

## Synthesis of Silica-supported Nanoiron for Cr(VI) Removal: Application of Box-Behnken Statistical Design (BBD)

(Sintesis Besi Nano Disokong Silika untuk Penyingkiran Cr(VI):  
Aplikasi Reka Bentuk Statistik Box-Behnken (BBD))

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### ABSTRACT

*This study aimed to optimize the condition of silica-supported nanoscale zero valent iron (NZVI/SiO<sub>2</sub>) synthesis by colloidal impregnation method. Box-Behnken design (BBD) was used as a tool to create and analyze the 17 synthesized conditions of NZVI/SiO<sub>2</sub> samples. The independent variables included ethanol concentration (0-100 vol%), amount of silica (0.025-0.125 g) and agitation speed (100-400 rpm). In addition, analysis of variance (ANOVA) for a response surface quadratic model was used to approximate statistical relationship of independent variables. The reducing performance of the synthesized NZVI/SiO<sub>2</sub> was examined through removal of Cr(VI) contaminated in water. The optimum of NZVI/SiO<sub>2</sub> synthesis was validated with 100 vol% of ethanol concentration, 0.075 g of silica amount, and 100 rpm of agitation speed. The materials were characterized using X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), and nitrogen adsorption/desorption which showed the existence of NZVI phase, composition, and morphology. The Cr(VI) removal efficiency of the NZVI/SiO<sub>2</sub> was tested further at the solution pH 4, 7 and 10 in comparison with that by pristine NZVI and silica-unsupported NZVI (NZVI + SiO<sub>2</sub>). Among the three materials, NZVI/SiO<sub>2</sub> presented the highest Cr(VI) removal, especially at pH 7 and 10 with 98 and 94.41%, within 60 min. This was due to the adsorption of Cr(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> precipitates over SiO<sub>2</sub> resulting in availability of NZVI/SiO<sub>2</sub>'s active sites. The proposed mechanism of Cr(VI) removal by NZVI/SiO<sub>2</sub> was also described.*

*Keywords: Box-Behnken design; chromium; NZVI; silica-supported nanoiron*

### ABSTRAK

*Kajian ini bertujuan untuk mengoptimalkan keadaan sintesis besi skala nano disokong silika bervalensi sifar (NZVI/SiO<sub>2</sub>) melalui kaedah pepadatan koloid. Reka bentuk Box-Behnken (BBD) telah digunakan sebagai alat untuk mencipta dan menganalisis sampel 17 keadaan sintesis NZVI/SiO<sub>2</sub>. Pemboleh ubah bebas termasuk kepekatan etanol (0-100 vol%), silika (0.025-0.125 g) dan kelajuan goncangan (100-400 rpm). Selain itu, analisis varians (ANOVA) untuk model quadratik tindak balas permukaan telah digunakan untuk menganggar hubungan statistik pemboleh ubah bebas. Pengurangan prestasi sintesis NZVI/SiO<sub>2</sub> telah disemak melalui penyingkiran Cr(VI) tercemar dalam air. Sintesis NZVI/SiO<sub>2</sub> optimum telah disahkan dengan 100 vol% kepekatan etanol, 0.075 g silika dan 100 rpm kelajuan goncangan. Bahan ini telah dicirikan menggunakan pembelauan sinar-x (XRD), mikroskop elektron imbasan dengan spektroskopi tenaga serakan sinar-x (SEM-EDX) dan nitrogen penyerapan/penyahjerapan yang menunjukkan kewujudan fasa NZVI, komposisi dan morfologi. Kecekapan penyingkiran Cr(VI) NZVI/SiO<sub>2</sub> telah diuji selanjutnya pada larutan pH 4, 7 dan 10 berbanding dengan NZVI asli dan NZVI tidak disokong silika (NZVI/SiO<sub>2</sub>). Antara ketiga-tiga bahan, NZVI/SiO<sub>2</sub> menunjukkan penyingkiran Cr(VI) tertinggi, terutamanya pada pH 7 dan 10 dengan 98 dan 94.41% dalam masa 60 minit. Ini disebabkan penyerapan Cr(OH)<sub>3</sub> dan mendakan Fe(OH)<sub>3</sub> ke atas SiO<sub>2</sub> yang mengakibatkan ketersediaan tapak aktif NZVI/SiO<sub>2</sub>. Mekanisme cadangan penyingkiran Cr(VI) oleh NZVI/SiO<sub>2</sub> turut dibincangkan.*

*Kata kunci: Besi nano disokong silika; kromium; NZVI; reka bentuk Box-Behnken*

### INTRODUCTION

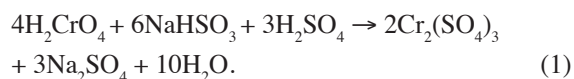
Modification of nanoscale zero valent iron (NZVI) is one of the most important ways to improve the removal efficiency of chromium contaminated in water (Fu et al. 2016; Li et al. 2016; Shih et al. 2015; Toli et al. 2016; Wu et al. 2015; Yirsaw et al. 2016; Zhou et al. 2015). Since chromium is widely applied in several kinds of industrial work such as metallurgy, industrial dyes, paint pigments, chrome

tanning and electroplating operations, it is mostly found in industrial wastewater (Liu et al. 2016; Padmavathy et al. 2016). In addition, chromium could be found in groundwater in regard to leaching from contaminated soil in mine (Coller-Myburgh et al. 2014). Due to its toxicity and carcinogenicity, the World Health Organization (WHO) has set a drinking water limit for chromium of 0.05 mg/L (WHO 2004). In order to avoid contamination of chromium

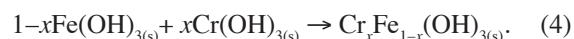
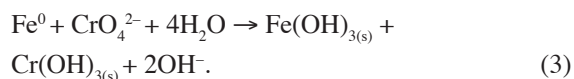
in natural water sources used for public supply, the removal of chromium from industrial wastewater and groundwater become necessary.

Generally, chromium exists in water in two oxidation states including Cr(III) and Cr(VI). However, Cr(VI) compounds are categorized as carcinogen and was confirmed to be 10- to 1000-fold more toxic than Cr(III) compounds (Katz et al. 1993). With the high water solubility of Cr(VI), it readily diffuses in the environment and accumulates in living cells (Anderson 1997; Costa 2003).

In conventional techniques, Cr(VI) is firstly reduced to Cr(III) using a chemical reducing agent, like NaHSO<sub>3</sub>, that reduces Cr(VI) to Cr(III) in the form of Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Afterwards, the reduced Cr(VI) can be removed as insoluble Cr(OH)<sub>3</sub> by precipitation using a coagulating agent, such as NaOH. The chemical equation is given in (1) and (2) (Chang et al. 2005, 2003; Chen et al. 2006; Guha & Bhargava 2005). Consequently, the treatment requires a significant amount of reducing and coagulating agent.



Recently, there was considerable interest in using NZVI to treat Cr(VI) contaminated in groundwater (Chang 2003). In this process, NZVI (Fe<sup>0</sup>) acts as a reducing agent or an electron donor, while CrO<sub>4</sub><sup>2-</sup> acts as reducible species or an electron acceptor, which is shown in (3) and (4) (Wu et al. 2015),



The reaction between Fe(OH)<sub>3(s)</sub> and Cr(OH)<sub>3(s)</sub> generated from the reduction of Cr(VI) using NZVI can produce Cr<sub>x</sub>Fe<sub>1-x</sub>(OH)<sub>3</sub> that has a low water solubility and readily precipitates (Sass & Rai 1987). Therefore, one advantage in using NZVI is that a coagulant is no longer needed. However, the efficiency of Cr(VI) reduction is decreased as the solution pH increases while the NZVI's surface might be blocked by the precipitated forms of Cr<sub>x</sub>Fe<sub>1-x</sub>(OH)<sub>3</sub> or Fe(OH)<sub>3</sub> (Wu et al. 2015). In order to prevent the blockage of undesired adsorptive substrates onto NZVI, not only decreasing of the solution pH but also supported NZVI and composited NZVI are the interesting alternatives to enhance Cr(VI) removal efficiency (Fu et al. 2016; Li et al. 2016; Toli et al. 2016; Wu et al. 2015).

A mixture of NZVI and silica (SiO<sub>2</sub>) was reported to be effective for Cr(VI) reduction (Oh et al. 2007; Powell et al. 1995). However, the mixture was not adhered together resulting in NZVI allowed the direct adsorption of precipitated Cr(III) onto its surface. Consequently, the available reactive surface area and Cr(VI) reduction rate

of NZVI was decreased. As a result, synthesized method as well as synthesized condition of silica-supported NZVI (NZVI/SiO<sub>2</sub>) is probably a key factor in improving the efficiency of Cr(VI) removal. It is, therefore, necessary to determine the condition of NZVI/SiO<sub>2</sub> synthesis that provides the highest Cr(VI) removal efficiency.

Box-Behnken design (BBD) has been used as a tool to determine optimal condition for desired responses in diverse studies, such as the optimization of dye removal by the laccase-mediator system (Dassi et al. 2012), Zn extraction from pyrometallurgical sludge in the steel manufacturing industry (Mocellin et al. 2015) and an azo dye batch adsorption (Tripathi et al. 2009). In addition, it was applied to optimize photocatalytic degradation system of paraquat (Tantriratna et al. 2011) and preparation of Fe-ZnO catalyst used for 2,4-dichlorophenol degradation (Kiattisaksiri et al. 2014). These studies confirmed that BBD could assist to disclose the optimum of each parameter by maximizing the response variables, and was suitable for optimizing the NZVI/SiO<sub>2</sub> synthesized condition in this study.

From previous study, some important synthesized condition parameters influenced the property and reducing activity of NZVI was reported. Agitation speed of 100 rpm compared with that of 300 rpm was investigated in mixing FeCl<sub>3</sub> solution and NaBH<sub>4</sub> droplets to synthesize NZVI (Tanboonchuy et al. 2012). It was found that the higher reducing power of NZVI was obtained at the higher agitation speed because of more dispersion and higher surface area of NZVI particles. Concentration of ethanol in the ethanol/water solvent was the one of parameter concerned with NZVI synthesis (Wu et al. 2016). Absolute ethanol concentration of 0-100 vol% showed the differences of NZVI characteristics (Wang et al. 2009). As the ethanol concentration increased, the particle size of NZVI decreased leading to its surface area increased. This was due to the lower polarity of ethanol/water solvent which encouraged the stabilized NZVI particles to disperse in the solvent and inhibited the particle agglomeration. Besides the agitation speed and concentration of ethanol; however, the amount of silica was addressed as the parameters involved in this study for NZVI/SiO<sub>2</sub> synthesis, as previously mentioned.

Thus, in this study, the BBD was applied to evaluate the optimal condition for the synthesis of NZVI/SiO<sub>2</sub>. The three parameters including the ethanol concentration, the amount of silica and the agitation speed were investigated. The synthesized NZVI/SiO<sub>2</sub> were then tested for their ability to reduce a 40 mg/L of Cr(VI) solution at three different pH values (4, 7 and 10) in direct comparison with pristine NZVI and silica-unsupported NZVI (NZVI + SiO<sub>2</sub>).

## RESEARCH METHODS

### MATERIALS

The chemical reagents used in this study were FeCl<sub>3</sub> (99%, Merck), NaBH<sub>4</sub> (> 96%; Merck), C<sub>2</sub>H<sub>5</sub>OH (99.99%, RCI Labscan) and SiO<sub>2</sub> extracted from rice husk (Tantriratna et al. 2011). The Cr(VI) stock solution was prepared by

dissolving  $K_2Cr_2O_7$  (99-100%, J.T. Baker) into deionized water (18.2 M $\Omega$ , Mill-Q).

#### SYNTHESIS METHOD OF NZVI/SiO<sub>2</sub> AND NZVI + SiO<sub>2</sub>

NZVI/SiO<sub>2</sub> and NZVI + SiO<sub>2</sub> were synthesized by *in-situ* and *ex-situ* colloidal impregnation method, respectively. For the *in-situ* synthesis, SiO<sub>2</sub> was mixed with FeCl<sub>3</sub> in ethanol/water solvent for 7 h with vigorous stirring. Then, it was added by NaBH<sub>4</sub> solution (0.25 M, 50 mL) at pumping rate of 10 mL/min. The mixture was stirred for 30 s after completion of NaBH<sub>4</sub> addition. The NZVI/SiO<sub>2</sub> occurred in the mixture was separated using a magnet and then applied immediately to examine its Cr(VI) removal efficiency. For *ex-situ* method, SiO<sub>2</sub> was not mixed with FeCl<sub>3</sub> in the first step, but added after NZVI synthesis. The material obtained from *ex-situ* method was named as NZVI + SiO<sub>2</sub>.

#### BOX-BEHNKEN STATISTICAL DESIGN

In order to optimize synthesized condition of the NZVI/SiO<sub>2</sub>, the 3-level 3-factor BBD was calculated to design the experiment and analyze the experimental data for validating the independent variables which affect to the Cr(VI) removal efficiency. The highest Cr(VI) removal efficiency was evaluated by BBD in a range of independent variables limits. The independent variables included X<sub>1</sub> = ethanol concentration (0, 50 and 100 vol%), X<sub>2</sub> = amount of silica (0.025, 0.075 and 0.125 g) and X<sub>3</sub> = agitation speed (100, 250 and 400 rpm). The set up range values of the independent variables were created as low (-1), middle (0) and high (+1). The BBD generated 17 different synthesized conditions of the NZVI/SiO<sub>2</sub> samples used for 17 experimental runs of Cr(VI) removal as shown in Table 1. Analysis of variance (ANOVA) for a response surface quadratic model was used to approximate statistical relationship of independent variables.

#### CHARACTERIZATION OF NZVI/SiO<sub>2</sub>

Both fresh and spent NZVI and NZVI/SiO<sub>2</sub> were analyzed for their crystallinity phases by X-ray diffraction (XRD) instrument (Model D8 Advance, Bruker AXS, Germany). The morphology of the materials was characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) technique (S-3000N, Hitachi, Japan). Additionally, the Brunauer-Emmett-Teller (BET) analysis of nitrogen adsorption/desorption (NOVA 1200e, Quantachrome, USA) was used to measure the specific surface area of the fresh NZVI, NZVI/SiO<sub>2</sub> and NZVI + SiO<sub>2</sub>.

#### BATCH EXPERIMENTS FOR CR(VI) REMOVAL

Synthetic wastewater was prepared with an initial Cr(VI) concentration of 40 mg/L in 500 mL to which 0.1 g of NZVI/SiO<sub>2</sub> was then introduced into the reaction beaker. Batch experiment was performed under 200 rpm at 30°C. At 40 min, 20 mL of the synthetic Cr(VI) wastewater was collected and measured by UV-vis spectrophotometer (V-630, Jasco, Germany) at  $\lambda_{max} = 540$  nm via colorimetric method. The percentage of Cr(VI) removal efficiency was applied to BBD and ANOVA. Then, the NZVI/SiO<sub>2</sub> experimental run which provided the optimal synthesized condition and the highest Cr(VI) removal efficiency was tested in the same manner at initial Cr(VI) solution pH 4, 7 and 10 to compare with NZVI and NZVI + SiO<sub>2</sub>.

#### RESULTS AND DISCUSSION

##### OPTIMIZATION OF NZVI/SiO<sub>2</sub> SYNTHESIZED CONDITION

The NZVI/SiO<sub>2</sub> was synthesized by modifying the procedure described by Zhang et al. (2011). In this study, three independent variables including ethanol concentration, amount of silica and agitation speed were investigated in

TABLE 1. Combinatorial optimization of NZVI/SiO<sub>2</sub> synthesis for Cr(VI) removal (controlled condition: Cr(VI) initial concentration = 40 mg/L, NZVI/SiO<sub>2</sub> = 0.1 g/500 mL, sampling time = 40 min and temperature = 30°C)

Run order	Independent variables (determined by BBD)			Results (Cr(VI) removal (%))	
	Ethanol concentration (vol%)	Amount of silica (g)	Agitation speed (rpm)	Experimental	Predicted (from equation (6))
1	0	0.075	400	46.17	43.73
2	50	0.125	100	47.96	48.00
3	50	0.125	400	32.68	36.56
4	0	0.025	250	37.82	30.69
5	100	0.075	100	89.63	78.35
6	0	0.075	100	48.86	55.17
7	50	0.075	250	63.82	61.04
8	50	0.025	400	41.04	36.56
9	50	0.075	250	62.11	61.04
10	50	0.075	250	61.45	61.04
11	50	0.025	100	45.60	48.00
12	50	0.075	250	59.20	61.04
13	100	0.025	250	58.07	53.87
14	100	0.125	250	43.26	53.87
15	0	0.125	250	31.82	30.69
16	50	0.075	250	61.71	61.04
17	100	0.075	400	66.43	66.91

terms of their effects upon the resultant of Cr(VI) removal efficiency. The experimental runs with respect to NZVI/SiO<sub>2</sub> synthesized conditions were designed by BBD. With BBD, the experimental and predicted Cr(VI) removal efficiency is given in Table 1. The significant changes in those parameters were then evaluated by ANOVA. A quadratic regression model was found to fit reasonably to the experimental results. In Figure 1(a), the plot of the residuals against the percentage of Cr(VI) removal collected from all experiments mostly fell on the reference diagonal line. Thus, the results fitted with a normal distribution could verify the assumption of ANOVA. In Figure 1(b), the analysis of ANOVA residuals on the fitted values showed a somewhat scattered and non-specific distribution away from zero. This indicated the variance of the residuals was constant leading to the validation of the ANOVA.

The relationship of the ethanol concentration, amount of silica and agitation speed to the percentage of Cr(VI) removal at 30°C is shown in Figure 2. The optimized condition for Cr(VI) removal appeared to be ethanol concentration of 90-100 vol%, silica amount of 0.07-0.08 g and agitation speed of 100-120 rpm. Besides the contour and surface plots for Cr(VI) removal, the main effects of the independent variables are presented clearly in Figure 3. It was showed that the ethanol concentration of 100%, silica amount of 0.075 g and agitation speed of 100 rpm were the most effective synthesized condition for Cr(VI) removal. Because ethanol provides lower polarity than water, it can be used to stabilize the NZVI, which is neutral, during the synthesis. However, aggregation of the NZVI is rarely formed in the lower polar solvent (Wang et al. 2009; Wu et al. 2016) leading to the improvement of Cr(VI) removal efficiency by NZVI/SiO<sub>2</sub> synthesized in the ethanol/water solvent. On the other hand, while silica is capable of directly absorbing the precipitate of Cr(III), it also releases a proton from the silanol group (Oh et al. 2007) that can increase the solubility of the precipitated Cr(III). Thus, the inclusion of higher proportion of silica reduced the Cr(VI) removal level. For agitation speed, it was observed that the resulting size of the NZVI particle is

smaller at a high agitation, which implies a likely increased adsorption surface on the NZVI particles (Tanboonchuy et al. 2012). However, the decreased particle size and increased total surface area per unit mass of nanoparticles may result in some of the surfaces not being fully coated by silica during the synthesis. Therefore, the low agitation speed was still more suitable than the high agitation speed.

#### CHARACTERISTICS OF NZVI/SiO<sub>2</sub>

The NZVI and NZVI/SiO<sub>2</sub> were synthesized under the optimal condition determined by BBD. The materials were characterized by XRD, SEM-EDX and BET surface area.

The XRD patterns of fresh and spent NZVI and NZVI/SiO<sub>2</sub> are presented in Figure 4. The peaks at 2θ of 44.55° and 64.85° confirmed the existing of Fe<sup>0</sup> and the successful synthesis of NZVI and NZVI/SiO<sub>2</sub> (Wang et al. 2009; Wu et al. 2016). After 60 min of Cr(VI) removal, the peaks of the spent NZVI and NZVI/SiO<sub>2</sub> demonstrated the NZVI corrosion products including magnetite (Fe<sub>3</sub>O<sub>4</sub>), maghemite (Fe<sub>2</sub>O<sub>3</sub>) and lepidocrocite (FeOOH) (Shih et al. 2015; Zhou et al. 2015). The intensity of the peak at 44.55° was lower in the spent NZVI than that in the spent NZVI/SiO<sub>2</sub> (Shih et al. 2015). It was due to the reaction between NZVI and Cr(VI) that formed the Cr(III) precipitate and resulted in a decreased level of available surface area and active sites on the NZVI. In contrast, for the NZVI/SiO<sub>2</sub>, the Cr(III) precipitate can form together with the SiO<sub>2</sub> component resulting in an increase of the remaining unreacted surface of the NZVI, which was congruent with the previously reported (Kohn et al. 2005; Vikesland et al. 2003).

The SEM analysis, in Figure 5, shows that the NZVI had a higher degree of particle agglomeration compared to that for NZVI/SiO<sub>2</sub>. The addition of SiO<sub>2</sub> to the NZVI resulted in an increased dispersion of the NZVI particles which in turn provided a higher contact area between NZVI and Cr(VI). In addition, the EDX profiles showed that the major elemental components were O, Cl, Fe and Si for the NZVI/SiO<sub>2</sub> sample (Wu et al. 2016) except Cl originated from the FeCl<sub>3</sub>·6H<sub>2</sub>O as a precursor of the NZVI synthesis.

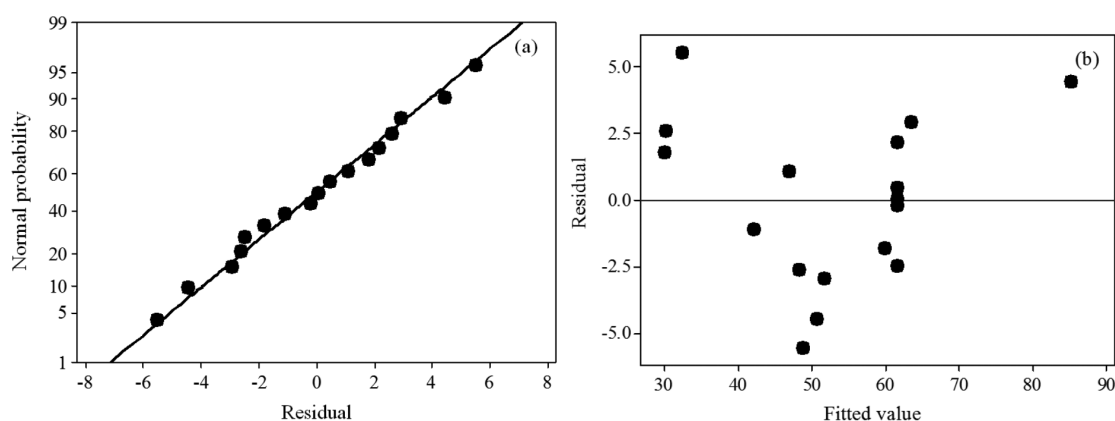


FIGURE 1. (a) Plot of normal probability and residual and (b) residual versus fitted value plot (Response is the percentage of Cr(VI) removal)



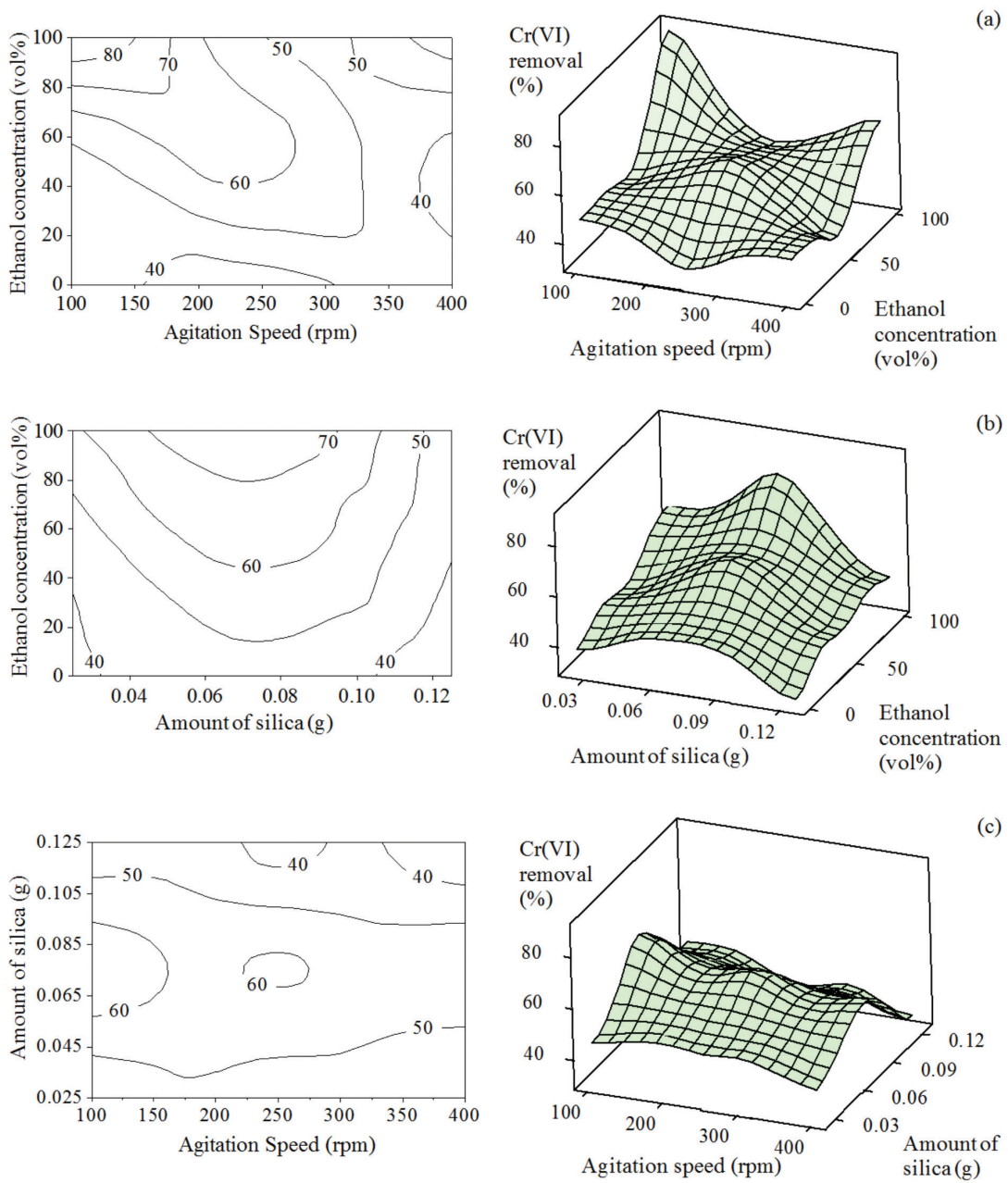


FIGURE 2. Contour and surface plots for Cr(VI) removal on the effects of (a) ethanol concentration and agitation speed, (b) ethanol concentration and amount of silica and (c) amount of silica and agitation speed

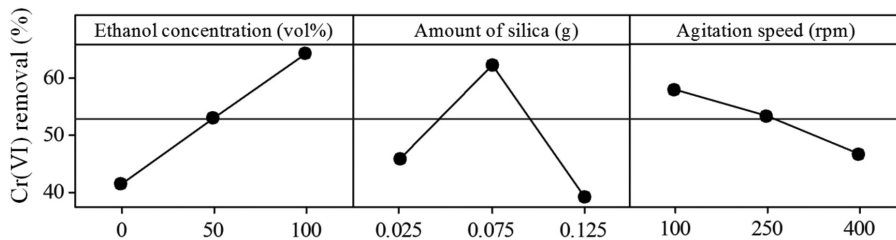


FIGURE 3. Main effect plots for Cr(VI) removal (controlled condition: Cr(VI) initial concentration = 40 mg/L, NZVI/SiO<sub>2</sub> = 0.1 g/500 mL, sampling time = 40 min and temperature = 30°C)

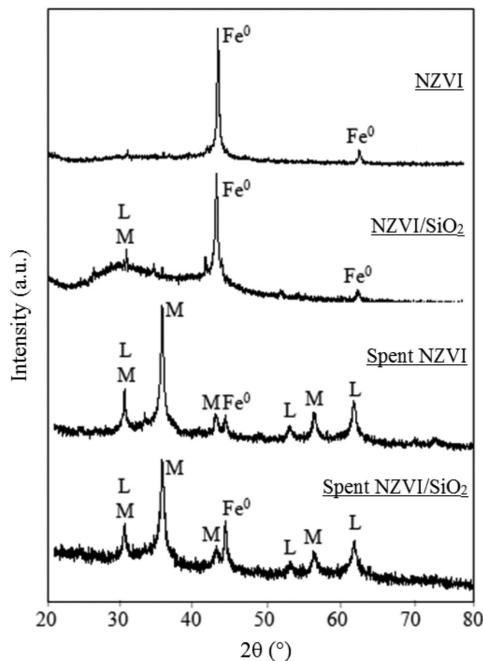


FIGURE 4. XRD patterns of NZVI, NZVI/SiO<sub>2</sub>, spent NZVI and spent NZVI/SiO<sub>2</sub> (M= magnetite (Fe<sub>3</sub>O<sub>4</sub>) and/or maghemite (Fe<sub>2</sub>O<sub>3</sub>) and L = lepidocrocite (FeOOH))

The BET results showed that the specific surface areas of the NZVI and NZVI/SiO<sub>2</sub> were 12.35 and 8.89 m<sup>2</sup>/g, respectively, while that of SiO<sub>2</sub> was 240.12 m<sup>2</sup>/g. The surface areas of the NZVI and NZVI/SiO<sub>2</sub> tended to insignificantly different by this physical property.

#### QUADRATIC REGRESSION MODEL

From ANOVA in Table 2, an approximate function of the Cr(VI) removal efficiency based on the quadratic regression model is derived as presented in (5);

$$Y = 59.66 + 11.59X_1 - 3.35X_2 - 5.72X_3 + 2.02X_1^2 - 18.93X_2^2 + 1.1X_3^2 - 2.2X_1 * X_2 - 5.13X_1 * X_3 - 2.68X_2 * X_3, \quad (5)$$

where Y is the predicted percentage of Cr(VI) removal; and X<sub>1</sub>, X<sub>2</sub>, and X<sub>3</sub> represent the ethanol concentration, amount of silica and agitation speed, respectively. The correlation between the observed values and those predicted from (5) was high, with a coefficient of determination (R<sup>2</sup>) of 0.917. However, only the ethanol concentration (X<sub>1</sub>), agitation speed (X<sub>3</sub>) and the interaction between the amount of silica and the amount of silica (X<sub>2</sub><sup>2</sup>) were significant. The ANOVA of the response surface reduced quadratic model which excluded the terms of the insignificant factors is shown in Table 3. The final equation obtained in terms of the significant factors is given in (6).

$$Y = 61.04 + 11.59X_1 - 5.72X_3 - 18.76X_2^2. \quad (6)$$

The ANOVA result for the Cr(VI) removal showed an F-value of 22.43. The model represents the significant

factors that affect the response as there is only a 0.01% chance that is due to noise and insignificant lack of fit of F-value (1.29) related to the pure error. Thus, the model shown in (6) can be used to reasonably estimate the percentage Cr(VI) removal under these conditions. The predicted values for Cr(VI) removal by NZVI/SiO<sub>2</sub> were accordingly calculated, as shown in Table 1, while Figure 6 shows the close agreement between the experimental values and the predicted values from (6) with R<sup>2</sup> = 0.8381.

#### COMPARISON OF Cr(VI) REMOVAL PERFORMANCE

The removal of Cr(VI) from solution at 30°C by the NZVI/SiO<sub>2</sub>, along with that for NZVI + SiO<sub>2</sub> and the pure NZVI, at pH 4, 7 and 10 is shown in Figure 7. At pH 4, the pure NZVI gave the highest percentage of Cr(VI) removal (94.37%) while the NZVI/SiO<sub>2</sub> and NZVI + SiO<sub>2</sub> did not exhibit any significant removal. In contrast, the NZVI/SiO<sub>2</sub> showed the highest percentage of Cr(VI) removal with 98 and 94.41% at pH 7 and 10, respectively, within 60 min whereas the removal efficiency of Cr(VI) by the pure NZVI were decreased.

The reported pH<sub>pzc</sub> for the synthesized NZVI is 7.8 (Li et al. 2008; Tanboonchuy et al. 2011). At a solvent pH above 7.8, the pristine NZVI surface has a negative charge and CrO<sub>4</sub><sup>2-</sup> is formed. The same charge creates an electrostatic repulsion that results in a decreased removal of Cr(VI). In addition, the Cr(VI) can be reduced to Cr(III) by NZVI and then precipitated in the form of Cr(OH)<sub>3</sub>. When the solution pH is above 7, the Cr(III) is co-precipitated with Fe(OH)<sub>3</sub>, as shown in (3) and (4)

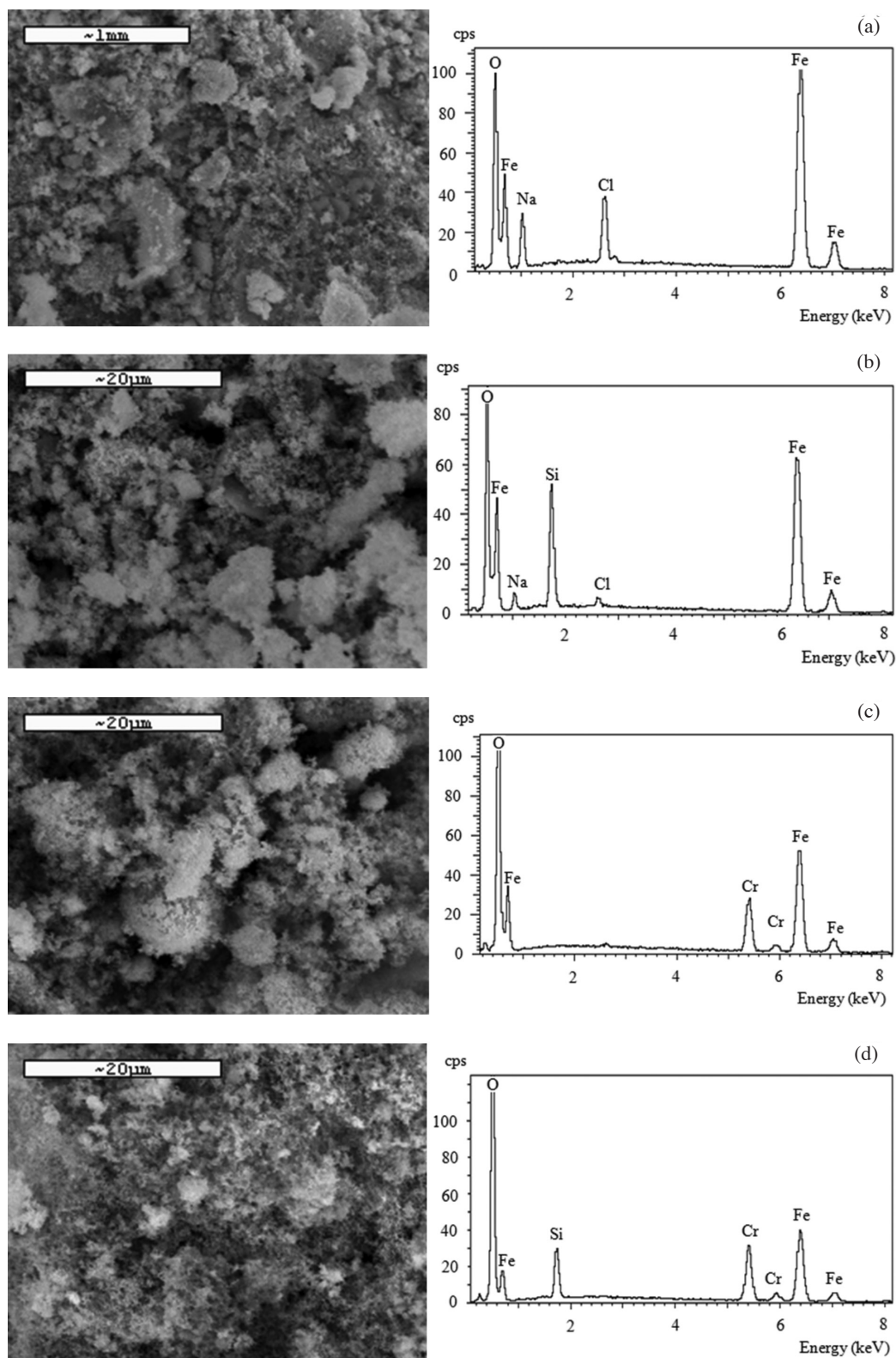


FIGURE 5. SEM images and EDX analysis of (a) NZVI (b) NZVI/SiO<sub>2</sub>, (c) spent NZVI and (d) spent NZVI/SiO<sub>2</sub>

(Astrup et al. 2000; Blowes et al. 1997; Powell & Puls 1997). Therefore, the Cr(III) can be adsorbed onto the NZVI's surface without the adsorption of Cr(OH)<sub>3</sub> and

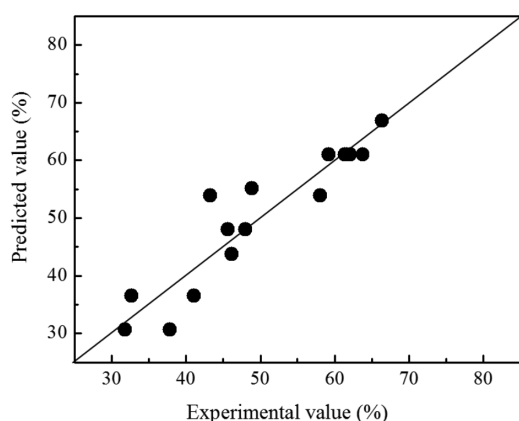
Fe(OH)<sub>3</sub> by SiO<sub>2</sub>. This led to the inferiority of the pristine NZVI to remove Cr(VI) comparing to NZVI/SiO<sub>2</sub> and NZVI + SiO<sub>2</sub>.

TABLE 2. ANOVA for response surface quadratic model

Term	Coefficient	F-Value	P-value
Constant	59.66	-	-
Ethanol concentration (vol. %) ( $X_1$ )	11.59	26.89	0.0013
Amount of silica (g) ( $X_2$ )	-3.35	2.25	0.1774
Agitation speed (rpm) ( $X_3$ )	-5.72	6.54	0.0377
Ethanol concentration (vol. %)*Ethanol concentration (vol. %) ( $X_1*X_1$ )	2.02	0.49	0.5333
Amount of silica (g)*Amount of silica (g) ( $X_2*X_2$ )	-18.93	2.63	0.0005
Agitation speed (rpm)*Agitation speed (rpm) ( $X_3*X_3$ )	1.10	0.72	0.7325
Ethanol concentration (vol. %)*Amount of silica (g) ( $X_1*X_2$ )	-2.20	0.43	0.5084
Ethanol concentration (vol. %)*Agitation speed (rpm) ( $X_1*X_3$ )	-5.13	37.77	0.1488
Amount of silica (g)*Agitation speed (rpm) ( $X_2*X_3$ )	-2.68	0.13	0.4245
Model		8.60	0.0049
Lack of fit		1.33	0.3825
R-squared = 0.9171			
Adj R-squared = 0.8104			

TABLE 3. ANOVA for the response surface reduced quadratic model

Term	Coefficient	F-Value	P-value
Constant	61.04	-	-
Ethanol concentration (vol. %) ( $X_1$ )	11.59	25.58	0.0002
Agitation speed (rpm) ( $X_3$ )	-5.72	6.22	0.0269
Amount of silica(g)*Amount of silica (g) ( $X_2*X_2$ )	-18.76	35.48	< 0.0001
Model		22.43	0.0001
Lack of fit		1.29	0.4326
R-squared = 0.8381			

FIGURE 6. Parity plot of actual and predicted Cr(VI) removal ( $R^2 = 0.8381$ )PROPOSED MECHANISM OF CR(VI) REMOVAL BY NZVI/SiO<sub>2</sub>

The proposed mechanism of Cr(VI) removal over NZVI/SiO<sub>2</sub> is shown in Figure 8. Firstly, the CrO<sub>4</sub><sup>2-</sup> was reduced by NZVI to form Cr<sup>3+</sup>, Fe<sup>3+</sup> and OH<sup>-</sup> ions. Then, under the alkaline environment of OH<sup>-</sup>, the Cr<sup>3+</sup> and Fe<sup>3+</sup> were readily precipitated in the forms of Cr(OH)<sub>3(s)</sub> and Fe(OH)<sub>3(s)</sub>. Moreover, the Cr<sup>3+</sup>, Fe<sup>3+</sup> and OH<sup>-</sup> ions could possibly combine simultaneously to form Cr<sub>x</sub>Fe<sub>1-x</sub>(OH)<sub>3(s)</sub>

complexes (Wu et al. 2015). All the precipitated species can directly adsorb on the SiO<sub>2</sub> surface, as confirmed by the EDX profiles (Figure 5). Since the surface availability of SiO<sub>2</sub> is considerably higher than that of NZVI, the precipitation of the various Cr(OH)<sub>3(s)</sub>, Fe(OH)<sub>3(s)</sub> and Cr<sub>x</sub>Fe<sub>1-x</sub>(OH)<sub>3(s)</sub> complexes would mainly take place on the SiO<sub>2</sub> surface. With less precipitation on the NZVI surface, the NZVI accordingly retained a higher level of available active sites for further Cr(VI) removal, as shown in steps (1)-(3) in Figure 8.

## CONCLUSION

The NZVI/SiO<sub>2</sub> was synthesized via colloidal impregnation method. The optimal synthesized condition of NZVI/SiO<sub>2</sub> was designed, analyzed and validated by BBD and ANOVA. The ethanol concentration, amount of silica and agitation speed influenced the efficiency of the NZVI/SiO<sub>2</sub> to remove Cr(VI) and were set as the independent variables. The morphology of NZVI/SiO<sub>2</sub> can be significantly controlled by effects of ethanol concentration and agitation speed. The optimal condition for the synthesis of NZVI/SiO<sub>2</sub> for Cr(VI) removal was 100 vol% of ethanol concentration, 0.075 g of silica amount and 100 rpm of agitation speed. The Cr(VI) removal efficiency was highly obtained over the NZVI/SiO<sub>2</sub> compared to that by the pristine NZVI and NZVI



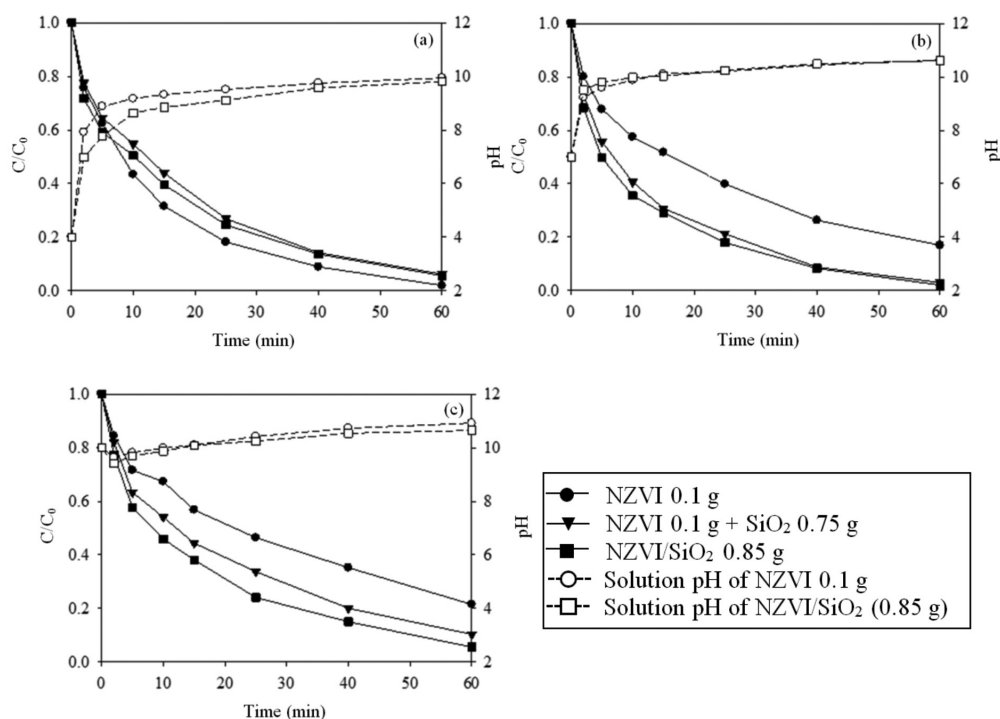


FIGURE 7. Cr(VI) removal by synthesized materials at initial Cr(VI) solution pH (a) 4, (b) 7, and (c) 10 (controlled condition: Cr(VI) initial concentration = 40 mg/L, NZVI/SiO<sub>2</sub> = 0.1 g/500 mL, sampling time = 40 min and temperature = 30°C)

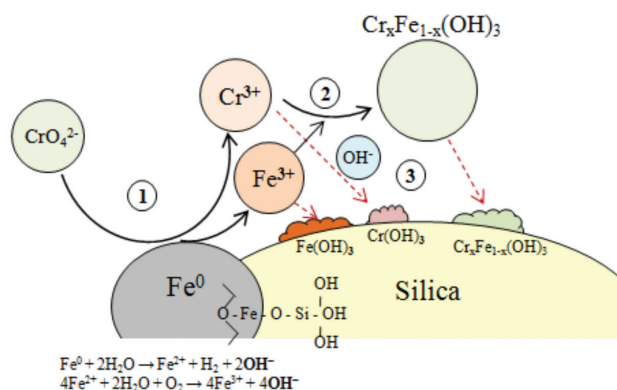


FIGURE 8. Proposed mechanism of Cr(VI) removal by NZVI/SiO<sub>2</sub>

+ SiO<sub>2</sub>, especially at pH 7 and 10 with 98 and 94.41% of Cr(VI) removal, respectively, at 60 min. As SiO<sub>2</sub> played the important role on the adsorption of Cr(OH)<sub>3(s)</sub>, Fe(OH)<sub>3(s)</sub> and Cr<sub>x</sub>Fe<sub>1-x</sub>(OH)<sub>3(s)</sub> precipitates, which were by-product of Cr(VI) reduction, the available active sites of NZVI/SiO<sub>2</sub> were still remained for further Cr(VI) removal.

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