilibrium time)	Selectivity	References
Fe ₃ O ₄ 50%-PANI@GO hybrid composite	aniline groups	(multi-step)	98.5 mg g ⁻¹ (50 min)	Not obvious	(Chinnathambi and Alahmadi 2021)
Imidazole functionalized mesoporous SBA-15	Imidazole groups	Chemical modified (multi-step)	113 mg g ⁻¹ (60 min)	Not mentioned	(Li et al. 2007)
Ion-exchange resin	Tertiary amino	Chemical modified (one-step)	152.52 mg g ⁻¹ (60 min) ; 120.48 mg g ⁻¹ (60 min); 156.25 mg g ⁻¹ (60 min)	Not mentioned	(Shi et al. 2009)
Cr(VI) imprinted polymers	Quaternized pyridine	Free radical polymerization, quaterisation (one-step)	45.23 mg g ⁻¹ (90 min)	Cr(VI) ions	(Pakade et al. 2011)
Magnetic Cr(VI) imprinted nano composites	Amino and imidazole	Free radical polymerization and sol-gel method (one-step)	2.49 mg g ⁻¹ (30 min)	Cr(VI) ions	(Qi et al. 2017)
Cr(VI)IMS	Imidazole groups	Sol-gel method (one-step)	45.6 mg g ⁻¹ (10 min)	Cr(VI) ions	This work

Conclusions

In this study, we developed Cr(VI) imprinted mesoporous silica synthesis method which combined the advantages between mesoporous material with ion imprinted technology. The positive charged imidazolyl groups were be integrated into the mesoporous silica successfully, proved by FT-IR and NMR and showed strong electrostatic attraction to anions. Compared to NIMS, Cr(VI)IMS exhibited specific adsorption to Cr(VI) anions. Benefited by highly ordered MCM-41 mesoporous structure, Cr(VI)IMS showed large adsorption capacity and short adsorption time at acid and weak acid conditions. The Cr(VI) concentration of wastewater is lower than emission standard limit (0.5 mg L⁻¹) after treatment by the optimized amount of Cr(VI)IMS. The combination of imprinted technology and highly ordered

mesoporous silica synthesized by one-step co-condensation shows a prospective method for development of specific and efficient pollutant adsorbents.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Funding

We gratefully acknowledge the financial support from National Natural Science Foundation of China (No: 21773072), the Natural Sciences Foundation of Guangdong Province (Grant No.218A0303130135) and the foundation of Guangdong Industry Technical College (Grant No. KYRC2018-016).

Availability of data and materials

All data generated or analysed during this study are included in this published article.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions:

Conceptualization: **Shuibin Cen**

Methodology: **Shuibin Cen**

Formal analysis and investigation: **Shuibin Cen, Jiean Tan**

Writing - original draft preparation: **Shuibin Cen**

Writing - review and editing: **Shuibin Cen, Ruimin Li, Shengzhao Gong, Lixi Zeng**

Funding acquisition: **Shuibin Cen, Ruimin Li**

Resources: **Lixi Zeng**

Supervision: **Lan Yang**

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Figures

Figure 1

Schematic procedure for synthesis of Cr(VI) ions imprinted mesoporous silica.

Figure 2

(a) FT-IR spectra of MCM-14 (1) and Cr(VI)IMS (2); (b) solid-state ^{13}C NMR spectra of Cr(VI)IMS; (c) The low-angle XRD pattern of MCM-14 (1), Cr(VI)IMS (2); (d) N_2 adsorption-desorption isotherms of Cr(VI)IMS

Figure 3

SEM and TEM images of Cr(VI)IMS.

Figure 4

(a) The effect of pH on the binding capacities and IF values of Cr(VI)IMS (experimental conditions: used 10 mL of 200 mg L⁻¹ Cr(VI) ion solution, solid weight 10 mg, T=25 °C); (b) Adsorption isotherm experiments of Cr(VI)IMS (experimental conditions: used 10 mL of different concentrations of Cr(VI) ion solution, solid weight 10 mg, T=25 °C, pH=3).

Figure 5

Scatchard plot of Cr(VI)IMS and NIMS.

Figure 6

Langmuir adsorption model analysis of Cr(VI)IMS.

Figure 7

Adsorption kinetics of Cr(VI)IMS. (experimental conditions: used 10 mL of 200 mg L⁻¹ and 50 mg L⁻¹ Cr(VI) ion solution, solid weight 10 mg, T=25 °C, pH=3)

Figure 8

The pseudo-first-order(a) and pseudo-second-order(b) model of adsorption kinetics of Cr(VI)IMS

Figure 9

Selective adsorption experiments of Cr(VI)IMS. (experimental conditions: used 10 mL of 1 mmol L⁻¹ anion solution, solid weight 10 mg, T=25 °C, pH=3)

Figure 10

(a) Reusability of Cr(VI)IMS; (b) Reproducibility of Cr(VI)IMS. (experimental conditions: used 10 mL of 200 mg L⁻¹ of Cr(VI) ion solution, solid weight 10 mg, T=25 °C, pH=3)