



## Comparative Study for Reduction of Hexavalent Chromium by High Carbon Iron Filings and Electrolytic Iron: Mass Transfer Limitations

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Received: 17 May 2014;

Accepted: 26 July 2014;

Published online: 4 February 2015;

AJC-16800

Reduction of chromium(VI) by electrolytic iron and high carbon iron filings (HCIF) was carried out in batch reactors. The pseudo-first order reaction rates for reduction of Cr(VI) by HCIF were nearly one order of magnitude higher than electrolytic iron. It was revealed that the adsorption of Cr(VI) to graphite inclusions, present on HCIF, played an important role in quick decline of aqueous concentration in comparison to electrolytic iron. Further the reduction of Cr(VI) with HCIF was studied in completely mixed and non-mixed conditions. The pseudo-first order reduction rates of Cr(VI) in completely mixed conditions were nearly 20 times that of rates obtained in stationary batch reactors. The rates for electrolytic iron and HCIF stationary batch reactors were comparable which is due to reduction in adsorption of Cr(VI) to non reactive sites in non mixed conditions. This suggests that the reduction of Cr(VI) in permeable reactive barriers, built in sub-surface, for *in situ* remediation of groundwater, may be subjected to mass transfer limitations as the conditions in subsurface are poorly mixed. Further reduction of Cr(VI) lead to the formation of Cr(III). Elution of Cr(III) was also found to be lower in case of HCIF, probably due to adsorption of Cr(III) to non reactive sites on HCIF.

**Keywords:** Hexavalent chromium, Electrolytic iron, High carbon iron filings (HCIF), Adsorption, Mass transfer limitations.

### INTRODUCTION

Chromium compounds are used in various industries (*e.g.* textile dyeing, tanneries, metallurgy, metal electroplating and wood preserving); hence, large quantities of chromium have been discharged into the environment due to improper disposal and leakage. Chrome waste from leather processing poses a significant disposal problem. It occurs in three forms: liquid waste, solid tanned waste and sludge. Fat liquoring has a heavy influence on formation of chromate in leather<sup>1</sup>. Wastewaters rejected by the industries often contain chromium at concentrations above local discharge limits. US Environmental Protection Agency (EPA) has set a maximum contaminant level (MCL) of 0.1 mg/L for total chromium in drinking water<sup>2</sup>. Indian Standards (IS: 10500) has set a desirable limit of 0.05 mg/L for drinking water and an effluent standard of 0.1 mg/L for Cr<sup>6+</sup>. Industrial application has resulted in widespread contamination of chromium in soil, surface and groundwater.

Oxidation states of chromium range from -4 to +6, but only the +3 and +6 states are stable under most natural environments. In natural waters, chromium exists in Cr(VI) and Cr(III). Chromium(III) species are much less soluble and relatively stable. However, Cr(VI), such as chromate (CrO<sub>4</sub><sup>2-</sup>, HCrO<sub>4</sub><sup>-</sup>)

and dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) are highly soluble and mobile in aqueous solutions<sup>3</sup>. Chromium(VI) is known to be toxic to humans, animals, plants and microorganisms. Because of its significant mobility in the subsurface environment, the potential risk of groundwater contamination is high. Chromium(III), is less toxic and readily precipitates as Cr(OH)<sub>3</sub> or as mixed Fe(III)-Cr(III) (oxy)hydroxides under alkaline or even slightly acidic conditions<sup>4</sup>. Chromium(III) may also have toxic effects but its concentration is usually very low (below water quality standards) due to the low solubility in the pH range of natural waters<sup>3</sup>. Therefore, reduction of Cr(VI) to Cr(III) is favourable for the environment and could be a feasible method in the remediation of polluted environmental sites<sup>5</sup>. Chromium is considered as a significant pollutant because of its carcinogenic, mutagenic and teratogenic behaviour in biological systems<sup>6</sup>. In humans, chromium(VI) pose significant health hazards like irritation, inflammation, ulcers, skin allergy, damage to lungs and kidney and may be carcinogenic.

There are several wastewater treatment techniques including physical, chemical or biological processes *i.e.*, coagulation, flocculation, adsorption, reverse osmosis, activated sludge and chemical precipitation, adsorption, electrokinetic remediation, membrane separation processes, bioremediation *etc.* Conven-

tional methods of treatment of waste water laden with Cr(VI) like activated sludge process and upflow anaerobic sludge blanket (UASB) may result in high Cr(VI) in their effluents and sludge. Physico-chemical methods like reverse osmosis, ion exchange and electrolysis, employed for further removal of chromium, may prove to be expensive. Use of zero-valent iron ( $\text{Fe}^0$ ) as reactive medium for wastewater treatment is one of the most promising techniques because the iron metal is of low-cost, is easy-to-obtain and has good effectiveness and ability of degrading contaminants<sup>7</sup>. In addition, iron waste particles from industrial filings can be used as a zero-valent iron. Zero-valent iron ( $\text{Fe}^0$ ) (ZVI) based permeable reactive barriers (PRBs) have been recognized as a viable and cost-effective technology for *in situ* remediation of groundwater contaminated with redox active inorganics (such as chromate, nitrate and uranate) as well as chlorinated organics<sup>8-10</sup>. Zero-valent iron could potentially stabilize several elements in contaminated soil, because its oxidation would cause minor changes in pH and provide effective surfaces for sorption of both cations and anions. Hexavalent chromium [Cr(VI)], which is a strong oxidant, a potential carcinogen and more mobile in soils and aquifers, is transformed to trivalent chromium [Cr(III)], which is less hazardous and less water soluble and associated with solids<sup>7</sup>.

Reduction kinetics of chromium by zero-valent iron depends upon the initial pH of the solution. The results with scrap iron indicate zero order kinetics at pH 2.10 and first-order kinetics over the pH range of 2.98-7.10<sup>3</sup>. Rate of reduction increased as the particle size decreased, the rate being in the order nano-zero-valent iron > powder-zero-valent iron > Filings zero-valent iron<sup>11</sup>. The reduction rate of Cr(VI) by zero-valent iron is accelerated when mineral surfaces like goethite and aluminium oxide are present<sup>12</sup>. High zero-valent iron doses and temperature and low pH values and Cr(VI) concentration favoured Cr(VI) reduction by zero-valent iron and the reduction could be described by pseudo-first-order kinetics<sup>5</sup>.  $\text{Ca}^{2+}$  ions did not impact the zero-valent iron reactivity toward Cr(VI) reduction, Humic acid introduced a marginal influence, whereas  $\text{HCO}_3^-$  greatly enhanced Cr(VI) removal by maintaining the solution pH near neutral<sup>13</sup>. The effects of ferrous cation ( $\text{Fe}^{2+}$ ), copper cation ( $\text{Cu}^{2+}$ ) and calcium cation ( $\text{Ca}^{2+}$ ) on the reduction of Cr(VI) by zero-valent iron showed that  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  could improve the reduction of Cr(VI) but  $\text{Ca}^{2+}$  might inhibit the reduction of Cr(VI) by zero-valent iron<sup>14</sup>. Amorphous silica and sand enhanced the rate and extent of Cr(VI) removal by zero-valent iron in batch reactors<sup>15</sup>. Reduction of Cr(VI) by zero-valent iron seems to be unaffected by mass transfer limitations as the rate coefficients measured under flow conditions were comparable to those measured under batch conditions<sup>16</sup>.

Most of the studies conducted till date pertains to use of pure iron (electrolytic iron) as a reductive medium<sup>5,13,14,17-19</sup>. Few studies pertain to the use of scrap iron as reductive medium<sup>3,4</sup>. This study was conducted to compare the reduction of Cr(VI) by using high carbon iron filings (HCIF) and electrolytic iron as reductive medium. Researchers have shown that the halogenated organic compounds not only get reduce but are also sorbed to the graphite inclusions present on high

carbon iron filings (HCIF)<sup>10,20-23</sup>. These may also act as non reactive and adsorptive sites for Cr(VI) which may enhance the reduction of Cr(VI) aqueous concentration. Further the partitioning of Cr(VI) may be hampered in groundwater condition where poorly mixed conditions prevail. Hence, the batch studies with HCIF were conducted in mixed and stationary mode to evaluate the mass transfer limitations.

## EXPERIMENTAL

The chemicals used in the study were potassium dichromate, sulphuric acid, methyl orange indicator, ammonium hydroxide, potassium permanganate, sodium azide, diphenyl carbazide and acetone. All chemicals were of AR grade and were procured from Merck. Electrolytic iron was also procured from Merck (100 Mesh). Commercially available high carbon iron was chipped on a lathe machine and then ground into iron filings in a ball mill. The fraction of filings passing through 425  $\mu\text{m}$  (40 mesh) sieve and retained on 212  $\mu\text{m}$  (80 mesh) sieve was used. The quantitative determination of  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$  was done by colorimetric method (Standard Methods, APHA) on UV Spectrophotometer, Fe content by AAS (GBS Avanta) and pH by Cyber Scan 510 (Oakton Instruments, USA) pH meter. Both the iron were pre-treated with acid, washed with acetone and stored in air tight containers.

To study the kinetics of reduction by electrolytic iron and HCIF, batch studies were conducted. All the batch studies with electrolytic iron were conducted in duplicate polyethylene bottles (Tarson Co. Ltd., India) of 125 mL capacity with synthetic Cr(VI) solution of 60 mg/L concentration. Dissolved oxygen (D.O.) was not removed from the aqueous solutions. 10 g of electrolytic iron and HCIF was added to the bottles and the bottles were shaken for desired period. The bottles were taken out from the shaker at pre-determined intervals and the content was filtered using Whatman No-42 filter paper to separate the iron and filtrate. 1 mL filtrate was taken for analysis and determination of residual Cr(VI) and Cr(III) with the help of colorimetric method. Adsorption studies were conducted by adding various amount of HCIF *i.e.*, 2.5, 5, 10, 15 and 20 g HCIF in batch reactors and measuring the aqueous concentration of Cr(VI) after 10 min of mixing.

## RESULTS AND DISCUSSION

### Mixed batch reactors

**Kinetic studies with electrolytic iron:** For studying the kinetics of reduction by electrolytic iron batch studies were conducted using 10 g of iron in 125 mL polyethylene bottles. The batch reactors were shaken for desired period and vials were taken out after predetermined time period and analyzed for Cr(VI) as well as Cr(III). Fig. 1 shows the reduction of Cr(VI) when reacting with 10 g  $\text{Fe}(0)$  powder (80 g/L). About 95 % Cr(VI) reduction occurred during 24 h of observation. The product of Cr(VI) reduction, Cr(III) concentration in aqueous phase increased with time revealing that Cr(VI) is being converted to Cr(III). The blank concentration remained unchanged during 24 h. pH increased from 5.1-9.8 during 24 h and ORP varied between 200 to -250 mV. Mass balance studies for chromium reveals that the Cr(VI) is getting reduced to

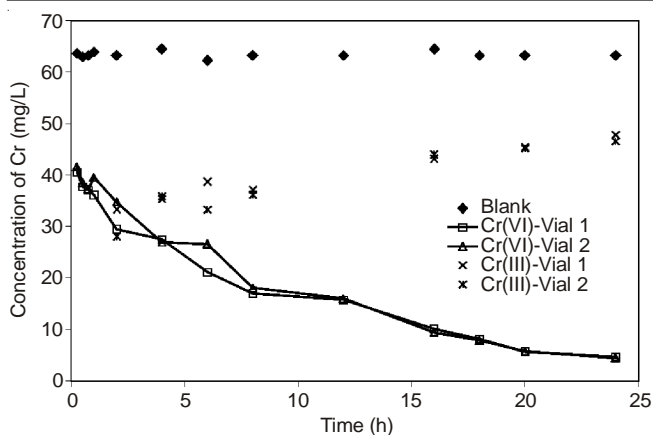


Fig. 1. Variation of Cr(VI) and Cr(III) concentration with time in electrolytic iron mixed batch reactors

Cr(III) which remains in the solution till pH 7 after which Cr(III) may be precipitating due to formation of  $\text{Cr(OH)}_3$  or mixed Fe(III)-Cr(III) (oxy)hydroxides<sup>4</sup>. Fig. 2 shows that the Cr(III) is present in the aqueous phase solution and total Cr [Cr(III)+Cr(VI)] is nearly equal to the mass added initially. The mass balance declines at the end of 24 h due to precipitation of Cr(III).

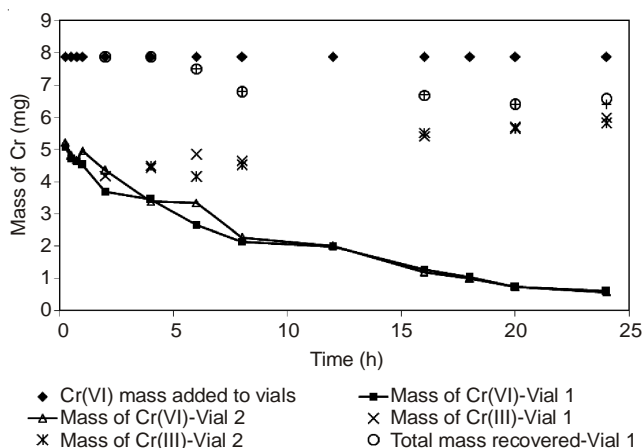


Fig. 2. Variation of mass of Cr with time in electrolytic iron mixed batch reactors

Assuming that the reduction of Cr(VI) by zero-valent iron follows pseudo-first order reaction, the change in aqueous Cr(VI) concentration at any time  $t$  can be expressed by following expression:

$$C_t = C_0 e^{-k_{\text{obs}} t} \quad (1)$$

where,  $C_t$  = aqueous phase Cr(VI) concentration at any time  $t$  (mg/L),  $C_0$  = initial Cr(VI) concentration added (mg/L),  $k_{\text{obs}}$  = observed pseudo-first order rate constant ( $\text{h}^{-1}$ ).

This expression can be linearized as follows:

$$\ln\left(\frac{C_t}{C_0}\right) = -k_{\text{obs}} t \quad (2)$$

Thus plotting the  $\ln(C_t/C_0)$  values against time  $t$  for batch reactors containing 80 g/L iron resulted in a straight line (Fig. 3). Further the reduction rates may be normalized to the concentration of iron and the observed reduction rates may be expressed as:

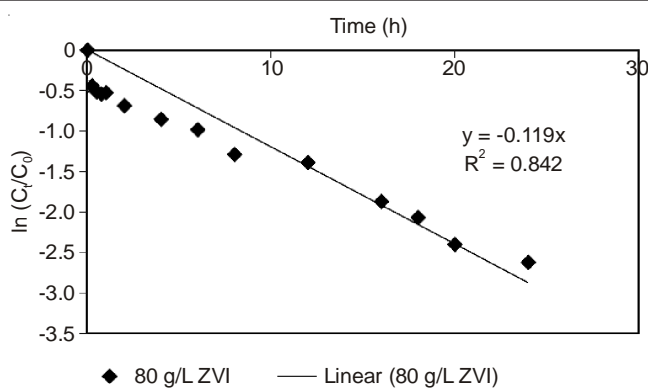


Fig. 3. Graph between  $\ln(C_t/C_0)$  vs time for electrolytic iron mixed batch reactors

$$k_{\text{obs}} = kM \quad (3)$$

where,  $M$  = concentration of iron (g/L),  $k$  = normalized reduction rate ( $\text{h}^{-1} \text{g}^{-1} \text{iron L}$ ).

Equation of the fitted line ( $r^2 = 0.84$ ) resulted in observed pseudo-first order constant as  $k_{\text{obs}} = 1.19 \times 10^{-1} \text{h}^{-1}$ . Thus the variation of concentration of Cr(VI) when contacted with electrolytic iron at above mentioned conditions can be expressed as  $C_t = C_0 e^{-0.119t}$ . Pseudo first order rate constant normalized to concentration of iron is  $1.4875 \times 10^{-3} \text{h}^{-1} \text{g}^{-1} \text{L}$ . No adsorption of Cr(VI) or Cr(III) was observed in this case as the mass balance during first few hrs did not declined. It may be concluded that only reduction reactions are contributing to the decline of Cr(VI) in aqueous phase.

#### Kinetic studies with high carbon iron filings (HCIF):

Kinetic studies with HCIF were conducted taking 10 g iron in 32 mL HDPE bottles as batch reactors. 60 mg/L Cr(VI) aqueous solution was added to each vial and mixed for 2 h. Bottles were taken at regular intervals and analyzed for Cr(VI) and Cr(III) concentrations. Fig. 4 shows the reduction of Cr(VI) and total Cr and elution of Cr(III) with time. pH increased from 4.5-9.94 during the 2 h of observation. ORP varied between 200 mV to -200 mV.

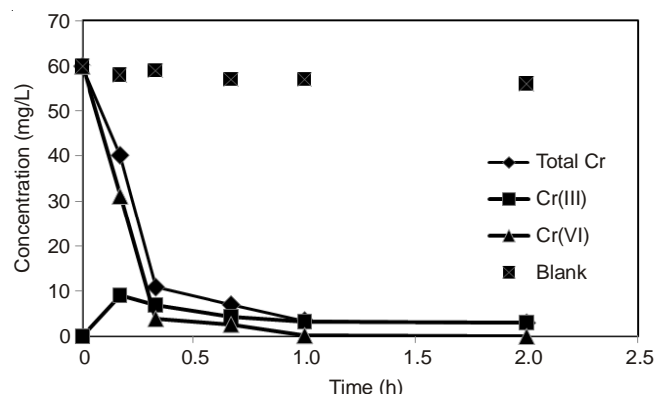


Fig. 4. Variation of concentration of Cr(VI), Cr(III) and total Cr with time in HCIF mixed batch reactors

The kinetic studies for the data revealed that the reduction of Cr(VI) in mixed conditions follow pseudo first order kinetics and the first order rate constant is  $4.291 \text{h}^{-1}$ . HCIF normalized rate is  $1.373 \times 10^{-2} \text{h}^{-1} \text{g}^{-1} \text{HCIF L}$  (Fig. 5). Chromium(VI) partitions to graphite inclusions present in HCIF. It is assumed that such partitioning is non-specific in nature, *i.e.*, the number

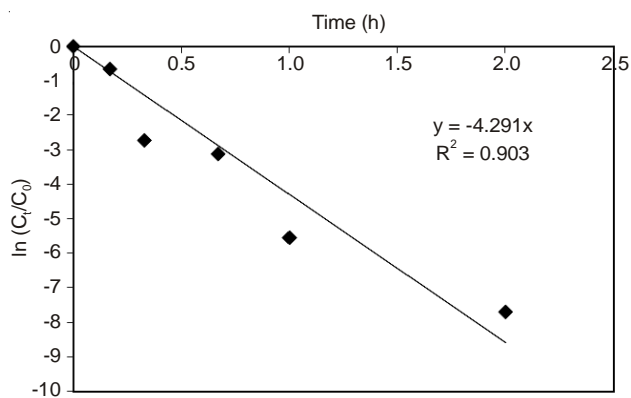
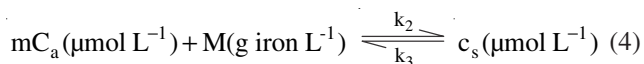


Fig. 5. Graph between  $\ln(C_t/C_0)$  vs. time for HCIF mixed batch reactors

of adsorption sites on the graphite surface is constrained only by the number of Cr(VI) molecules that can be fitted on the graphite surface. At low surface coverage, such partitioning can be represented by the general equation,



where  $c_s = M.C_s$ .

Under such conditions, partitioning of Cr(VI) between solid and aqueous phases can be represented by a Freundlich isotherm,

$$C_s = K[C_a]^m \quad (5)$$

A plot of  $\log C_a$  versus the corresponding  $\log C_s$  for Cr(VI) is presented in Fig. 6, which shows that the data could be adequately represented by the Freundlich isotherm with  $m = 1.014$  and  $K = 0.0026 \text{ g}^{-1} \text{ L}$ .

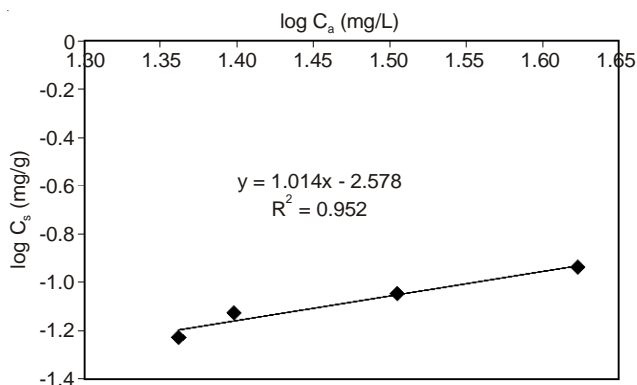


Fig. 6. Plot of  $\log C_a$  vs.  $\log C_s$  for Cr(VI) adsorption in HCIF mixed batch reactors

**Stationary batch reactors:** To evaluate the impact of mixing on reduction of Cr(VI), batch studies were conducted in non-mixed (stationary) conditions. The vials were kept for 20 h and were used at regular intervals for determination of aqueous phase Cr(VI) and Cr(III). Chromium(VI) reduced from 60-2.06 mg/L in the observation period *i.e.* 20 h. The results of the reduction of Cr(VI) and elution of Cr(III) with time are presented in Fig. 7. pH increased from 4.5-9.95 while ORP varied from 200 to -166 mV during observation period. Concentration in blank vials did not decline. Kinetic studies performed on the observed data revealed that the pseudo first order rate for reduction of Cr(VI) in non-mixed conditions was  $7.392 \times 10^{-4} \text{ h}^{-1} \text{ HCIF L}$  (Fig. 8). Hence the reduction

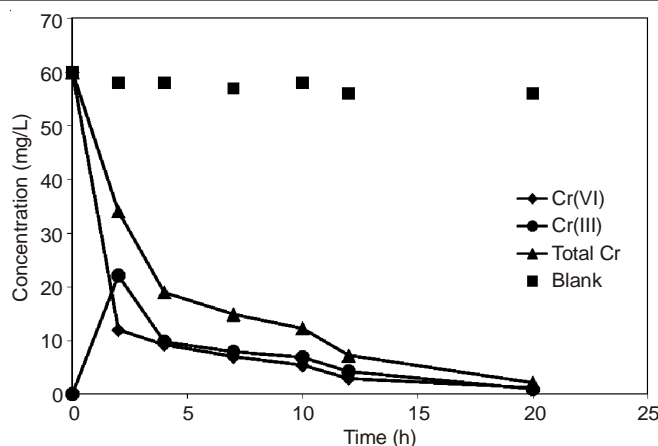


Fig. 7. Temporal variation of Cr(VI), Cr(III) and total Cr concentrations in HCIF static batch reactors

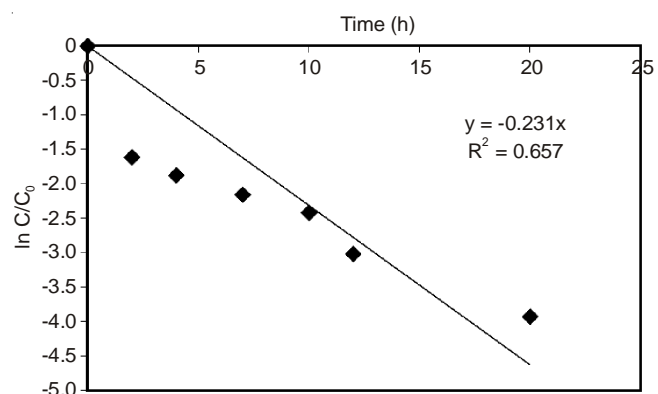


Fig. 8. Plot of  $\ln C/C_0$  vs. time for Cr(VI) reduction in HCIF stationary batch reactors

rates decreased by an order of magnitude in comparison to the well mixed batch reactors. This may be due to the mass transfer limitations for Cr(VI) to the surface of HCIF in static conditions which hampers the adsorption as well as the reduction reactions. Further the adsorption of total chromium in static batch reactors was studied. The adsorption studies for total Cr in stationary batch reactors revealed that the adsorption can be defined by Freundlich isotherm with  $m = 0.04$  and  $K = 9.12 \times 10^{-47} \text{ g}^{-1} \text{ L}$  (Fig. 9). This suggests that the adsorption phenomenon is seriously impacted due to non-mixing of the batch reactors.

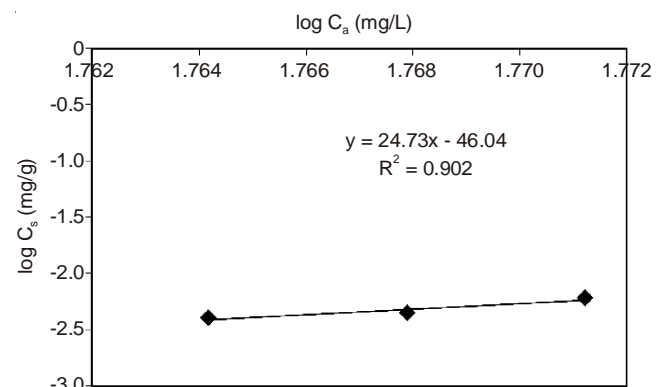


Fig. 9. Plot of  $\log C_s$  vs.  $\log C_a$  for total Cr adsorption in HCIF stationary batch reactors



TABLE-1  
COMPARISON OF PSEUDO-FIRST ORDER REDUCTION RATES OF Cr(VI) BY ELECTROLYTIC IRON AND HCIF

Pseudo first order reduction rates for HCIF (mixed batch reactors)	Pseudo first order reduction rates for HCIF (static batch reactors)	Pseudo first order reduction rates for electrolytic iron (mixed batch reactors)
$1.373 \times 10^{-2} \text{ h}^{-1} \text{ g}^{-1} \text{ HCIF L}$	$7.392 \times 10^{-4} \text{ h}^{-1} \text{ g}^{-1} \text{ HCIF L}$	$1.4875 \times 10^{-3} \text{ h}^{-1} \text{ g}^{-1} \text{ iron L}$

**Comparison of reduction rates by electrolytic iron and HCIF:** The reduction rates for electrolytic iron in mixed batch reactors was  $1.4875 \times 10^{-3} \text{ h}^{-1} \text{ g}^{-1} \text{ iron L}$  where as for HCIF the reduction rate was  $1.373 \times 10^{-2} \text{ h}^{-1} \text{ g}^{-1} \text{ HCIF L}$ . The reduction of Cr(VI) was ten times faster by high carbon iron filings in comparison to the electrolytic iron. This was due to the adsorption of Cr(VI) on to the non reactive sites (carbon) on HCIF. This can be explained by comparing the reduction rates of electrolytic iron with HCIF static batch reactors, where no adsorption is taking place. Table-1 shows the comparison of reduction rates of HCIF and electrolytic iron.

**Elution of Cr(III):** The reduction of Cr(VI) by electrolytic iron lead to the formation of Cr(III) as it is evident from Figs. 1 and 2. The mass balance of total Cr in two vials under observation declined slightly after 15 h of observation. This may be due to the precipitation of Cr as Cr(OH)<sub>3</sub> or as mixed Fe(III)-Cr(III) (oxy)hydroxides under alkaline or even slightly acidic conditions. The pH at 15 h of observation was around 7 and rose rapidly thereafter 9.8. No adsorption of Cr(III) was observed till the pH 7 and all the Cr(III) was found in aqueous phase only (Fig. 2). In comparison to this, the Cr(III) eluted due to reduction by HCIF in mixed conditions didn't appeared in the solution and remained adsorbed to the HCIF (Fig. 4). Small amount of Cr(III) eluted till 20 min of observation and reduced thereafter probably due to precipitation of Cr as Cr(OH)<sub>3</sub> or as mixed Fe(III)-Cr(III) (oxy)hydroxides as the pH after 40 min rose beyond 7. In static batch reactors a higher amount of Cr(III) eluted in comparison to the mixed case, this may be due to low adsorption of Cr(III) to the HCIF surface and mass transfer limitations induced due to non mixing (Fig. 7).

### Conclusion

The reduction of Cr(VI) by HCIF was due to reduction as well as adsorption of Cr(VI) to the graphite nodules present on HCIF. The reduction rates of Cr(VI) reduced to nearly 20 times in absence of mixing. Further, the adsorption of Cr(VI) decreased drastically in non mixed conditions due to mass

transfer limitations of Cr(VI) to HCIF surface. Hence, it may be concluded that mass transfer limitation of Cr(VI) to HCIF surface may reduce the reduction of Cr(VI) by HCIF permeable reactive barriers (PRBs). Mass transfer limitations may also lead to higher amount of Cr(III) in the effluent of HCIF permeable reactive barriers.

### ACKNOWLEDGEMENTS

The authors are grateful to Indian School of Mines for providing the financial support for this project (2010/MRP/ESE/09/Acad).

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