

# Removal of hexavalent chromium ion from aqueous solution using nanoscale zero-valent iron particles immobilized on porous silica support prepared by polymer template method

Minchae Jang\*, Boyeong Park\*, Hyunseung Lee\*, Tae-Yong Kim\*, and Yangsoo Kim<sup>\*,\*\*,†</sup>

\*Department of Nanoscience & Engineering, Inje University, Gimhae 50834, Korea

\*\*High Safety Vehicle Core Technology Research Center, Inje University, Gimhae 50834, Korea

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**Abstract**—Porous silica supported nanoscale zero-valent iron was prepared by a polymer template method in order to effectively remove a hexavalent chromium ion (Cr(VI)) in an aqueous solution. It did not show a deterioration of Cr(VI) removal efficiency, which could be caused by the surface oxidation and agglomeration of nanoscale zero-valent iron (NZVI) particles. Porous silica by the polymer template method showed quite unique structure, which we named as quasi-inverse opal silica (QIOS), and it showed high surface area (375.4 m<sup>2</sup>/g) and fine pore size (76.5 nm). NZVI immobilized on the surface of QIOS (NZVI@QIOS) was added to an aqueous Cr(VI) solution at 0.025 g/L, and it showed over 96% Cr(VI) removal efficiency. Such a high removal efficiency of Cr(VI) was maintained over two weeks after preparation (92% after 16 days). Morphology of porous silica supported nanoscale zero-valent iron was analyzed by TEM and FE-SEM. Identification of the reaction compounds produced by the reaction of Cr(VI) and zero-valent iron (Fe(0)) was made by the application of XPS.

Keywords: Diphenylcarbazide Method, Hexavalent Chromium, Nanoscale Zero-valent Iron, Polymer Template, Porous Silica

## INTRODUCTION

Nanoscale zero-valent iron (NZVI) with core-shell structure has been known to show a remarkable efficiency in the reductive removal of various types of toxic compounds and heavy metal ions contained in contaminated soil and water [1]. Hexavalent chromium, Cr(VI), showing highly toxic, carcinogenic and mutagenic properties is one of major heavy metal ions found in the wastewater discharged from a variety of chemical plants and reportedly a suitable target substance that could be effectively removed by NZVI [2]. An outstanding oxidation capability of NZVI allows the conversion of Cr(VI) into relatively nontoxic trivalent chromium, Cr(III), in which a few mechanisms such as reduction, adsorption and coprecipitation are involved [3]. However, there are still some problems to be solved in practical applications of NZVI. NZVI shows an agglomeration in time due to both the van der Waals forces occurring among the nanoscale particles having high surface to volume ratio and its magnetization properties. Besides, a shell surface surrounding the NZVI core is easily oxidized in the atmospheric environment due to its high reactivity and low stability. These characteristic problems of NZVI make a Cr(VI) removal efficiency worse with time and are a serious impediment to the remediation of Cr(VI) in contaminated soil and water. One of the feasible solutions to the agglomeration and surface oxidation problems regarding NZVI is an immobilization of NZVI on the silica support for the removal

of Cr(VI) from the aqueous hexavalent chromium solution [3-10]. It is noted that an utilization of highly publicized porous silica such as MCM-41 [3] and SBA-15 [4] as a support material for NZVI was applied for the removal of Cr(VI).

There is an interesting report regarding the preparation of porous silica having quite unique structure and controllable surface area by the application of polymer template method [11]. Polymer particles including a precursor of silica (i.e., tetraethyl orthosilicate (TEOS)) were first prepared by the application of dispersion polymerization of methyl methacrylate, and then TEOS was transformed into silica by the application of sol-gel reaction process. And, finally, a porous silica material was prepared by removing polymeric components from the polymer particles including silica via a calcination process. In this study, we prepared porous silica material showing the quasi-inverse opal structure on the basis of the polymer template method [11] and made an immobilization of NZVI on the quasi-inverse opal silica (QIOS).

The main objectives of this work were (a) preparation of nanoscale zero-valent iron particles immobilized on porous silica having the quasi-inverse opal structure, (b) achievement of high removal efficiency of Cr(VI) from the aqueous hexavalent chromium solution by using the porous silica (QIOS) supported NZVI (NZVI@QIOS), (c) confirmation of a prolonged superiority of a Cr(VI) removal efficiency for the QIOS supported NZVI.

## MATERIALS AND METHODS

### 1. Materials

Methyl methacrylate (MMA; 99.5%, Junsei Chemical) was puri-

<sup>†</sup>To whom correspondence should be addressed.

E-mail: cheykim@inje.ac.kr

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fied by passing through an inhibitor remover column (Aldrich) before use. The following chemicals were used as-received in this study: polyvinyl alcohol (PVAL; MW=66,031, Wako Pure Chemical), n-hexane (95%, Aldrich), tetraethyl orthosilicate (TEOS; 98%, Aldrich), lauroyl peroxide (LPO; 97%, Aldrich), potassium dichromate ( $K_2Cr_2O_7$ ; 99%, Aldrich), iron(III) chloride ( $FeCl_3$ ; 97%, Aldrich), hydrochloric acid (HCl; 37%, Aldrich), methacryloxypropyl-terminated polydimethylsiloxane (PDMS; 97%, Gelest), 1,5-diphenyl-carbazide (DPC; 98%, Aldrich), sodium borohydride ( $NaBH_4$ ; 99%, Aldrich). Reagent-grade (>99%) acetone, ethanol and isopropyl alcohol (IPA) were also used in this study.

## 2. Preparation of Porous Silica Supported Nanoscale Zero-valent Iron

Polymethylmethacrylate (PMMA) particles used as polymeric template materials for the preparation of porous silica having unique morphology (i.e., QIOS) were prepared by the application of dispersion polymerization process based on the report by Choi et al. [11]. An aqueous PVAL solution of 15 g/L solubilized in deionized water (DI-water) and an organic LPO solution of 42.2 g/L dissolved in n-hexane were prepared, respectively. A reaction mixture of MMA (0.448 M), TEOS (0.124 M) and PDMS (22.7 g/L) was thoroughly mixed with the organic LPO solution, and then the prepared organic mixture including MMA, TEOS, PDMS and LPO was added to the aqueous PVAL solution. The reaction mixture was thoroughly agitated and maintained at 70 °C for 3 hours under a nitrogen atmosphere, and solid particles were retrieved after the completion of dispersion polymerization process.

The prepared PMMA particles including TEOS were added to an aqueous solution of IPA (429.6 g/L), HCl (79.6 g/L) and DI-water, and then a sol-gel reaction process continued to proceed for a certain time. The sol-gel reaction made TEOS in the surface of PMMA particles convert into silica. After the sol-gel reaction process, PMMA particles with silica were transferred to a tube-type furnace and a calcination process was carried out at 500 °C for 5 hours by passing argon gas through the tube. The calcination process made PMMA burned away and only silica component remained, which resulted in a unique porous structure of silica, i.e., the quasi-inverse opal silica.

An immobilization of NZVI on the porous silica materials proceeded in the following order. A certain quantity of ethanol solution containing iron(III) chloride (90 g/L) was slowly added to the prepared porous silica materials, and then they continued to stay in dampened state for 10 minutes. A weight ratio of iron(III) chloride to the silica was maintained at about 2.0 in this study. The whole mixture was heated at 80 °C for 2 hours to let ethanol dry out completely. A certain amount of ethanol was additionally put into the silica and a specified quantity of  $NaBH_4$  ( $NaBH_4 : FeCl_3 = 1 : 10$ ) was slowly added. A reduction reaction changing from Fe(III) to Fe(0) was carried out for 15 minutes, and the vacuum-dried solid materials were retrieved and immediately transferred to a desiccator for further use of them.

## 3. Reductive Removal of Cr(VI) from the Aqueous Hexavalent Chromium Solution by Using an Immobilized NZVI on the Porous Silica Support

An aqueous solution of  $K_2Cr_2O_7$  solubilized in DI-water was prepared with the variation of concentration of Cr(VI) and used as a

target solution for the reductive removal of Cr(VI) in this study. A certain amount of the NZVI immobilized on a porous silica support was added to a fixed volume of the aqueous  $K_2Cr_2O_7$  solution with the specified concentration of Cr(VI), and a reduction process changing from Cr(VI) to Cr(III) was carried out maintaining the pH at 6 unless specified. After the completion of reduction process, the solid products settled down were separated from the upper liquid by a centrifugation, and then the obtained liquid was transferred to the quantitative analysis of Cr(VI) remained after a reductive removal process. In this study, the amount of QIOS supported NZVI (NZVI@QIOS) added in a specific volume of the aqueous  $K_2Cr_2O_7$  solution was maintained at a constant value of 0.001 g/mL.

## 4. Characterization of the Prepared Samples

The concentration of Cr(VI) in the aqueous  $K_2Cr_2O_7$  solution was estimated by using the DPC method combined with the application of spectrophotometric analysis using UV-spectroscopy (Shimadzu Model UV-1280). It has been known that a hexavalent chromium ion reacts with DPC in acidic condition and it produces a highly colored carbazone inner complex salt of a chromous ion (Cr(III)), which is quantified by spectrophotometrically measuring at 540 nm with extremely high detection power [12]. Morphology of the immobilized NZVI on a porous silica support was analyzed by transmission electron microscopy (TEM) operating at 200 kV (JEOL Model JEM-2010). Samples for the field emission-scanning electron microscopy (FE-SEM) analysis were coated with Pt/Pd by sputtering for 150 s. The FE-SEM images were obtained on a Hitachi Model S-4700. The X-ray diffraction (XRD) pattern was taken with 40 kV, 30 mA Cu  $K\alpha$  radiation using a Philips Model X'Pert MPD. The detector was moved step by step ( $\Delta 2\theta = 0.04-0.05^\circ$ ) in a scanning range from  $2\theta = 10-90^\circ$  at a speed of  $6^\circ/\text{min}$ . Specific surface area and pore size of the prepared porous silica were analyzed using BELSORP-mini II. The chemical state and composition of the products were analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific Model MultiLab 2000 X-ray photoelectron spectrometer with twin anode Mg/Al (300/400 W) X-ray source.

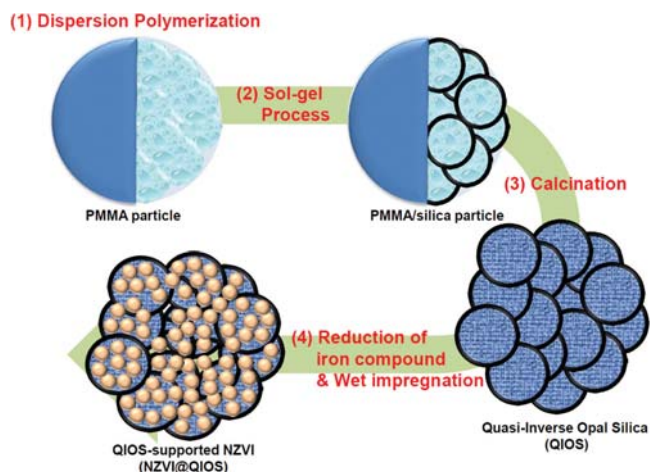


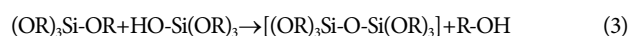
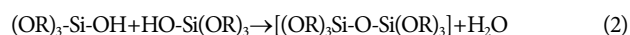
Fig. 1. Schematic preparation process flow of the QIOS supported NZVI (NZVI@QIOS).

## RESULTS AND DISCUSSION

## 1. Morphology Analysis

The overall preparation process of QIOS supported NZVI (NZVI@QIOS) is schematically presented in Fig. 1. SEM microphotographs of the PMMA particles including TEOS show that they are composed of outer supraparticles of 100-300  $\mu\text{m}$  (Fig. 2: a<sub>L</sub>) and inner subparticles of 1-3  $\mu\text{m}$  (Fig. 2: a<sub>H</sub>). After the dispersion polymerization process, a sol-gel reaction process applied to the prepared PMMA particles made TEOS convert into silica according

to the following hydrolysis (Eq. (1)) and condensation (Eq. (2) & (3)), where the alkyl group of R indicates ethyl group, i.e., C<sub>2</sub>H<sub>5</sub> [13].



The SEM microphotographs of PMMA particles retrieved after the completion of sol-gel process (Fig. 2: b<sub>L</sub> and b<sub>H</sub>) show that the surface of inner and outer particles turned out to be remarkably cor-

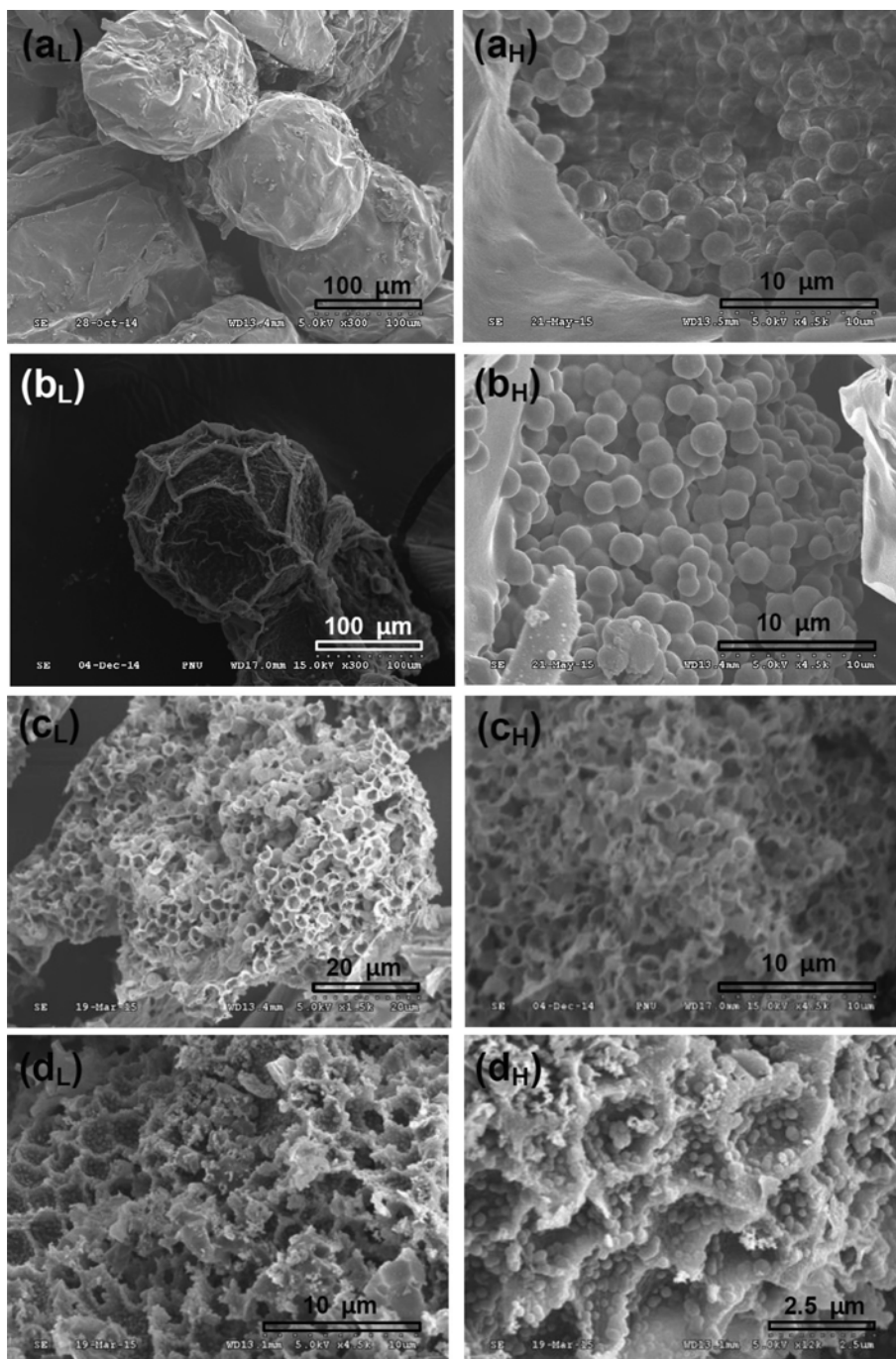


Fig. 2. SEM microphotographs of (a) PMMA/TEOS particles, (b) PMMA/silica particles, (c) QIOS and (d) NZVI@QIOS.

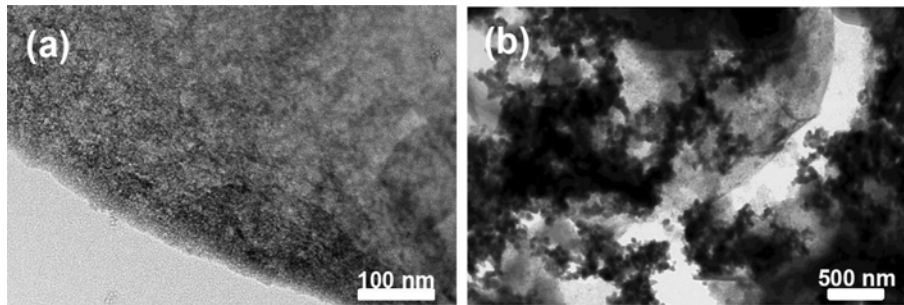


Fig. 3. TEM microphotographs of porous silica supported NZVI (NZVI@QIOS).

rugated and is quite different from the previous appearance, which means that solid silica was formed in the surface of PMMA particles. After the sol-gel reaction process, a complete removal of organic materials from the PMMA particles containing silica was carried out by a calcination process maintained at 500 °C for 5 hours. A SEM microphotograph (Fig. 2:  $c_L$  and  $c_H$ ) of the material obtained by the completion of calcination process clearly shows that porous silica was successfully prepared and its shape has a likeness of an inverted opal structure [14]. The obtained porous silica is called quasi-inverse opal silica (QIOS) in this study. The Brunauer-Emmett-Teller (BET) analysis results combined with Barrett-Joyner-Halenda (BJH) analysis regarding the QIOS obtained in this study showed a high surface area (375.4 m<sup>2</sup>/g) and fine pore size (average 76.5 nm). The NZVI particles were immobilized on the porous silica by the wet impregnation process and the SEM microphotographs (Fig. 2:  $d_L$  and  $d_H$ ) of them clearly show that solid NZVI particles (2-150 nm) were immobilized on the surface of porous silica (QIOS).

A TEM microphotograph of the NZVI@QIOS confirms that NZVI particles are present on the silica surface (Fig. 3), and they were produced according to the following reversible reaction showing the reduction of Fe(III) to metallic Fe<sup>0</sup> [4].

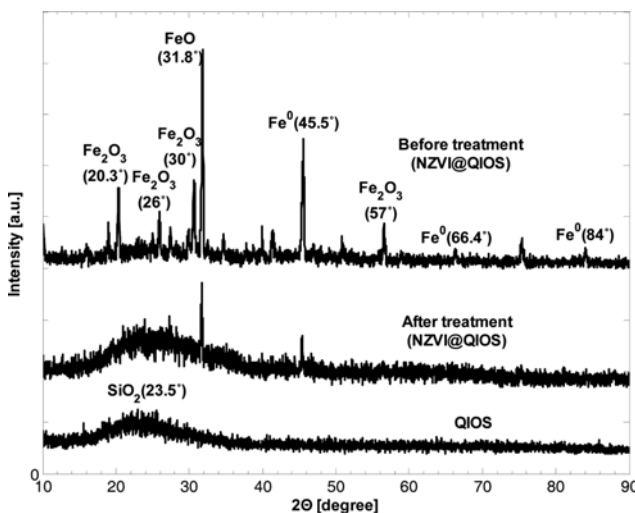
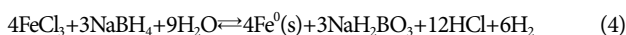


Fig. 4. XRD patterns of QIOS, NZVI@QIOS-Before treatment and NZVI@QIOS-After treatment.

Fig. 4 shows the XRD patterns for the porous silica itself (QIOS) and two kinds of the QIOS supported NZVI, which are the NZVI@QIOS before and after the Cr(VI) removal treatment process (NZVI@QIOS-Before treatment & NZVI@QIOS-After treatment). A broad diffraction peak at the  $2\theta$  of 23.5° regarding the QIOS is assigned to amorphous silica and the apparent peaks at the  $2\theta$  of 45.5° (1,1,0), 66.4° and 84° are attributed to the zero-valent iron ( $\alpha$ -Fe) in the QIOS supported NZVI (NZVI@QIOS-Before treatment) [15]. The XRD spectrum regarding the NZVI@QIOS before the Cr(VI) removal treatment process (NZVI@QIOS-Before treatment) shows a number of conspicuous peaks for the two types of crystalline iron oxides, which are FeO (31.8°) [16] and Fe<sub>2</sub>O<sub>3</sub> (20.3°, 26°, 30°, 57°) [17].

## 2. Reductive Removal of Cr(VI) from the Aqueous Hexavalent Chromium Solution

A specific amount of the QIOS supported NZVI (NZVI@QIOS) was added into the aqueous K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution at the specified concentration of hexavalent chromium ion, and it brought about a reductive removal of Cr(VI) from the solution. Fig. 5 shows that the removal efficiency of hexavalent chromium ion highly decreases with the increase of an initial concentration of hexavalent chromium ion in the aqueous K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution, [Cr(VI)]<sub>0</sub>, which means a steep increase of the ratio of Cr(VI) to [Cr(VI)]<sub>0</sub> as shown in the right

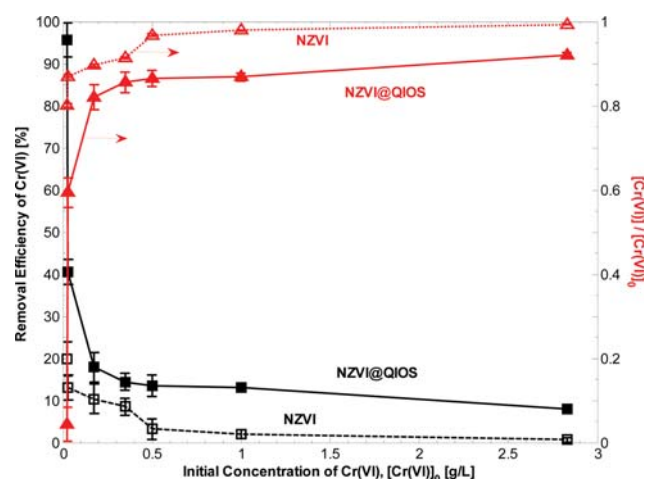


Fig. 5. Removal efficiency of hexavalent chromium ion depending on the initial concentration of hexavalent chromium ion in the aqueous K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution at pH 2.

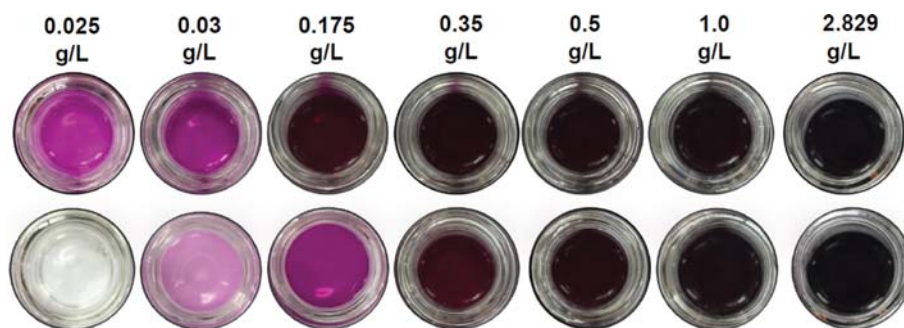


Fig. 6. Color change of Cr(II)-diphenylcarbazone complex depending on  $[\text{Cr(VI)}]_0$ ; top and bottom pictures - before and after adding NZVI@QIOS.

y-axis of Fig. 5. A removal efficiency of hexavalent chromium ion in this study is defined as follows:

$$\text{RE}(\%) = \frac{[\text{Cr(VI)}]_0 - [\text{Cr(VI)}]}{[\text{Cr(VI)}]_0} \times 100 \quad (5)$$

where  $[\text{Cr(VI)}]$  is a concentration of hexavalent chromium ion remained in the solution after the Cr(VI) removal treatment process. This experimental observation that a  $[\text{Cr(VI)}]_0$  increase adversely affects a Cr(VI) removal efficiency coincides with the previous reports [5,6,8] regarding the application of silica supported  $\text{Fe}^0$  nanocomposites for the removal of Cr(VI). It reveals addition of the NZVI@QIOS removed over 95.6% of a hexavalent chromium ion from the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution at 0.025 g/L of  $[\text{Cr(VI)}]_0$ ; however, a Cr(VI) removal efficiency at 2.829 g/L of  $[\text{Cr(VI)}]_0$  highly decreased to about 7.9%. The addition of the unsupported NZVI to the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution was also tried for comparison, and the results for both a Cr(VI) removal efficiency and the ratio of Cr(VI) to  $[\text{Cr(VI)}]_0$  are presented in Fig. 5. Note that a hexavalent chromium ion was removed at most 19.9% from the solution at 0.025 g/L of  $[\text{Cr(VI)}]_0$  in case of using the unsupported NZVI.

Fig. 6 shows that a magenta color (Fig. 6-Top) of the Cr(II)-diphenylcarbazone complex, which is the reaction product of Cr(VI) and DPC, completely disappeared and it turned colorless (Fig. 6-Bottom) by treating the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution at 0.025 g/L of  $[\text{Cr(VI)}]_0$  with the NZVI@QIOS. The disappearance of magenta color in the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution by adding the NZVI@QIOS indicates that Cr(VI) was virtually removed from the solution. The magenta color (Fig. 6-Top) appearing in the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution at 0.03 g/L of  $[\text{Cr(VI)}]_0$  faded into a light pink (Fig. 6-Bottom) after the completion of a Cr(VI) removal treatment process. With an increase of  $[\text{Cr(VI)}]_0$  in the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, the magenta color of the Cr(II)-diphenylcarbazone complex gradually darkened (Fig. 6-Top), and thus a discoloration of magenta color, which is a color change from top to bottom, caused by a reductive removal of Cr(VI) with the NZVI@QIOS, became unclear. Another clear indication that a Cr(VI) in the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution was removed by adding the NZVI@QIOS to the solution was confirmed by an experimental observation for a color change of the solution from black opaque state to white transparent, which occurred in less than 10 minutes.

The effect of pH and treatment time on the removal efficiency of hexavalent chromium ion from the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is

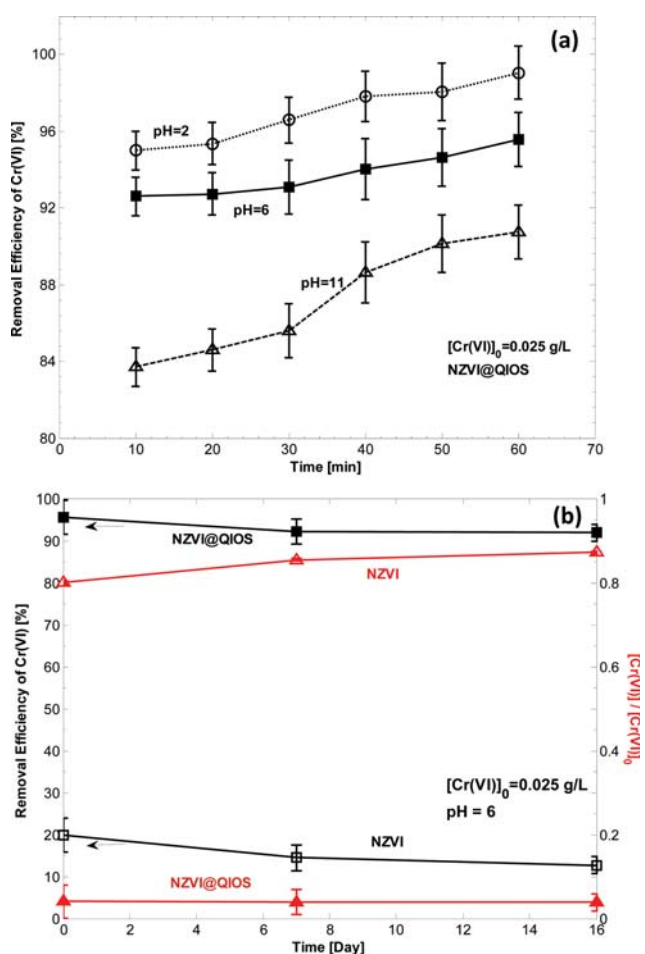


Fig. 7. Effect of pH and treatment time on the hexavalent chromium ion removal efficiency (a); hexavalent chromium ion removal efficiency depending on the time elapsed after preparation (b).

shown in Fig. 7(a). It shows that the removal efficiency of Cr(VI) from the solution reached an equilibrium value after 50 minutes from the start of Cr(VI) removal treatment process. The hexavalent chromium ion at 50 minutes after adding the NZVI@QIOS to the solution was removed as much as 98.1% at pH 2, 94.6% at pH 6 and 90.2% at pH 11, which means that the removal efficiency of Cr(VI) could be improved by changing the solution state from

basic (pH 11) to acidic condition (pH 2). The application of the NZVI@QIOS prepared in this study could remove hexavalent chromium ion over 90% from the aqueous  $K_2Cr_2O_7$  solution in highly basic state (pH 11). A decrease of Cr(VI) removal efficiency, which corresponds to the increase of the ratio of Cr(VI) to  $[Cr(VI)]_0$ , with the increase of pH value was also reported in the application of silica supported  $Fe^0$  nanocomposites [3,5,6].

One of the research objectives of this study was to secure stability against oxidation and agglomeration in the NZVI@QIOS. Fig. 7(b) reveals that the NZVI@QIOS prepared in this study shows an outstanding Cr(VI) removal efficiency without a drastic decline even more than two weeks after preparation. It still showed a high Cr(VI) removal efficiency as much as 91.9% when over 16 days since the QIOS supported NZVI had initially showed 95.6% of Cr(VI) removal efficiency. Note that a Cr(VI) removal efficiency (19.9%) in the unsupported nanoscale zero-valent iron (NZVI) is far lower than that (95.6%) in the NZVI@QIOS from the beginning of the preparation of samples, and it decreased from 19.9% to 12.8% after 16 days. A relatively low Cr(VI) removal efficiency for the NZVI could be attributed to either the occurrence of NZVI agglomeration or the formation of oxidized shell layer around the core NZVI, as previously mentioned.

### 3. Analysis of Cr(VI) Reactivity with NZVI@QIOS and NZVI

Chemical and valence states of the elements in the surface of the QIOS supported NZVI (NZVI@QIOS) were analyzed by using a X-ray photoelectron spectrometer, and a comparison was made of changes occurring before and after the Cr(VI) removal treatment process from the aqueous  $K_2Cr_2O_7$  solution. Whole XPS survey analysis of NZVI@QIOS before and after its utilization in the Cr(VI) removal treatment process is shown in Fig. 8(a) and Fig. 8(b), respectively. The principal elements on the surface of NZVI@QIOS were silicon, boron, carbon, oxygen, chromium and iron. Silicon and oxygen peaks are ascribed to the utilization of TEOS in the preparation of NZVI@QIOS, and the carbon peak is likely caused by carbon dioxide contamination during the whole sample preparation process [7]. Boron peak is also caused by a residue of sodium borohydride utilized in the conversion of Fe(III) into Fe(0) regarding the preparation of NZVI@QIOS [7]. Fig. 8(b) shows that a new peak for Cr(2p) around 577 eV [i.e., Cr(III)] apparently turned up and a peak for Fe(2p) around 706 eV [i.e., Fe(0)] was weakened after disposing of Cr(VI) with the NZVI@QIOS. A reduction of Cr(VI) to Cr(III) occurs in the aqueous  $K_2Cr_2O_7$  solution by adding the NZVI@QIOS to the solution, which is caused by the reaction of Cr(VI) with Fe(0). Thus, it results in the decrease of Fe(0)

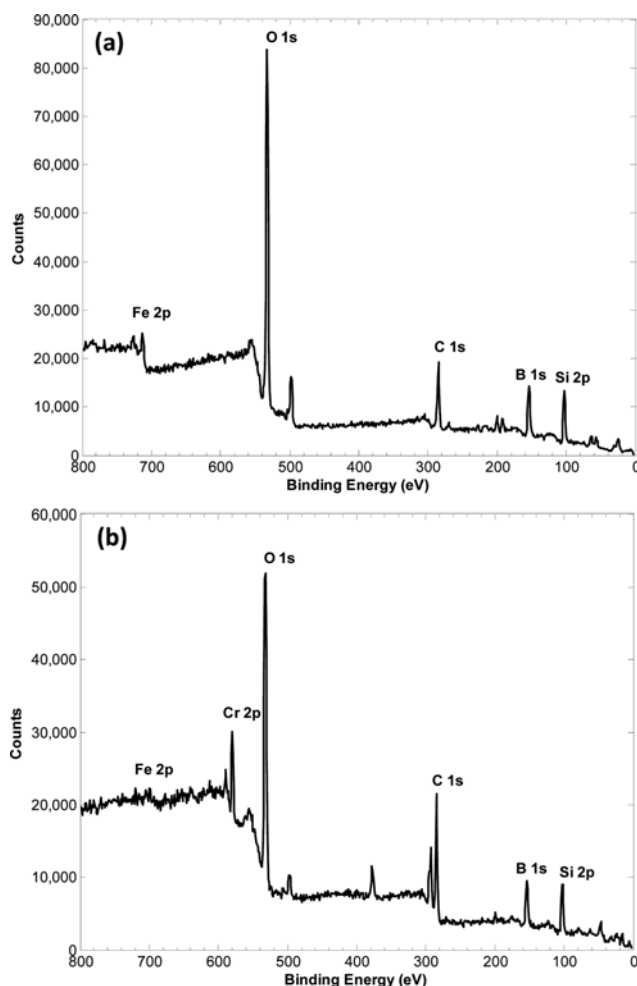


Fig. 8. Whole XPS survey analysis of NZVI@QIOS: Pristine NZVI@QIOS (a); retrieved NZVI@QIOS (b) after utilization in the Cr(VI) removal treatment process.

component and the formation of Cr(III) compound on the surface of NZVI@QIOS as shown in Fig. 8(b). XRD analysis results shown in Fig. 4 also show that most of the XRD peaks corresponding to Fe(0) disappeared after the completion of a treatment process for Cr(VI) removal from the aqueous hexavalent chromium solution.

With the deconvoluted spectra quantitative analysis results (Table 1), Fig. 9(a) and Fig. 9(b) show a deconvoluted XPS spectra analy-

Table 1. Deconvoluted XPS spectra quantitative analysis results for both iron (2p) and chromium (2p) on the surface of NZVI@QIOS and NZVI, respectively

	NZVI@QIOS		NZVI	
	Binding energy (eV)	Composition (%)	Binding energy (eV)	Composition (%)
Fe(III) [Fe(2p <sub>3/2</sub> )]	718.3	9.4	716.7	33.8
Fe(II) [Fe(2p <sub>3/2</sub> )]	711.4	90.6	711.6	66.2
Cr(VI) [Cr(2p <sub>3/2</sub> )]	579.4	48.1	580.1	87.3
Cr(III) [Cr(2p <sub>3/2</sub> )]	577.2	41.4	577.9	12.7
	576.2	10.5		

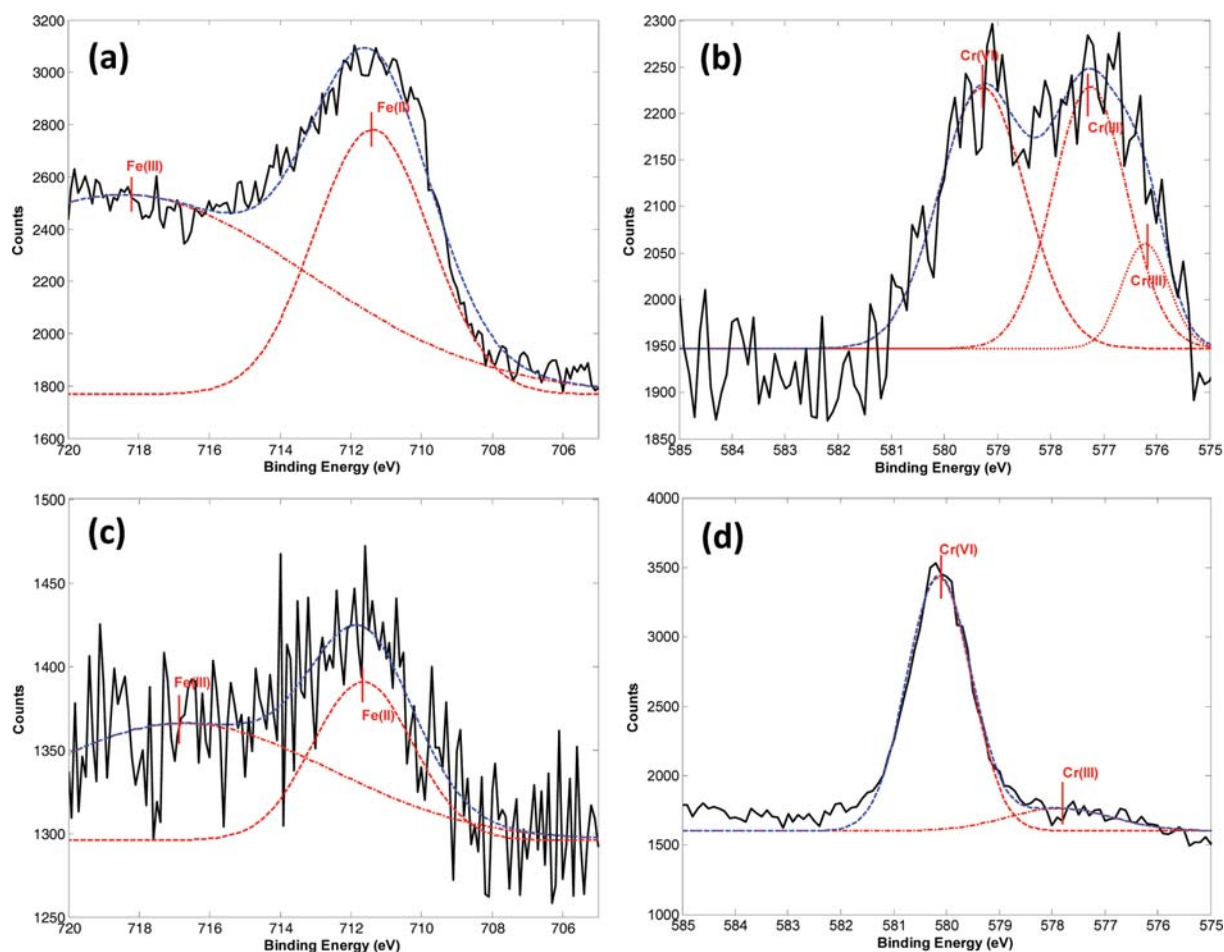


Fig. 9. Deconvoluted XPS spectra analysis: Iron (2p) for NZVI@QIOS (a); chromium (2p) for NZVI@QIOS (b); iron (2p) for NZVI (c); chromium (2p) for NZVI (d).

sis for iron 2p and chromium 2p on the surface of NZVI@QIOS retrieved after the treatment process for Cr(VI) removal from the aqueous  $K_2Cr_2O_7$  solution by reacting with the NZVI@QIOS. Note that no peak around 706 eV corresponding to Fe(0) [16,18,19] is observed in Fig. 9(a). There are shown a large peak at 711.4 eV (90.6%) for Fe(2p<sub>3/2</sub>) and a small peak at 718.3 eV (9.4%) for Fe(2p<sub>3/2</sub>) in Fig. 9(a), and these are assigned to Fe(II) (chromite, FeCr<sub>2</sub>O<sub>4</sub>) [18] and Fe(III) (Fe<sub>2</sub>O<sub>3</sub> or FeOOH) [18,19], respectively. It indicates that most of the NZVI, Fe(0), on the surface of QIOS was transformed into iron chromium oxide (FeCr<sub>2</sub>O<sub>4</sub>) (90.6%), which is a product of the reaction of Fe(0) with Cr(VI) in the aqueous  $K_2Cr_2O_7$  solution, and few of the Fe(0) components were oxidized (9.4%). Fig. 9(b) shows a large peak at 577.2 eV (41.4%) and a small shoulder peak at 576.2 eV (10.5%) for Cr(2p<sub>3/2</sub>), which are assigned to Cr(III) compound (e.g., Cr<sub>2</sub>O<sub>3</sub> or Cr(OH)<sub>3</sub>) [19] and chromite (Cr(III)) (FeCr<sub>2</sub>O<sub>4</sub>) [18], respectively. Another large peak at 579.4 eV (48.1%) is clearly shown in Fig. 9(b), which is assigned to Cr(VI) oxide [18,19]. The relative composition on the surface of NZVI@QIOS retrieved after the Cr(VI) removal treatment process is 48.1% for Cr(VI) (579.4 eV, Cr(VI) oxide) and 51.9% (41.4% at 577.2 eV plus 10.5% at 576.2 eV) for Cr(III).

With the deconvoluted spectra quantitative analysis results (Table

1), a deconvoluted XPS spectra analysis for iron 2p and chromium 2p on the surface of the unsupported nanoscale zero-valent iron (NZVI) retrieved after a treatment process for Cr(VI) removal from the aqueous  $K_2Cr_2O_7$  solution was made in Fig. 9(c) and Fig. 9(d), respectively. Fig. 9(c) shows two peaks at 711.6 eV (66.2%) for Fe(II) (Fe-2p<sub>3/2</sub>) and 716.7 eV (33.8%) for Fe(III) (Fe-2p<sub>3/2</sub>), which are assigned to chromite (FeCr<sub>2</sub>O<sub>4</sub>, Fe(II)) [18] and Fe<sub>2</sub>O<sub>3</sub> or FeOOH regarding Fe(III) [18,19], respectively. It reveals that a majority of two-thirds of the unsupported nanoscale zero-valent iron was used in a reduction of Cr(VI) to Cr(III) (chromite, FeCr<sub>2</sub>O<sub>4</sub>) and the rest of them remain in an oxidized state of iron, which is Fe<sub>2</sub>O<sub>3</sub> or FeOOH. The relative composition on the surface of NZVI retrieved after the treatment process of Cr(VI) removal is 33.8% for Fe(III) (716.7 eV) and 66.2% for Fe(II) (711.6 eV). Fig. 9(d) shows a distinct large peak at 580.1 eV and a marginal peak at 577.9 eV, which are assigned to Cr(VI) oxide [18,19] and Cr(III) compound (e.g., Cr<sub>2</sub>O<sub>3</sub> or Cr(OH)<sub>3</sub>) [19], respectively. The relative composition on the surface of NZVI retrieved after a treatment process of Cr(VI) removal is 87.3% for Cr(VI) at 580.1 eV and 12.7% for Cr(III) at 577.9 eV.

The relative composition for the reaction product obtained by reacting Cr(VI) with Fe(0), which corresponds to FeCr<sub>2</sub>O<sub>4</sub>, decreased

from 90.6% regarding the NZVI@QIOS to 66.2% for NZVI. The relative composition for Cr(III) also decreased from 51.9% regarding the NZVI@QIOS to 12.7% for NZVI. These differences between the NZVI@QIOS and NZVI regarding the relative composition of  $\text{FeCr}_2\text{O}_4$  and Cr(III) coincide with the experimental results regarding the Cr(VI) removal efficiency for the NZVI@QIOS and NZVI shown in Fig. 5, where 95.6% for the NZVI@QIOS remarkably decreased to 19.9% for NZVI. Any peak around 706 eV attributed to the  $2p_{3/2}$  peak of zero-valent iron is not observed in both Fig. 9(a) and Fig. 9(c), which means that zero-valent iron was transformed into other iron compound, which is either iron chromium oxide ( $\text{FeCr}_2\text{O}_4$ ) produced by the reaction of Fe(0) with Cr(VI) or Fe(III) compound ( $\text{Fe}_2\text{O}_3$  or  $\text{FeOOH}$ ) due to the oxidation of Fe(0). It has been known that the reduction of Cr(VI) by Fe(0) produces Cr(III), which may be further transformed into various types of Cr(III) compounds as shown in Eq. (6), (7), (8) and (9) [20]. Chromium occurs in the environment primarily in two valence states, trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. Exposure may occur from natural or industrial sources of chromium. Cr(III) is much less toxic than Cr(VI) as shown that it is  $0.5 \text{ mg/m}^3$  for Cr(III) and  $0.001 \text{ mg/m}^3$  for Cr(VI) at 8-hour time-weighted average (TWA) according to the National Institute for Occupational Safety and Health (NIOSH) standards. A chromite compound ( $\text{FeCr}_2\text{O}_4$ ), which is produced by the addition of NZVI@QIOS particles to the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution in this study, is a kind of natural mineral and could be easily separated out of the final solution by the sedimentation operation.

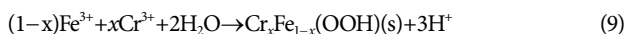
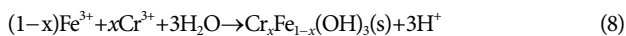
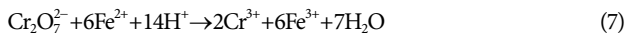
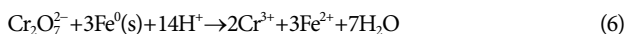


Fig. 10 shows the SEM microphotograph for the regenerated NZVI@QIOS particles, which were retrieved after a series operation of washing with water and ambient air drying for the solid particles separated out of the solution after the completion of a treatment process for Cr(VI) removal from the aqueous hexavalent chromium solution. The physical appearance of the porous silica remained intact and was free from NZVI particles on the surface. It indicates that it could be reused as a porous support for the immobilization of zero-valent iron.

## CONCLUSION

Porous silica having a distinctive structure named as “quasi-inverse opal silica (QIOS)” in this study was prepared by a polymer template method, which consists of a sol-gel reaction and calcination process. Porous silica (i.e., QIOS) showed as high as  $375.4 \text{ m}^2/\text{g}$  of surface area and  $76.5 \text{ nm}$  of a pore size. Nanoscale zero-valent iron particles less than  $150 \text{ nm}$  were successfully supported on the silica by the successive application of a reduction of iron(III) chloride to metallic zero-valent iron and then a wet impregnation process for the particle immobilization. Porous silica supported nanoscale zero-valent iron (NZVI@QIOS) was used for a reductive removal of hexavalent chromium ion from the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. Addition of a specified amount of NZVI@QIOS particles to the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, which is  $0.001 \text{ g}$  per  $1 \text{ mL}$  of the solution, showed a quite high removal efficiency of hexavalent chromium ion as much as 95.6% from the solution at  $0.025 \text{ g/L}$  of the initial concentration of hexavalent chromium ion (i.e.,  $[\text{Cr(VI)}]_0$ ). However, it revealed a removal efficiency of hexavalent chromium ion as low as 19.9% in case of adding a specific amount of unsupported nanoscale zero-valent iron (NZVI) to the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution at the same concentration of  $[\text{Cr(VI)}]_0$ . A removal efficiency of hexavalent chromium ion from the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution regarding the NZVI@QIOS was slightly reduced from 95.6% to 91.9% when passing 16 days after its preparation, and thus it is a clear indication of stability against probable oxidation and agglomeration occurring in the unsupported nanoscale zero-valent iron particles. Reactivity of chromium ion with the NZVI@QIOS and NZVI was analyzed by the application of X-ray photoelectron spectroscopy (XPS) in great detail. It clearly showed that a hexavalent chromium ion (Cr(VI)) was reduced to a trivalent chromium ion (Cr(III)), in which a reaction product resulting from the reaction of Fe(0) with Cr(VI) was a chromite compound ( $\text{FeCr}_2\text{O}_4$ ). A deconvoluted XPS spectra analysis regarding the NZVI@QIOS retrieved after a Cr(VI) removal process in the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution showed 90.6% of  $\text{FeCr}_2\text{O}_4$  at  $711.4 \text{ eV}$  and 9.4% of an iron oxide compound ( $\text{Fe}_2\text{O}_3$  or  $\text{FeOOH}$ ) at  $718.3 \text{ eV}$ , while in case of the application of NZVI the composition of  $\text{FeCr}_2\text{O}_4$  and iron oxide compound was 66.2% and 33.8%, respectively. A porous structure of the NZVI@QIOS prepared in this study was intact after its utilization in the reductive removal process of Cr(VI) from the aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. Accordingly, it could be reused as a support material for NZVI after its retrieving and washing.

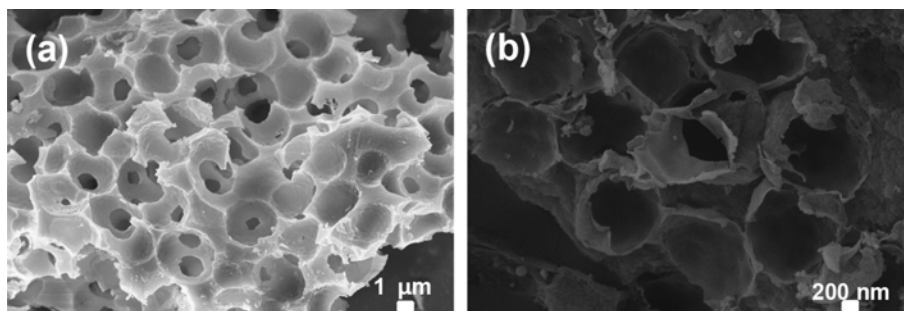


Fig. 10. SEM microphotographs for the regenerated “NZVI@QIOS” particles after employing them in the Cr(VI) removal treatment process.



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