Hexavalent chromium removal using iron bearing industrial sludges

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Received 29 September 2000; revised 26 April 2001; accepted 21 May 2001

The use of iron bearing metallic and mineral materials for the treatment of highly toxic Cr(VI) containing industrial wastewater have received increased attention for the past decade. In conventional treatment, a large amount of chromium hydroxide generates as secondary solid waste which poses a serious problem of disposal. In the presence of iron bearing materials, Cr(VI) reduces to Cr(III) and Fe(II) oxidises to Fe(III) generating mixed complexes from which separation probability of individual element reduces. Based on this chemical principle it is expected that such industrial solid wastes containing iron as a major constituent have potential to reduce highly toxic Cr(VI) to less toxic Cr(III). In view of this, present investigation was aimed to utilise iron bearing industrial wastes like sludges of steel tube making industry and aluminium industry for removal of Cr(VI). Studies include identification of suitable pH for the Cr(VI) reduction, optimisation of dosage and contact time and determination of reaction kinetics. No Cr(VI) was detected from the reacted wastes and total chromium was measured as Cr(III). Toxicity characteristics leaching procedure (TCLP) has been employed to estimate the leachability of chromium, iron etc from the reacted wastes. TCLP results indicate a negligible amount of chromium as Cr(III) and iron leachability from the reacted wastes.

The use of chromium bearing salts in various industrial applications like leather tanning, electro-plating and metal finishing etc ultimately makes its way in the soil and water through wastewater/solid wastes disposal. Once chromium enters into the environment, it exists in two most stable oxidation states i.e, Cr(III) and Cr(VI). Among them, trivalent form of chromium is comparatively innocuous and nearly immobile, while hexavalent chromium moves rapidly through soil and water. This form of chromium generally acts as irritant to plant and animal tissues and carcinogenic in nature. Because of toxic nature of Cr(VI), its treatment becomes essential before final disposal of the wastes. In conventional method of removal, Cr(VI) is reduced to Cr(III) at low pH (~2 to 3) by addition of reducing chemicals. Then again solution is made alkaline (pH~8) in which Cr(III) precipitates as chromium hydroxide. The generation of a huge amount of solid chromium hydroxide in this process poses environmental problem for its safe disposal due to susceptibility of further oxidation of Cr(III) into Cr(VI) in the presence of oxidising elements in the soil. Addition of reducing and neutralising chemicals during removal also increases the treatment cost. To overcome the above problems, investigations are being carried out for replacement of the conventional method by treating with zero-valent iron bearing materials including minerals, soil etc.

Extensive research works have established effectiveness of zero-valent metallic iron for reduction of Cr(VI). Several studies have shown that different kinds of soils like acidic subsoil, alkaline soil, wetland soil, alluvial river sand, aquifer materials etc. can also be used for the Cr(VI) removal. Iron bearing minerals namely biotite, hematite, pyrite, magnetite etc. have also demonstrated their effectiveness in Cr(VI) removal. These studies have suggested that the rate of removal is completely dependent on rate of release of ferrous iron (Fe(II)) from the iron bearing materials. This indicates that those iron bearing solids which are able to release soluble ferrous iron in the aqueous solution, have potential for the reduction of hexavalent chromium to its trivalent form. Industrial solid wastes like sludge generated from the effluent treatment plant of steel tube making industry or red mud discharged after reclamation of bauxite ore in aluminium industry contain a considerable quantity of iron. These wastes can also release soluble ferrous iron which could be utilised in Cr(VI) removal. Based on this assumption present investigations were carried out in order to assess the potential use of these wastes in the removal of highly toxic hexavalent chromium. The main objective of the present work is to explore possibilities of potential use of these wastes in the treatment of chromate or dichromate ion containing
ETP sludge and red mud were taken in conical flasks containing solution. In optimisation process, different quantities of sludge were added to the flasks to study the effect of solid waste doses and contact time for Cr(VI) removal, batchwise shaking was performed at room temperature. The pH of the solution was adjusted by addition of HCl and NaOH containing extraction fluid (64.3 mL of 1N NaOH and 5.7 mL acetic acid in 1000 mL remaining distilled water) at pH 4.93. Initial and final concentrations of hexavalent chromium during removal process were determined by 1.5 diphenyl carbohydrazide method in 500 mL extraction fluid (500 mL) as described earlier, filled up in the liquid to solid weight ratio of 1:20. A glass fibre filter of 0.8 μm pore size used for extraction, was placed in-between support screen of ZHE barrel. The primary leachate was collected in the syringe, fitted at the top of ZHE for every 10 psi increased upto 50 psi pressure in 5 step and total 50 mL leachate was collected. After collection of primary leachate or extract, ZHE volume was maintained by extraction fluid and kept for agitation for 18 h. Then secondary leachate or extract was collected by the same procedure as it was adopted for collection of primary leachate. Details of TCLP experiment are given elsewhere.

### Table 1 — Presence of various metals in ETP sludge and red mud (in percentage)

<table>
<thead>
<tr>
<th>Waste</th>
<th>Fe</th>
<th>Al</th>
<th>Cr</th>
<th>Mn</th>
<th>Zn</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETP</td>
<td>52.50</td>
<td>0.10</td>
<td>0.25</td>
<td>1.51</td>
<td>0.1</td>
<td>0.25</td>
<td>0.30</td>
</tr>
<tr>
<td>Redmud</td>
<td>29.75</td>
<td>9.50</td>
<td>Nil</td>
<td>0.15</td>
<td>0.15</td>
<td>0.20</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Experimental Procedure

For carrying of present study, two types of industrial sludge generated in effluent treatment plant (ETP) of steel tube making industry and red mud from aluminium industry, were collected. After drying, sludges were analysed to determine iron and other metal concentrations. The results of detailed chemical analysis for various metals present in ETP sludge and red mud are presented in Table 1. Chemical analysis results indicated the presence of nearly 52% and 30% iron in ETP sludge and red mud respectively. pH measurement in the range of 9 to 10 of both wastes indicated their alkaline nature. Presence of nearly 2% titanium in red mud was confirmed by EDAX analysis.

All the chemicals used for preparation of solutions were of analytical grade. Stock solution of hexavalent chromium of 1000 mg/L strength was prepared by dissolving 2.8289 g K$_2$Cr$_2$O$_7$ in triple distilled water. Working solutions used for Cr(VI) removal, were prepared by successive dilution of stock solution with distilled water. pH of the working solutions were adjusted by addition of HCl and NaOH.

Leachability test of Cr(VI)-reacted wastes was conducted in acetic acid and sodium hydroxide containing extraction fluid (64.3 mL of 1N NaOH and 5.7 mL acetic acid in 1000 mL remaining distilled water) at pH 4.93. Leachability test was conducted in acetic acid and sodium hydroxide containing extraction fluid (64.3 mL of 1N NaOH and 5.7 mL acetic acid in 1000 mL remaining distilled water) at pH 4.93. Initial and final concentrations of hexavalent chromium during removal process were determined by 1.5 diphenyl carbohydrazide method in 500 mL extraction fluid (500 mL) as described earlier, filled up in the liquid to solid weight ratio of 1:20.

To estimate leachability of chromium and iron from Cr(VI) reacted solid wastes, toxicity characteristic leaching procedure (TCLP) was employed. TCLP determines the mobility of organic and inorganic contaminants of liquid, solid or multiphasic wastes in the form of primary and secondary leachability. Primary extract is the measure of immediate leachability, while secondary extract determines the long term mobility of the contaminant. For performing this test 25 g Cr(VI) reacted solid waste was taken in Zero Head Extractor (ZHE) in which extraction fluid (500 mL) as described earlier, filled up in the liquid to solid weight ratio of 1:20. A glass fibre filter of 0.8 μm pore size used for extraction, was placed in-between support screen of ZHE barrel. The primary leachate was collected in the syringe, fitted at the top of ZHE for every 10 psi increased upto 50 psi pressure in 5 step and total 50 mL leachate was collected. After collection of primary leachate or extract, ZHE volume was maintained by extraction fluid and kept for agitation for 18 h. Then secondary leachate or extract was collected by the same procedure as it was adopted for collection of primary leachate. Details of TCLP experiment are given elsewhere.

Fig. 1 — Cr(VI) removal rate in the presence of 14 g ETP sludge and red mud in 20 mg/L Cr(VI) containing 100 mL dichromate solution at different pH.
Results and Discussion

Effect of pH on Cr(VI) removal

After passing through 210 μ size sieve of dried ETP sludge and red mud, batch shaking experiments were performed to see the effect of pH on Cr(VI) removal. In this study 14 g each ETP sludge and red mud were added in 20 mg/L Cr(VI) containing 100 mL dichromate solution at pH 2 to 7 separately and kept for shaking up for one hour. Before start of shaking, pH of each solution was adjusted properly because of alkaline nature of both of the wastes. After batch shaking, unreduced (residual) Cr(VI) was analysed and percentages of Cr(VI) removal was determined (Fig. 1). As seen in Fig. 1, Cr(VI) removal rate occurs slightly higher at pH 2 as compared to other pH in both the systems. With the increase of pH, removal rates decrease and show a minimum value at pH 5. At pH 3 removal efficiency of around 91% and 77% could be achieved using ETP sludge and red mud, respectively. Measurement of nearly 15% less removal by red mud in comparison to ETP sludge indicates its lesser removal capability than ETP sludge. Presence of Ti and Al in the red mud also helps in the removal process. This is due to the presence of their oxides which increases Cr(VI) removal due to adsorption on their surfaces. Solubility of iron was also measured for both wastes at different pH. As seen in Fig. 2, solubility of iron is lower for red mud than ETP sludge. Since solubility of iron from the solid materials mainly determines removal rate of Cr(VI), a lower solubility of iron in red mud as compared to ETP sludge is attributed for the occurrence of lower removal efficiency.

To determine the presence of unreacted iron in the treated dichromate solution, analysis of iron was carried out simultaneously after batch shaking. The unreacted iron obtained at different pH are given Fig. 3. Occurrence of minimum level of unreacted iron at pH 3 to 4 obviously suggests that this pH range is the most suitable solution condition for Cr(VI) removal as compared to other pH. A precipitation was also noticed after shaking at pH 5, 6 and 7. Reacted wastes were digested for the determination of Cr(VI) and total chromium as Cr(III). It was amazing to note that no Cr (VI) was detected in the digested solutions of ETP sludge and red mud and total chromium occurred as Cr(III).

Quantification of Cr(VI) and Cr(III)

To assess effectiveness of any treatment system, quantification of input and output concentrations of contaminants to be treated, is very necessary to be evaluated. In the present study since a hazardous Cr(VI) species is converted into a less hazardous Cr(III), therefore, identification and estimation of its reduced forms i.e., chromium as Cr(III) is essential. That’s why reacted ETP sludge, red mud and treated


Table 2 — Quantitative analysis results of Cr(VI) removal by using 14g of ETP sludge in 20 mg/L containing 100 mL dichromate solution at pH 2 to 7

<table>
<thead>
<tr>
<th>Description</th>
<th>pH 2</th>
<th>pH 3</th>
<th>pH 4</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr (VI) used in removal (mg)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Cr (VI) removal (mg)</td>
<td>1.90</td>
<td>1.82</td>
<td>1.78</td>
<td>1.74</td>
<td>1.77</td>
<td>1.84</td>
</tr>
<tr>
<td>Total Cr as Cr(III) obtained from ETP sludge (mg)</td>
<td>1.86</td>
<td>1.77</td>
<td>0.74</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Total Cr as Cr(III) in treated solution (mg)</td>
<td>ND</td>
<td>ND</td>
<td>0.95</td>
<td>0.3</td>
<td>0.28</td>
<td>0.27</td>
</tr>
<tr>
<td>Total Cr as Cr(III) (mg) mixed waste and precipitates</td>
<td>No ppt</td>
<td>No ppt</td>
<td>Colloidal</td>
<td>1.36</td>
<td>1.41</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Table 3 — Quantitative analysis results of Cr(VI) removal by using 14g of red mud in 20 mg/L containing 100 mL dichromate solution at pH 2 to 7

<table>
<thead>
<tr>
<th>Description</th>
<th>pH 2</th>
<th>pH 3</th>
<th>pH 4</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr (VI) used in removal (mg)</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Cr (VI) removal (mg)</td>
<td>1.61</td>
<td>1.54</td>
<td>1.48</td>
<td>1.43</td>
<td>1.49</td>
<td>1.55</td>
</tr>
<tr>
<td>Total Cr as Cr(III) obtained from reacted red mud (mg)</td>
<td>1.52</td>
<td>1.46</td>
<td>0.62</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cr as Cr(III) in treated solution (mg)</td>
<td>—</td>
<td>—</td>
<td>0.80</td>
<td>0.1</td>
<td>0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>Total Cr as Cr(III) (mg) mixed waste and precipitates</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.25</td>
<td>1.31</td>
<td>1.4</td>
</tr>
</tbody>
</table>

It is well known that ferrous ion in solution acts as suitable reductant for the chromate or dichromate ions reduction. Aqueous ferrous ion has been demonstrated to effectively reduce Cr(VI)\(^{22,23}\). The reduction of Cr(VI) to Cr(III) occurs very rapidly in the presence of three equivalents of ferrous ion as:

\[
\text{Cr(VI)} (aq) + 3\text{Fe(II)} (aq) \rightarrow \text{Cr(III)} aq + 3\text{Fe(III)} aq
\]

When Cr(VI) reduces to Cr(III) state in the presence of ferrous ion, simultaneously, Fe(II) is oxidised to ferric ion which apparently combined to Cr(III) and make a solid solution of chromium-iron hydroxide \((\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3\) via following reaction

\[
x\text{Cr(III)} + (1-x)\text{Fe(III)} + 3\text{H}_2\text{O} \leftrightarrow (\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3 + 3\text{H}^+
\]

Where \(x\) can vary from 0 to 1. However, stability of mixed chromium-iron hydroxide completely depends on the pH. Weng et al.\(^{25}\) found an increased amount of Cr(III) and Fe(III) in the pH <4. They also measured a steep decrease of concentration of soluble Fe(III) and Cr(III) with the increase of pH in the neutral direction. Eary and Rai\(^{24}\) reported the stability of \(\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3\) in the pH range of 3.91 to 11.06 and explained the stoichiometry of its formation. Based on above report it is hypothesised that reaction product film formed on the surfaces of iron containing grains at pH 2 and 3, could be iron and chromium oxides. Formation of their oxides can be represented by following reaction:

\[
2\text{Fe} + K_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + 2\text{KOH}
\]
Since Cr\textsuperscript{3+} and Fe\textsuperscript{3+} also meet the crystalline structure criteria having the same charge density and the same ionic radii 0.63 Å and 0.64 Å, respectively\textsuperscript{26}, it is assumed that both the oxides can be mixed together homogeneously and a solid layer can be made on the grains of the reacted solid waste. Thus, the possibilities of separation of either chromium or iron from the oxide layer reduces.

Over recent years corrosion mechanism has also been proposed\textsuperscript{27,28} to explain Cr(VI) reduction by metallic iron. Under this, an electrochemical cell formation\textsuperscript{29,30} is primarily required for commencing of oxidation and reduction reactions. When metal comes in contact of aqueous solution, an electrochemical redox reaction starts between the oxidising and reducing components of the system. Electrons are released by the oxidising metal forming cations and taken by reducing component at the cathode or anions of the solution. Based on above mechanism it can be proposed that iron from the wastes corrodes or oxidises as Fe\textsuperscript{2+} ion which further oxidises to Fe\textsuperscript{3+} in the presence of dichromate ion. Subsequently Cr\textsuperscript{6+} is reduced to Cr\textsuperscript{3+} ion and form Fe\textsubscript{2}O\textsubscript{3} and Cr\textsubscript{2}O\textsubscript{3} in the presence of oxygen at pH 2 and 3. Involvement of reduced Cr(III) with iron on the metallic iron surfaces at pH 2 and 3 has also been confirmed by EDAX analysis\textsuperscript{31}.

**Optimisation of dosages and time**

Present treatment studies have already indicated the suitability of pH 3 over other pH for Cr(VI) removal because of the estimation of minimum level of unreacted iron. To find out the optimum dosage for the complete removal of Cr(VI), an increased amount starting from 10 g of both wastes was batch shaken in 20 mg/L Cr(VI) containing 100 mL dichromate solution at this pH till the occurrence of a complete removal. After one hour of batch shaking, unreduced Cr(VI) present in the solution was analysed. Fig. 4 exhibits the concentration of unreduced Cr(VI) in mg/L obtained against the mass of ETP sludge and red mud used for the removal. Cr(VI) removal trend shows the concentration of unreduced Cr(VI) left in the solution at various time intervals during shaking. As shown in Fig. 5, after 45 min of shaking, a complete removal of Cr(VI) occurs in both the systems. This study attributes that 45 min of shaking is essential for production of appropriate concentration of ferrous ion in the presence of optimum dosage of both the sludges for removal of 2 mg Cr(VI) containing dichromate ion present in the solution at pH 3.

**Adsorption isotherms**

Freundlich and Langmuir\textsuperscript{32,33} adsorption isotherms were plotted by using treatment data related to Cr(VI) removal in the presence of various quantities of ETP sludge and red mud. Freundlich isotherm as shown in Fig. 6 is plotted as log \( q_e \) \( \gamma \) is the quantity of Cr(VI)
adsorbed per unit weight of the adsorbent) versus log $C_e$ ($C_e$ is the concentration of Cr (VI) after adsorption) while $1/(Q/e)$ is used against $1/C_e$ for plotting of Langmuir adsorption isotherm (Fig. 7). When linearity of both adsorption isotherms is compared, one can agree that Langmuir isotherm is most likely followed in both systems due to its linearity over Freundlich isotherm. Langmuir adsorption generally determines the occurrence of a homogeneous type of oxidation and reduction reaction in the system. Thus, it can be assumed that adsorption of dichromate ion and its subsequent reduction and ferrous ion oxidation are likely to occur simultaneously during removal reaction. Fig. 8 describes the initial rate plot with respect to concentration of Cr(VI) reduced by ferrous ion in the presence of both the sludges. Exhibition of a linear trend ($slop R^2=0.92$ for ETP sludge and 0.87 for red mud) with $n=1$ indicates the existence of first order reaction kinetics for Cr(VI) reduction in the presence of above wastes at pH 3. Fendrof and Li 34 have also reported the occurrence of first order reaction kinetics in the redox reaction of Cr(VI) and Fe(II) in aqueous solution. It may further be asserted that first order reaction rate of Cr(VI) reduction rate indicates the dependence of Cr(VI) reduction in the presence of Fe(II) ion.

**Maximum Cr(VI) removal and leachability determination**

As described earlier, the toxicity characteristic leaching procedure (TCLP) test estimates immediate and long term leachability of toxic contaminants from the hazardous wastes. Therefore, this specific test was employed to measure the leachability of chromium and iron from the Cr(VI)-reacted sludges. Before carrying of this test two consecutive treatments of once reacted waste was made in order to achieve maximum Cr(VI) removal. A noticeable decrease of 7% and 10% removal efficiency after second time treatment by both ETP sludge and red mud respectively indicated the decrease of removal rate after first time treatment. After third treatment, Cr (VI) removal became considerably low by 75% for ETP sludge and 60% to red mud. Reduction of removal efficiencies after each consecutive treatment is mainly due to less availability of ferrous iron at the surface of solid grains.

![Fig 6—Freundlich adsorption isotherm](image)

![Fig 7—Langmuir adsorption isotherm](image)

**Table 4—Primary and secondary leachability for chromium and iron for 1st, 2nd and 3rd time Cr(VI)-reacted ETP sludge**

<table>
<thead>
<tr>
<th></th>
<th>1&lt;sup&gt;st&lt;/sup&gt; treatment</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt; treatment</th>
<th>3&lt;sup&gt;rd&lt;/sup&gt; treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Primary</td>
<td>Secondary</td>
<td>Primary</td>
</tr>
<tr>
<td>Total Cr as Cr(III) (mg/L)</td>
<td>0.02</td>
<td>0.28</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>0.64</td>
<td>0.94</td>
<td>0.20</td>
</tr>
</tbody>
</table>

**Table 5—Primary and secondary leachability obtained for chromium and iron after 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> time reacted red mud**

<table>
<thead>
<tr>
<th></th>
<th>1&lt;sup&gt;st&lt;/sup&gt; treatment</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt; treatment</th>
<th>3&lt;sup&gt;rd&lt;/sup&gt; treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Primary</td>
<td>Secondary</td>
<td>Primary</td>
</tr>
<tr>
<td>Total Cr as Cr(III) (mg/L)</td>
<td>0.01</td>
<td>0.18</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>0.36</td>
<td>0.58</td>
<td>0.18</td>
</tr>
</tbody>
</table>
It has already been described that after redox reaction, Fe(III) and Cr(III) make their oxides at the surfaces which suppress further dissolution or corrosion of iron.

After estimation of maximum removal tendency, primary and secondary leachates were extracted by employing TCLP from the 1st, 2nd and 3rd time reacted wastes. Thereafter leachates were analysed for the Cr(VI), total chromium as Cr(III) and iron. The primary and secondary leachability obtained for chromium as Cr(III) and iron, respectively from the 1st time Cr(VI)-reacted ETP sludge and red mud, becomes somewhat more as 0.28 mg/L for total chromium as Cr(III) and 0.94 mg/L as iron. In case of Cr(VI)-reacted red mud, comparatively less leachability of chromium and iron was determined (Table 4). After 3rd time Cr(VI) removal by ETP sludge, the primary leachability of chromium occurred up to 0.08 mg/L which became significantly high (0.51 mg/L) for secondary leachability. However, iron leachability was slightly reduced. For 3rd time Cr(VI)-reacted red mud, chromium leachability was obtained slightly less to that estimated for reacted ETP sludge. But leachability of iron was appreciably reduced as compared to ETP sludge.

The total leachability of Cr(III) and iron was obtained by using relation as given in experimental part incorporating the primary and secondary leachability results. Figs 9 and 10 illustrate the total leachability measured for chromium as Cr(III) and iron from the 1st, 2nd and 3rd time Cr(VI)-reacted ETP sludge and red mud, respectively. Leachability trend clearly describes...
a reduced level of leachability of iron from 1st to 3rd treatment, while an increased level of leachability of chromium with the increased number of treatment. This level of leachability of chromium is well below the regulatory standard for chromium (5 mg/L) fixed for TCLP test as per US EPA\textsuperscript{18}. Leachability results suggest that both Cr(VI)-reacted waste may not pose any environmental contamination problems immediately or in long term whenever in contact with soil. In separate work it has been found that leachability of chromium and iron from Cr(VI)-reacted sludges reduces further after stabilisation with cement and clay\textsuperscript{35}.

**Leachability of other metals**

Since both sludges contain a noticeable level of metal elements, it is necessary to estimate their leachability in view to predict their impact on soil environment after disposal of reacted wastes. The total leachability of Zn, Cu, Ni, Co, Al and Mn from 3rd time reacted ETP sludge and red mud are given in Table 6. Leachability results describe that almost all the metals except Al in red mud and Mn in ETP sludge, are not leachable. Though, leachability of Al and Mn is in insignificant level which can be further minimised by stabilisation process\textsuperscript{35}.

**Conclusions**

ETP sludge generated in steel industry and red mud from aluminium industries have shown their potential for Cr(VI) removal in a very wide range of pH. Main findings from the present investigations are:

(i) After Cr(VI) removal at pH 2 to 7, total chromium was determined as Cr(III) from the reacted sludges. This confirmed the ability of ETP sludge and red mud for Cr(VI) removal in aqueous solution. Though, pH 3 was found as a suitable solution condition for the Cr(VI) removal due to the measurement of minimum unreacted iron in the treated solution as compared to other pH.

(ii) After optimisation, 16 g ETP sludge and 20 g red mud were found to be in their adequate quantities which are required for the removal of 2 mg Cr(VI) in aqueous solution at pH 3 after 45 min of contact period.

(iii) Visually, no precipitation was noticed in the reacted solution at pH 2 and 3, while precipitation started at pH 4 and above. This observation suggests the formation of hydrated Cr$_2$O$_3$ and Fe$_2$O$_3$ on the grains of the reacted wastes. At pH 4 and due to occurrence of precipitation reaction, reduced chromium Cr(III) along with Fe(III) occurs in the form of solid solution of chromium iron hydroxide.

(iv) TCLP testing of reacted waste at pH 3 indicated a very low level of 0.3 and 0.25 mg/L leachability of chromium from the reacted ETP sludge and red mud, respectively. Almost similar level of iron was also estimated from TCLP test. Measurements of minimum level of leachability of iron and chromium indicate the existence of strong bonding between chromium and iron which does not allow them to separate from the reaction product film.

(v) TCLP test also suggests that Cr(VI)-ETP sludge and red mud may not pose any contamination problem to the environment after their disposal.

**Acknowledgement**

The authors are grateful to Director, Regional Research Laboratory, Bhopal for his interest and providing laboratory facilities for conducting this work. They are also thankful to B.Chakradhar, RRL, Bhopal for discussions.

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