In-situ Reductive Regeneration of nZVI Immobilized on Cellulose for Atom Efficient Cr(VI) Adsorption

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Supporting information

Experimental Section

1. Chemicals

All chemicals used in the experiments were of analytical grade. Microcrystalline cellulose Avicel PH-101® was procured from Sigma Aldrich (St. Louis, USA). Deionized water was used for preparation of all the reagents. Total chromium and Cr(VI) were determined using diphenylcarbazide method. Iron in C-nZVI was analysed by phenanthroline method, upon HNO_3/H_2SO_4 digestion of the sample. Hydroxyl amine hydrochloride and acetic acetate buffer for oxime reaction.

2. Synthesis of Microcrystalline Cellulose Immobilized Zerovalent Iron Nanoparticle (C-nZVI)

MCC (3.50 g) was dissolved in 250 ml of deionized water for the synthesis of C-nZVI at room temperature. Upon dissolution, $FeCl_3$ (1.50 g) was added to reaction mixture with vigorous stirring. To this solution was added dropwise a 20% aqueous $NaBH_4$ solution (100 mL) at a rate of 1 mL/min. Upon subsequent addition of $NaBH_4$ solution, the reaction mixture turned black with foam formation. Excess of borohydride solution was added for complete reduction leading to the formation of suspended material. The black material was separated by filtration, washed with methanol and dried in vacuo.

3. Physical Characterization of C-nZVI

Fourier Transformed Infra-Red (FTIR) spectra of Microcrystalline Cellulose (MCC), C-nZVI and chromium adsorbed C-nZVI, were recorded on a BRUKER TENSOR 27 instrument. Morphological characterization was obtained upon analysis of gold coated sample using Scanning Electron Microscope (SEM JSM-6610LV) and EDX using oxford. BET surface area experiment was carried out by Belsorp adsorption/desorption data analysis software under nitrogen environment using BEL Inc. (Japan) Surface Area Analyzer for the determination of pore diameter and surface area of the nZVI particle. Thermogravimetric analysis (TGA) was carried out at a heating rate of $10^{\circ}C/min$ upto $500^{\circ}C$ using a Shimadzu TG-60H TG analyzer under N_2 environment. X-ray diffraction (XRD) analysis was carried out using Pan analytical X'Pert-Pro model. X-Ray photoelectron spectroscopy (XPS) measurment was performed using PHOBIOS HSA3500 DLSEGD analyzer with excitation energy of 1486.74eV. CHNS elemental analysis was carried out using Thermo Finningan elemental analyser.

4. Adsorption and Kinetics for Cr(VI) Adsorption by C-nZVI

Adsorption experiments were carried out by maintaining a 100 mL of Cr(VI) solution (1-10 mg/L) at pH 3. C-nZVI (10 mg) were added to the solutions and maintained under constant shaking at 25 ± 2°C for 24 h.

For the kinetic study, 10 mg of C-nZVI were added to a 100 mL solution of 10 mg/L Cr(VI) solution. The sample was, shaken at 25 ± 2°C for 24 h. A small aliquot was drawn and analysed at various time interval. The concentration of Cr(VI) adsorbed was plotted as a function of time. The kinetic data was studied for its pseudo–first order and pseudo-second order kinetic behaviour.

4.1. Adsorption Experiment

A stock solution (1mM) of chromium was prepared in deionized water by dissolving 294 mg of $K_2Cr_2O_7$ in 1000 mL of deionized water. Standard Cr(VI) solution (1-10) ppm, were prepared for adsorption study. To a 100 mL of Cr(VI) solution (1-10 ppm), 10 mg of C-nZVI was added and sample shaked at 200 rpm and 25 ± 2°C for 24h. upon equilibration for 24h the samples were filtered and analyzed.

4.2. pH optimization study

The influence of pH on Cr(VI) removal was studied by varying the pH from 3-10. The pH of 3 ppm Cr(VI) solution was adjusted to 3,5, 7,8 and 10 using 1N HCl and NaOH solution. To a 100 ml of pH adjusted Cr(VI) solution, 10 mg of C-nZVI was added and shaken at 25 ± 2°C, 200 rpm for 24h. The solution was filtered and analyzed for chromium.

5. Scanning Electron Microscopy (SEM)

To added 600 mg/L of C-nZVI to 40 mg/L of Chromium solution, maintain at pH3 and shaked for 24 h at 200 rpm. Filter the solution. The chromium adsorbed material was analyzed using SEM-EDX for the presence of chromium on to C-nZVI.
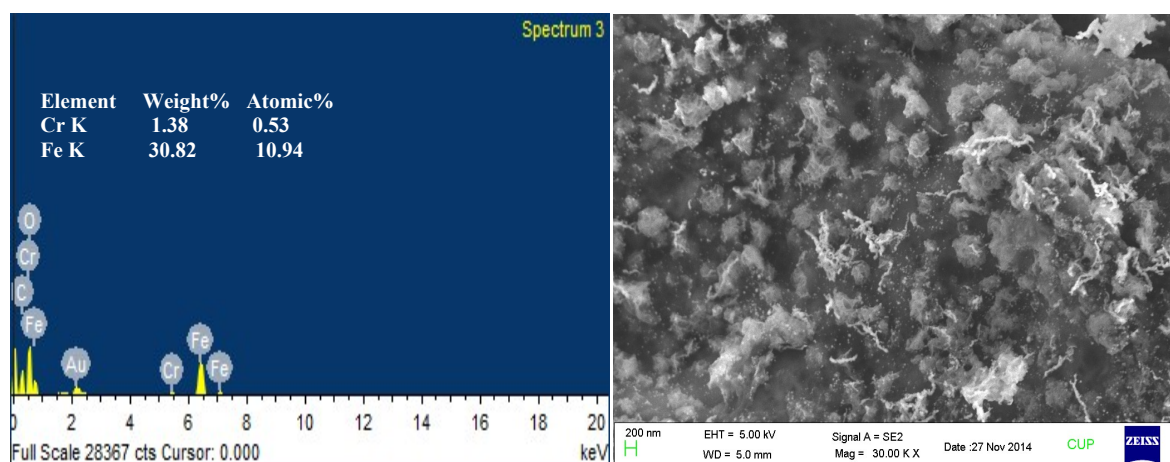
Figure S1: [A] SEM-EDX of chromium adsorbed C-nZVI [B] SEM image of Chromium adsorbed C-nZVI

6. Surface ara analysis using BET analyzer

CSMCRI, Bhavnagar

ASAP 2010 V5.02 H   Unit 1   Serial # 2529   Page 15

        Sample: MC-NW
      Operator: CSMCRI, Bhavnagar
     Submitter:
    File Name: C:\ASAP2010\2015\000-304.SMP

        Started: 7/30/2015 12:35:48PM Analysis Adsorptive: N2
      Completed: 7/30/2015 8:11:31PM   Analysis Bath: 77.56 K
   Report Time: 8/4/2015 10:15:15AM Thermal Correction: No
  Sample Weight: 0.2160 g   Smoothed Pressures: No
Warm Freespace: 16.0502 cm³   Cold Freespace: 49.1835 cm³
          MEASURED
Equil. Interval: 10 secs   Low Pressure Dose: None

Summary Report

Area

Single Point Surface Area at P/Po 0.27789150 :   9.8117 m²/g

BET Surface Area: 9.5581 m²/g

BJH Adsorption Cumulative Surface Area of pores
   between 17.000000 and 3000.000000 A Diameter: 8.3041 m²/g

BJH Desorption Cumulative Surface Area of pores
   between 17.000000 and 3000.000000 A Diameter: 20.2141 m²/g

Volume

Single Point Adsorption Total Pore Volume of pores less than
   875.5091 A Diameter at P/Po 0.97737708:   0.049088 cm³/g

BJH Adsorption Cumulative Pore Volume of pores
   between 17.000000 and 3000.000000 A Diameter: 0.048126 cm³/g

BJH Desorption Cumulative Pore Volume of pores
   between 17.000000 and 3000.000000 A Diameter: 0.049216 cm³/g

Pore Size

Adsorption Average Pore Diameter (4V/A by BET):   205.4316 A

BJH Adsorption Average Pore Diameter (4V/A):   231.8160 A

BJH Desorption Average Pore Diameter (4V/A):   97.3892 A
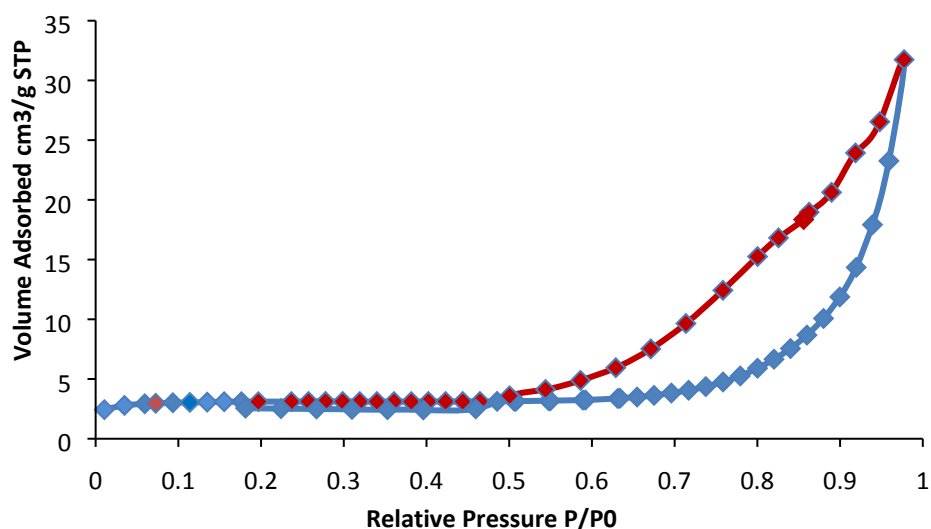
**Figure S2: Nitrogen desorption-adsorption isotherm for C-nZVI**

7. CHNS elemental analysis

CHNS elemental analysis of MCC, Fe^{3+} treated cellulose and chromium adsorbed C-nZVI were carried out for the investigation of cellulose dialdehyde. The iron was removed from cellulose by stirred the material in 1N HCl solution for 1h. The solution was washed with dionised water 3-4 time, filter and dried. The amount of dialdehyde in cellulose is determined by shiff base oxime reaction. The presence of nitrogen in cellulose dialdehyde determined the amount dialdehyde in cellulose.

### a. Preparation of sample for CHNS analysis using Oxime reaction

The dride 100 mg of cellulose dialdehyde was placed in 250 ml round bottom flask. To this added 1.39 g of hydroxyl amine hydrochloride and 100 ml of 0.1M acetic acetate buffer. The mixture was stirried for 48 h. The sample was washed with deionised water, filtered and dride.

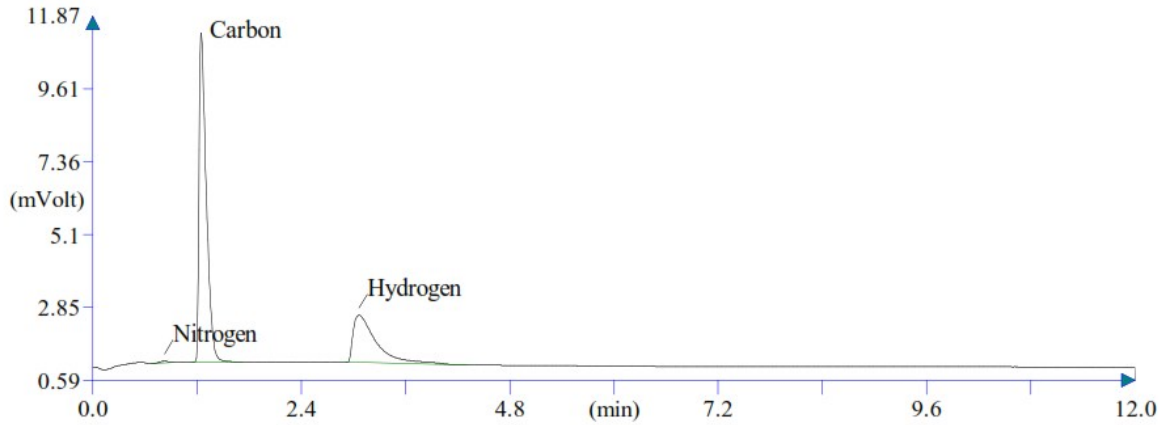The results of CHNS elemental analysis are given below:
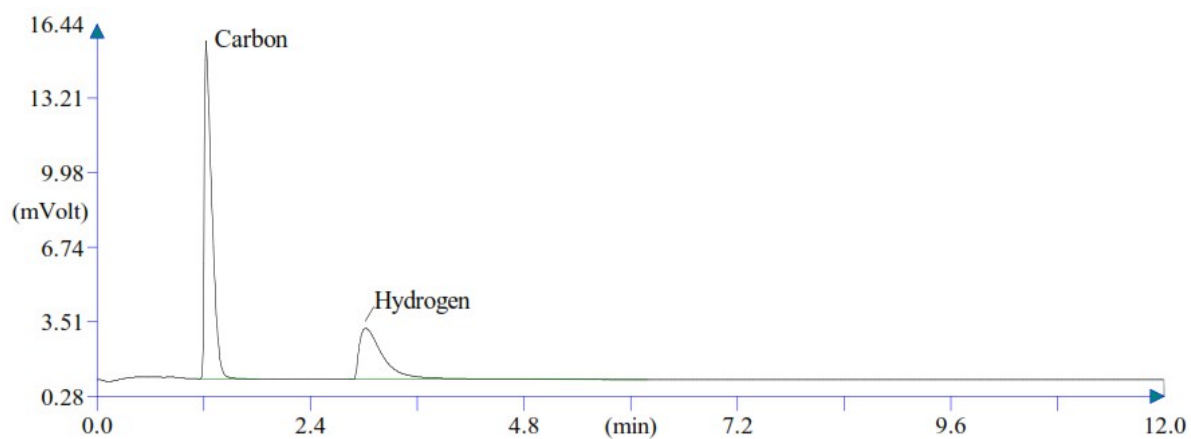
```
Retention Time    Component Name    Element %
(min)
----------------  ----------------  ---------
1.225             Carbon            41.460
3.017             Hydrogen           6.291
                                    ------
                                    47.751
```

Figure S3: CHN analysis of MCC
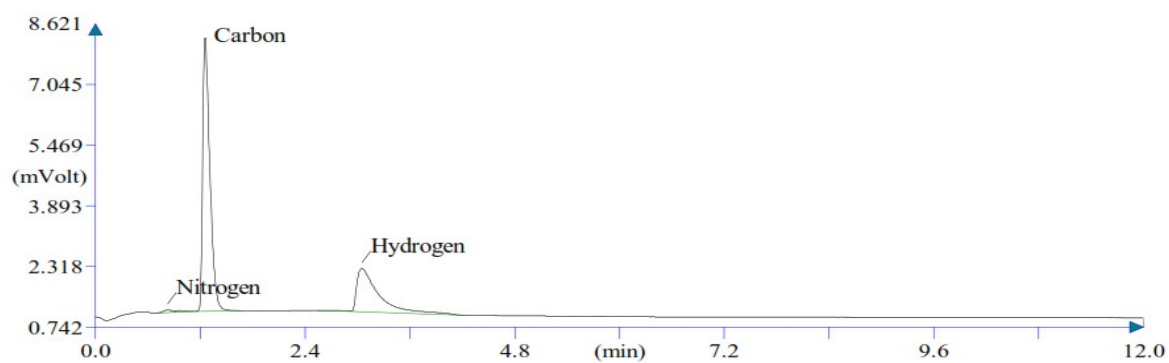

```
Retention Time    Component Name    Element %
(min)
----------------  ----------------  ---------
0.825             Nitrogen           1.244
0.958                                0.000
1.258             Carbon            41.802
2.575                                0.000
3.050             Hydrogen           6.352
                                    ------
                                    49.398
```

Figure S4: CHN analysis of Fe^{3+} treated cellulose

```
Retention Time      Component Name      Element %
(min)
- - - - - - - - - - - - - -     - - - - - - - - - - - - - -     - - - - - - - - - -
0.825               Nitrogen            0.702
1.250               Carbon              42.353
3.067               Hydrogen            5.974
                                        _____
                                        49.028
```

Figure S5: CHN analysis of Cr(VI) adsorbed C-nZVI cellulose dialdehyde

8. Freundlich Adsorption isotherm model

Freundlich adsorption isotherm model is applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption.

For a solute in solution as an adsorbate the nolinear equation is given by

$$qe = K_f C_e 1/n$$

Where *Kf* and *n* are the constants, which measure the adsorption capacity and intensity; respectively.

The equation is frequently used in the linear form by taking the logarithm of both sides.

Where *Ce* and *n* is equilibrium concentration of the adsorbate

$$l0gq_e = logK_f + \frac{1}{n} logC_e$$

Thus, plotting $log q_e$ versus $log C_e$ gives a straight line graph with a slope of $\left(\dfrac{1}{n}\right)$ and intercept of $log K_f$

The Freundlich constant K_f and $\dfrac{1}{n}$ are related to the adsorption capacity and the adsorption intensity, respectively.
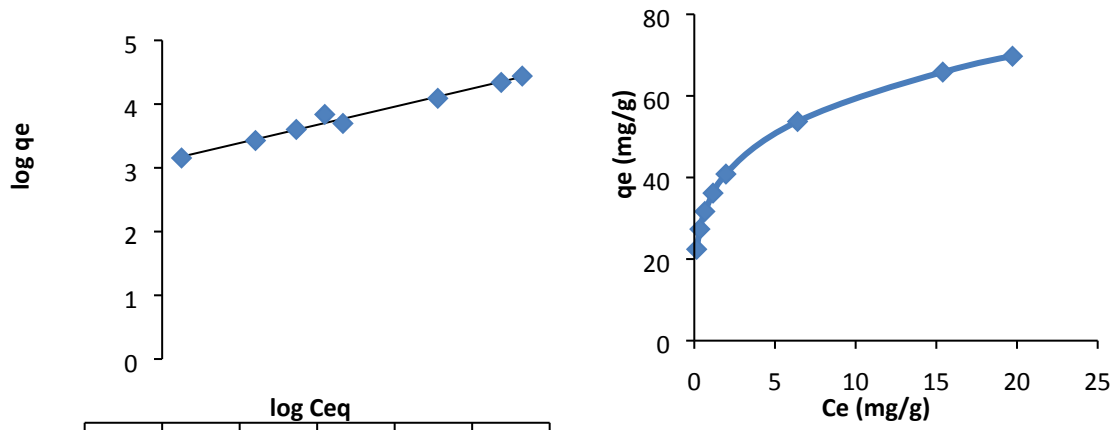
Fig S6: [A] Linear and [B] Nonlinear Freundlich isotherm of Cr(VI) adsorption by C-nZVI

The nonlinear fit for freundlich isotherm was also calculated in origin software. The parameters, *Kf* and *n* value were given below.

Parameters

		Value	Standard Error
Qe	n	4.31721	0.64675
	K	34.94676	2.73532

Iterations Performed = 1
Total Iterations in Session = 7
Fit converged - tolerance criterion satisfied.

Statistics

	Qe
Number of Points	8
Degrees of Freedom	6
Reduced Chi-Sqr	40.77263
Residual Sum of Squares	244.63575
R Value	0.95267
Adj. R-Square	0.89219
Root-MSE (SD)	6.38534
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged

Summary

	n		K		Statistics	
	Value	Standard Error	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
Qe	4.31721	0.64675	34.94676	2.73532	40.77263	0.89219

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
Qe	Regression	2	17309.49758	8654.74879	212.26862	6.55931E-6
	Residual	6	244.63575	40.77263		
	Uncorrected Total	8	17554.13333			
	Corrected Total	7	2647.24444			

Fitted Curves Plot
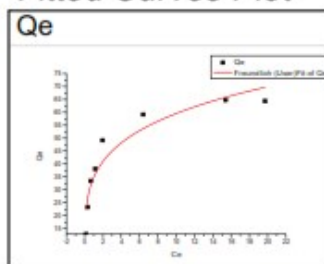
Residual vs. Independent Plot

9. **Langmuir Adsorption isotherm model**

Irvine Langmuir (1916) provided a kinetic explanation of the isotherm assuming the following.

(a) All the adsorption site are equivalent and uniformly spread over the surface of the adsorbent

(b) Adsorbed molecule do not interact

(c) Adsorption on the surface is independent of each entity of the adsorbate

(d) Only monolayer adsorption of adsorbate occurs on the adsorbent

This isotherm is related to the amount of gas adsorbed on the surface of adsorbent to the partial pressure of the gas.

Thus, based on this approximation, the derived equation known as Non-linear Langmuir equation is

$$q_e = \frac{q_{max}k_L C_e}{1 + k_L C_e}$$

This model was used to show the relationship between amount of Chromium adsorbed at equlibrium q_e in mg/g, equilibrium solute concentration C_e in mg/L, q_{max} is q_e for a complete monolayer in mg/g, K_L is constant.

The value of Langmuir constant q_{max} and K_L value obtanined by linear regression method using following equation,

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}}$$

The values of K_L and q_{max} were computed from the slope and intercept of the linear Langmuir plot of $1/q_e$ and $1/C_{eq.}$
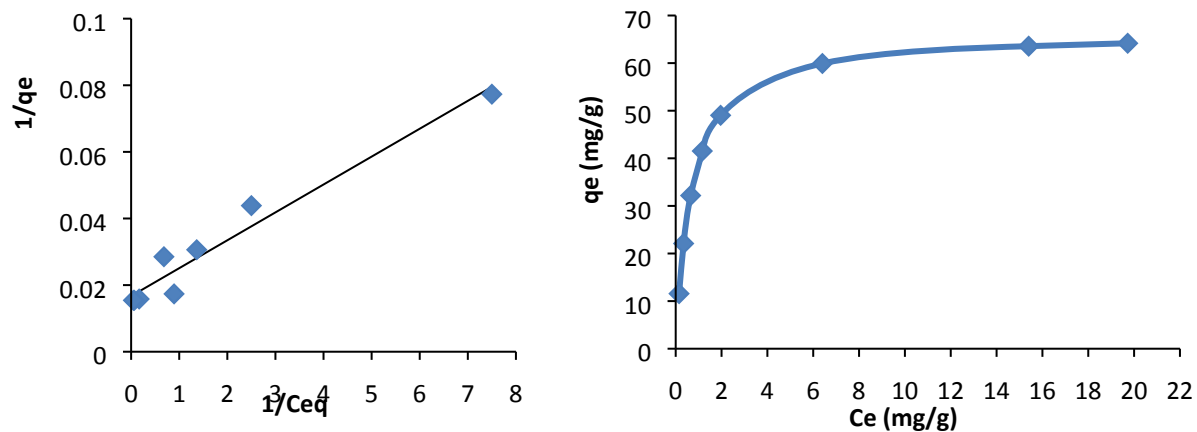
Figure S7: [A] Linear and [B] Nonlinear Langmuir isotherm of Cr(VI) adsorption by C-nZVI

The nonlinear fit for Langmuir isotherm was calculated in origin software. The parameters, K_L and q_{max} value were given below.

Parameters

		Value	Standard Error
Qe	Qm	66.42808	1.20113
	K	1.43857	0.10719

Iterations Performed = 1
Total Iterations in Session = 9
Fit converged - tolerance criterion satisfied.

Statistics

|	Qe
Number of Points	8
Degrees of Freedom	6
Reduced Chi-Sqr	3.06364
Residual Sum of Squares	18.38186
R Value	0.99652
Adj. R-Square	0.9919
Root-MSE (SD)	1.75033
Number of Iterations	1
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged

Summary

	Qm		K		Statistics	
	Value	Standard Error	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
Qe	66.42808	1.20113	1.43857	0.10719	3.06364	0.9919

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
Qe	Regression	2	17535.75147	8767.87573	2861.91073	2.86383E-9
	Residual	6	18.38186	3.06364		
	Uncorrected Total	8	17554.13333			
	Corrected Total	7	2647.24444			

Fitted Curves Plot
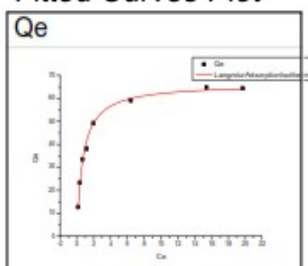
Residual vs. Independent Plot
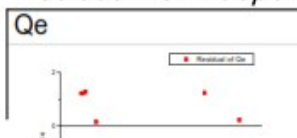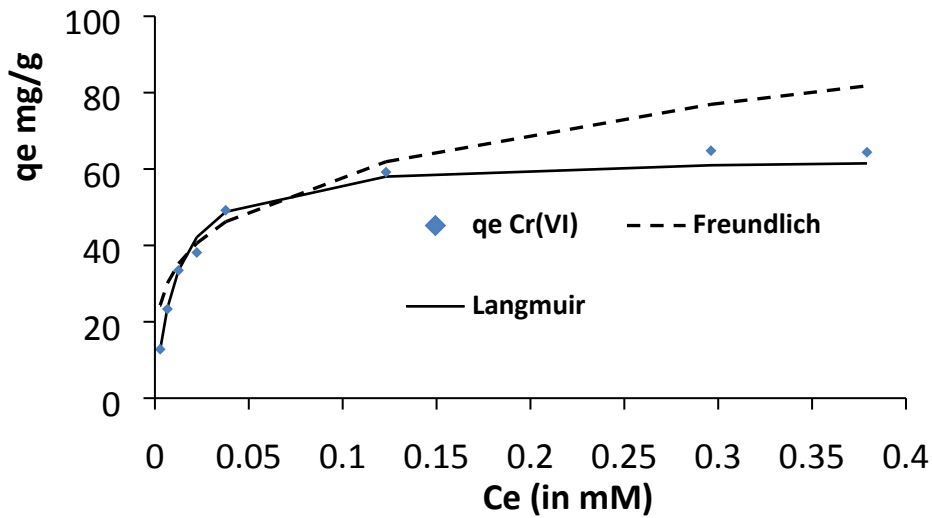
Figure S8: Linear adsorption isotherm of Cr(VI) adsorption by C-nZVI

10. Multilayer adsorption model

Multilayer adsorption is a multilayer surface phenomenon in which the first layer of adsorbate on adsoebent a solid material is covered by second layer of adsorbate. The first layered covered adsorbent doesnot take part in adsorption process, only uncovered first layer participate in adsorption.

The nonlinear multilayer adsorption equation are as follows:

$$q_e = \frac{Q_m K_1 C_e}{\left(1 - K_{2C_e}\right)\left[1 + (K_{1\_}K_2)C_e\right]}$$

Where, Q_m is adsorption maximum, K_1 and K_2 is equilibrium adsorption constants for first and second layer respectively, C_e is equilibrium constant.

Nonlinear Curve Fit (MultilayerFunction (User)) (7/20/2015 13:14:44)

Input Data

		Dep/Indep	Data	Range	Weight Type
Book1	ce	Indep	[Book1]Sheet1!A"ceq"	[1:8]	No Weighting
	qe	Dep	[Book1]Sheet1!B"qe"	[1:8]	No Weighting

Parameters

		Value	Standard Error
Book1	Qm	66.42808	1.31577
	K1	1.43857	0.11742
	K2	0	0

Reduced Chi-sqr = 3.67637285022
COD(R^2) = 0.99305622709317
Iterations Performed = 5
Total Iterations in Session = 9
Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.

Statistics

	Book1
Number of Points	8
Degrees of Freedom	5
Reduced Chi-Sqr	3.67637
Residual Sum of Squares	18.38186
Adj. R-Square	0.99028
Fit Status	Succeeded(100)

Fit Status Code :
100 : Fit converged. Chi-Sqr tolerance value of 1E-9 was reached.

Summary

	Qm		K1		K2		Statistics	
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
Book1	66.42808	1.31577	1.43857	0.11742	0	0	3.67637	0.99028

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
Book1	Regression	3	17535.75147	5845.25049	1589.9504	9.76529E-8
	Residual	5	18.38186	3.67637		
	Uncorrected Total	8	17554.13333			
	Corrected Total	7	2647.24444			

Fitted Curves Plot
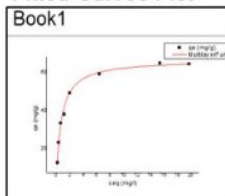
Residual vs. Independent Plot
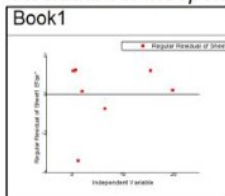
11. **Kinetics study**

For the investigation of mechanism of reduction, mass transport and chemical reaction process between C-nZVI and Cr(VI), pseudo first order and pseudo second order kinetics models are used.

Pseudo-first-order model is expressed as

$$\ln(q_e - q_t) = \ln q_e - K_t$$

q_e= amount of chromium adsorbed at an equilibrium in (mg/g)

q_t= amount of chromium adsorbed at time t

K= rate constant of pseudo-first-order reaction

Pseudo-second-order is expressed as

$$t/q_t = 1/k_p q_e^2 + t/q_e$$

Kp=Pseudo-second-order rate constant

$$\text{rate} = [Cr]^a \, [Fe]^b$$

$$\text{rate} = k[Cr]_o - [r]_t - [Cr]_o + [Cr]q_e$$

$$\text{rate} = k \, [Cr]q_e - [Cr]_t$$
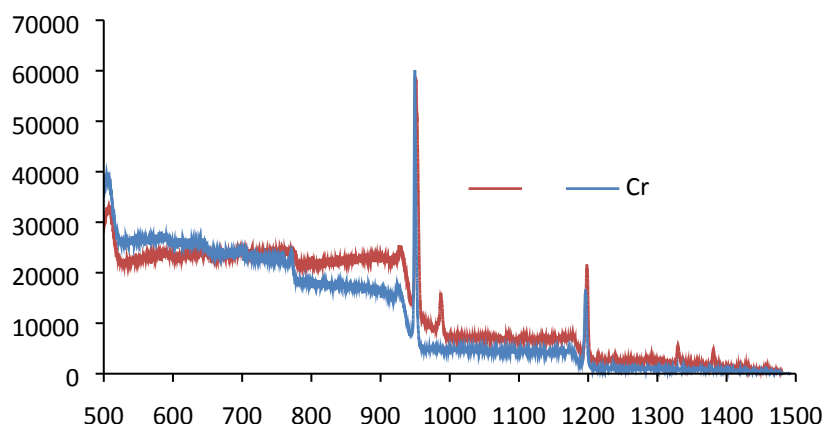
$$\text{rate} = k[Cr]q_e$$
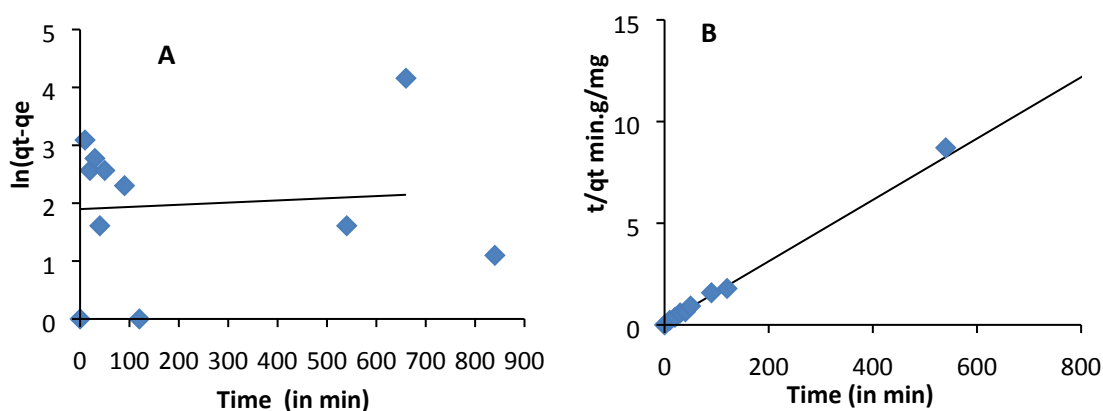
Figure S9: [A] Pseudo First order and **[B]** Pseudo Second order kinetic model of C-nZVI
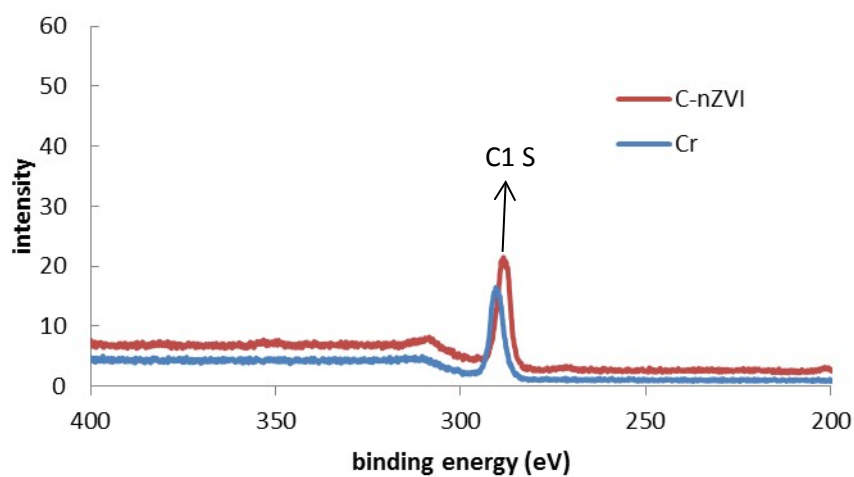
12. **Normalized maximum adsorption:** the smallest amount of material which expresses the adsorption maximum of analytes per gram of adsorbent.

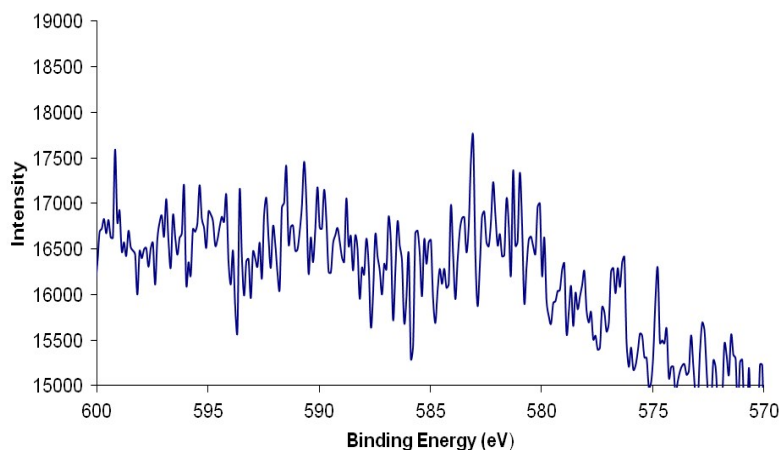$$\text{Normalized adsorption value} = q_{max} * 100 / \%Fe$$

13. XPS analysis of C-nZVI and chromium adsorbed C-nZVI

Figure S10: XPS picture of C-nZVI and chromium adsorbed C-nZVI

Figure S11: C 1s XPS spectra of C-nZVI and chromium adsorbed C-nZVI

Figure S12: XPS analysis of chromium adsorbed C-nZVI