Hexavalent chromium, Cr(VI) presence in chromite concentrate is a concern due to its environmental unfriendly and carcinogenic nature. Chromite concentrates typically contain Cr(VI) in the range of 2.0 to 4.0 mg-Cr/kg. The conventional methods of removing toxic Cr(VI) which includes the use of inorganic reductants are generally not preferred industrially due to their unavoidable environment unfriendly and cost ineffective nature. Therefore, in this study the use of Terminalia chebula, which is a naturally occurring organic product, is explored for Cr(VI) removal in chromite concentrates. The parameters in critical Cr(VI) removal process such as Terminalia chebula dosages, contact time and water requirements for application of this method are estimated and used at plant scale. It was found that 540 g of Terminalia chebula and contact time of 120 s is required for one ton concentrate treatment at plant for minimizing Cr(VI) to trace levels of 0.02 mg-Cr/kg. It was also observed that the water requirements in using Terminalia chebula method are insignificant. The application of Terminalia chebula for removing Cr(VI) in chromite concentrate is found to be suitable method for using in continuous production process of chromite concentrates at plant.

KEY WORDS: environment; chromite; hexavalent chromium; Terminalia chebula.

1. Introduction

Chromium in nature is stable in the environment mainly as trivalent, Cr(III) and hexavalent Cr(VI). The latter one—hexavalent chromium—is known to be the ‘rogue’ molecule. Highly toxic, hexavalent chromium, Cr(VI) in prolonged contact with the skin can cause skin ulcers and even cancer in humans. Therefore, chromium presence as Cr(VI) in any industrial product becomes a concern if its concentration is above the permissible exposure limit (PEL) of 0.5 mg-Cr/kg as per WHO (World Health Organization) standards.

Chromite concentrates typically contain Cr(VI) in the range of 2–4 mg-Cr/kg depending upon the nature of ore deposit. The common removal method (reducing toxic hexavalent chromium, Cr(VI) to non toxic trivalent chromium, Cr(III)) is by the use of inorganic (chemical) reductants which is an environmental unfriendly and cost ineffective option. Conventionally, treating chromite concentrates with chemical reductants is the industrial way. The following problems are well known: chemical reductants such as ferrous sulphate being corrosive in nature have an adverse effect on the production process and it also leaves behind high sulphur effluents which are environmentally degrading. Hence, there is need to look for alternative reductants. Unlike removing hexavalent chromium from water is a well researched topic, not much literature exists on removing Cr(VI) from chromite concentrates making newer reductant development a challenging task especially with solid chromite concentrates. In the recent times, there has been a considerable interest in low cost organic reductants due to their environmental friendly nature. Therefore, at Tata Steel an organic reductant known as Terminalia chebula is employed for the first time for removing Cr(VI) in chromite concentrates. In the current work, the critical Cr(VI) removal process parameters such as Terminalia chebula dosages, contact time and water requirements for treatment are established for using at plant scale to minimize Cr(VI) in chromite concentrates to trace levels (<0.1 mg-Cr/kg).

2. Aqueous Chromium Chemistry

Even though chromium can exists in valence states ranging from −2 to +6, the two important oxidation states under subsurface condition are trivalent, Cr(III) and hexavalent, Cr(VI). The hydration behaviour of Cr(III) is slower and tend to produce the mononuclear species as CrOH$^{2+}$, Cr(OH)$_2$$^{2+}$, Cr(OH)$_3$$^{-}$ and the neutral species Cr(OH)$_4$$^{0}$ as shown in Fig. 1. Cr(III) can also exists in polynuclear species such as Cr$_2$(OH)$_2$$^{2+}$ and Cr$_3$(OH)$_4$$^{2+}$ but these polynuclear species are never significant in natural systems. In acidic regions and at relatively low redox potentials, Cr(III) exists as Cr$^{3+}$ and cationic hydroxo complexes [Cr(OH)$_{1-x}$, Cr(OH)$_{2-x}$]$.^3,4$ Cr(III) precipitates as its hydroxides Cr(OH)$_3$$^{0}$ between pH 6.8 and 11.3, while at higher pH values, Cr(III) may form anionic hydroxo complexes [Cr(OH)$_{2-x}$, Cr(OH)$_{3-x}$]$.^5$

By contrast, hexavalent chromium, Cr(VI) hydrolyses extensively and hence only neutral or anionic (hydroxo or oxo) species are present in water. The anionic species form
varies according to pH and may be chromate (CrO$_4^{2-}$), hydrochromate (HCrO$_4^{-}$), or dichromate ion (Cr$_2$O$_7^{2-}$). At low pH, Cr(VI) exists predominantly as hydrochromate (HCrO$_4^{-}$) and at high pH >6.5 is in the form of chromate ion (CrO$_4^{2-}$).

2.1. Redox Behaviour of Chromium

Eh–pH diagrams are sometime used in assessing redox conditions in soil environments for chromium. Redox potential Eh–pH diagrams represent equilibrium data and indicate the oxidation states and chemical forms of the chemical substances which exist within specified Eh and pH ranges. Figure 2 is an Eh–pH diagram for chromium compounds representing typical aqueous ionic conditions. Although the diagram implies that the boundary separating one species from another is distinct, the transformation is so clear cut. Concentration, pressure, temperature, and the absence or presence of other aqueous ions can all affect the kind of species. Cr(III) exists in wide Eh and pH ranges, with specific species varying with pH, as seen in Fig. 2. Cr$^{3+}$ ion exists when pH is less than 3, and tri-valent chromium hydroxyl species [Cr(OH)$_2^{+}$, Cr(OH)$_3^{+}$, Cr(OH)$_3^{0}$, and Cr(OH)$_4^{1-}$] exist at pH greater than 3.5. Cr(III) can form the stable and soluble (and thus mobile) organic complexes with low to moderate molecular weight organics. The significance of these complexes is that they allow Cr(III) to remain in solution at pH levels above which Cr(III) would be expected to precipitate.

2.2. Toxicity of Chromium

The toxicity of chromium is highly dependent on the specific form present. Cr(VI), which is toxic and known to be carcinogenic in the environment, is also very soluble and mobile, and moves at a rate essentially same as groundwater. In contrast, the reduced form of Cr(VI), Cr(III) is relatively non toxic and immobile under moderately alkaline to slightly acidic conditions.

3. Occurrence of Hexavalent Chromium in Chromite Concentrates

The origin of Cr(VI) in chromite concentrates can be traced to the presence of MnO$_2$ in chromite ores. MnO$_2$ is thermodynamically capable of oxidizing Cr(III) to Cr(VI) in presence of reduced manganese oxide (MnO). Therefore, Cr(VI) content of natural chromites varies widely with the type and nature of ore deposit. At Tata Steel, chromite concentrates, which are usually obtained by wet physical beneficiation of natural chromite ores, contain Cr(VI) in the range of 2.0 to 4.0 mg-Cr/kg. A typical chemical composition of chromite concentrate is given in Table 1.

3.1. Difficulties in Conventional Cr(VI) Removal Approach

Historically, chromite concentrates are treated with ferrous sulphate for Cr(VI) removal. However, this method is environment unfriendly and cost ineffective due to the following two reasons. At first, FeSO$_4$ being highly corrosive in nature has an adverse effect on the production equipments. The way out is to add the chemical offline-by transporting the ore to the stockyard and then spraying it with FeSO$_4$—a batch process which is time consuming and costly due to high water requirements of about 200 L per ton for Cr(VI) treatment. It also leaves behind high sulphur containing effluents which are environmentally degrading. Secondly, ferrous sulphate in contact with air is converted into ferric oxide which decreases the chromium reducing ability. As a result, more amount of it is required to achieve the desired output, which means increased sulphur levels in the concentrate (a non desirable component in chromite concentrates beyond 0.007 mass%) and higher production costs. Thus, there is need for development of alternative low cost, easily available and environment friendly materials that can remove Cr(VI) in chromite concentrates which is mostly possible by using organic reductants such as Terminalia chebula.

| Constituent | Cr$_2$O$_7$ | Total Fe | Al$_2$O$_3$ | SiO$_2$ | MgO | MnO | TiO$_2$ |
|-------------|-------------|----------|-------------|---------|-----|-----|---------|
| Mass %      | 58.0        | 16.4     | 11.7        | 1.7     | 11.5 | 0.5 | 0.2     |
4. Experimental

4.1. Terminalia chebula

*Terminalia chebula* also known as myrobalan is a member of the Combretaceae family and commonly used as astringent, antitussive, anti-diarrhea and styptic agent in Indian and a traditional Chinese medicine.\(^8\)

*Terminalia chebula* (T. chebula, hereafter) is a dried fruit of an Indian tree and contains as much as 33% hydrolysable tannins, which may vary from 20 to 50% according to forestry research in India. Juang *et al.*\(^8\) found fourteen hydrolysable tannin constituents in *T. chebula* (Fig. 3), and categorized into four groups: (i) phenolcarboxylic acids: gallic acid, ellagic acid, and chebulic acid; (ii) gallotannins: 1,6-di-O-galloyl-β-D-glucose, 3,4,6-tri-O-galloyl-β-D-glucose, 1,2,3,4,6-penta-O-galloyl-β-D-glucose; (iii) ellagitannins: punicalagin, casuarinin, corilagin and terchebulin; (iv) others: chebulanin, neochebulinic acid, chebulagic acid and chebulinic acid. These tannin constituents are reported to have complex structures containing many polyhydroxyphenyl groups. In the current work, *T. chebula* powder used is analyzed by Fourier transform infrared spectroscopy (FTIR) for identifying the functional groups (chemical bonds) in this organic material. The result for FTIR spectra is shown in Fig. 4, which has confirmed the presence of phenol, carboxylic, hydroxyl and alcoholic groups as reported in previous paper.\(^9\)

4.2. Batch Experiments for Cr(VI) Removal

Chromite concentrate containing initially Cr(VI) of 4.1 mg-Cr/kg are fully mixed with *T. chebula* powder in lab scale stirred tank reactor at a constant room temperature (303 K). During the experiments, 60% (w/v) solids slurry was maintained considering the actual stream conditions at plant. In each experiment, after once treated with *T. chebula*, concentrates were separated from slurry by decanting the water, dried and analyzed for Cr(VI).

4.3. Plant Trials in Continuous Production Process Circuit

In order to conduct the plant trials, selection of location for *T. chebula* addition in process circuit was a critical task. Therefore, a sump location is identified such that the required contact time (obtained from lab studies) would be met without wastage of added *T. chebula* in the process stream. A constant dry concentrate (solids) rate of 50 tons per hour and slurry with 60% solids is maintained in this process stream during the trial period. The system was permitted to run continuously until steady state was achieved in each trial. The slurry samples were collected in known time intervals and repeated for three times to ensure accuracy in Cr(VI) removal results. Solid concentrates were then analyzed for Cr(VI).
4.4. Analysis Procedure of Hexavalent Chromium in Chromite Concentrate

4.4.1. Leaching of Cr(VI) from Chromite

Chromite concentrates are leached rigorously with pure distilled water (solids to water mixture ratio is 1 : 10) for 6 h using the horizontal shaking machine at rated speed of 100 rpm. Once leached, water is separated from concentrates by filtration using membrane filter having 0.10 μm open pore size (47 mm diameter). The filtrate contains almost 99% of total dissolvable Cr(VI) contained in solid chromite concentrates since Cr(VI) is highly soluble in water. Subsequently in order to identify the presence of Cr(VI), the filtrate is mixed with a special reagent as mentioned in Sec. 4.4.2.

4.4.2. Identifying Cr(VI) Using a Reagent

Diphenylcarbazide (DPC) is widely used reagent for identifying the dissolved Cr(VI) in water since DPC, in acidic pH, forms a red violet colour complex compound known as diphenylcarbazone by reacting with dissolved Cr(VI) in water. This colour is developed by mixing 25 mL of liquid filtrate (obtained after leaching chromite concentrate with distilled water) with 0.5 mL of H₂SO₄ (1 : 10 dilution) and 0.5 mL of DPC solution. The mixture is then allowed for the red violet colour development for 5 to 10 min. Thus, the absorbance of light (which is proportional to Cr(VI) concentration in solution) by this red violet complex in solution is measured using UV spectrophotometer for estimating Cr(VI) in chromite concentrate.

4.4.3. Cr(VI) Estimation

UV spectrophotometer method is commonly used for dissolved Cr(VI) estimation at trace levels. Hence all the absorbance measurements in the current study are carried out with UV-spectrophotometer at 540 nm light wavelength using distilled water as reference. This procedure was followed by adopting the method given in industrial standard for Cr(VI) analysis. Absorbance readings are corrected and compared with the standard calibration curve for Cr(VI) concentration which was obtained using chromium standard solution. The Cr(VI) in solid chromite concentrate is then estimated based on the results obtained by concentration measurement.

5. Results and Discussion

5.1. Estimation of Critical Cr(VI) Removal Process Parameters

5.1.1. Effect of T. Chebula Concentration

Chromite concentrates used in present study were containing Cr(VI) of 4.1 mg-Cr/kg. In order to get the first estimate of Cr(VI) removal, chromite concentrates are treated with T. chebula having different concentration in solution, ranging from 1 to 4 w/v%. These batch experiments are conducted for 300 s duration. The percentage of solids in each experiment is maintained at 60 w/v%. Figure 5 shows the effect of T. chebula concentration in solution on Cr(VI) minimization in chromite concentrates. It is observed that even at concentration of 1 w/v% T. chebula in solution, initial Cr(VI) in concentrate has dropped by almost 99.5% minimizing Cr(VI), to 0.02 mg-Cr/kg (i.e. traces) which is much below the permissible exposure limit (PEL) in chromite concentrates. An increase in T. chebula concentration, however, does not significantly contribute to the further Cr(VI) removal.

5.1.2. Effect of Contact Time

The contact time required for maximum Cr(VI) removal is established experimentally by contacting concentrate with T. chebula solution (1 w/v%) in batch reactor for different time ranging from 60 to 240 s. Figure 6 shows the effect of contact time on Cr(VI) minimization in chromite concentrates. It can be seen that with increase in contact time the concentration of Cr(VI) in concentrate decreases up to 120 s and falling flat thereafter at a constant Cr(VI) value of 0.02 mg-Cr/kg. Although Cr(VI) removal up to 96% was achieved in 60 s, contact time of 120 s is decided as suitable time for ensuring the maximum Cr(VI) removal up to trace values of 0.02 mg-Cr/kg.

5.1.3. Adsorption Mechanism of Cr(VI) Removal

As mentioned in Sec. 4.1, T. chebula contains as much as 33% hydrolysable tannins, which are basically plant phenolic compounds containing many polyhydroxyphenyl groups having high affinity towards heavy metals such as chromium. Therefore, the reduction of toxic Cr(VI) to non toxic Cr(III) essentially takes place by Cr(VI) adsorption to the tannin molecules. Nakano et al. have clarified this adsorption mechanism of Cr(VI) removal which consists of four reaction steps; (1) the esterification of Cr(VI) ion with tannin molecules, (2) the reduction of Cr(VI) to Cr(III), (3) the formation of carboxyl group by the oxida-
tion of tannin molecules and (4) the ion exchange between reduced Cr(III) with the carboxyl and/or hydroxyl groups created within tannin molecule. A schematic diagram representing the Cr(VI) removal mechanism by tannin molecules is shown in Fig. 7. The adsorption process as shown in this figure, begins with the attack on tannin polymer by Cr(VI) ion and proton in acidic solution followed by esterification of Cr(VI) ion with tannin. The esterification process (reaction step-1) is associated with a release of a water molecule. Further, the rearrangement of tannin structure takes place which is accompanied by the reduction of Cr(VI) into Cr(III) (reaction step-2) and formation of carboxyl group (reaction step-3) simultaneously by the oxidation of tannin molecule. It was reported that a large amount of proton was consumed during the reduction of Cr(VI) so that the initial acidic solution containing Cr(VI) was transferred automatically to neutral one. Therefore in this reaction process it is important to supply a large amount of proton for promoting the reduction of Cr(VI) into Cr(III). The carboxyl group which was created in reaction step-3, by the oxidation of tannin molecules parallel to reduction of Cr(VI) to Cr(III), contributed to an increase in the ion exchange sites of the reduced Cr(III) which acts effectively to increase the adsorption capacity of tannin molecules. The reduced Cr(III) is reported to be adsorbed on the sites of –OH and/or –COOH within the tannin particles indicating the ion exchange between reduced Cr^{3+} and carboxyl and/or hydroxyl groups. During this ion exchange process between reduced Cr^{3+} and carboxyl groups (reaction step 4), H^+ ions (protons) are released which are consumed during the process of Cr(VI) adsorption to the tannin molecules in reaction step 1.

5.1.4. Optimization of T. Chebula Dosages in Batch Experiments

The optimum requirement of T. chebula for maximum Cr(VI) removal in chromite concentrates is estimated in batch experiments by treating chromite concentrates with different dosages of T. chebula. For this, dry T. chebula of given mass is mixed with the concentrate slurry having percentage solids of 60% for 120 s and subsequently the solution was separated for Cr(VI) analysis. The results obtained in batch experiments are shown in Fig. 8. It is observed that about 99.5% Cr(VI) removal is completed at an optimum amount of 0.5 g/kg T. chebula, decreasing the Cr(VI) content to 0.02 mg-Cr/kg in chromite concentrates. Further increase in the T. chebula dosages does not show any effect on Cr(VI) removal. Thus, an optimum quantity of 0.5 g T. chebula per kg of chromite concentrate is established.

5.1.5. Crosscheck on Chromite Concentrate Quality

Apart from Cr(VI), the changes in quality of chromite concentrates after processing with T. chebula have been investigated. This is carried out by checking chemical composition and microstructure of concentrate obtained after treatment. It was seen that there is no change in chemical (composition) and physical properties such as colour of chromite concentrates after treatment with T. chebula. It was also observed that, no impurities such as sulphur are added to the concentrate product due to this treatment. The microscopic image of chromite concentrate before and after treatment with T. chebula is shown in Fig. 9. It is observed that there is no notable change in colour of concentrate after treatment with T. chebula. However, few traces of reddish coloured unreacted T. chebula particles are seen in microscopic image (Fig. 9(b)) but this phenomenon is not so strange since some T. chebula particles can remain adhered to chromite concentrate even after the solids are separated from process water carrying T. chebula particles.

5.2. Plant Scale Results

5.2.1. Optimization of T. Chebula Dosages at Plant

Once the process parameters (T. chebula dosages, contact time, etc.) are established at lab, it is necessary to carry out...
the Cr(VI) removal process in continuous plant production process. For this, the trials were conducted at chrome ore beneficiation plant. A constant dry solids rate of 50 tons per hour (slurry with 60 w/v% solids) is maintained in the process stream during the trial period. Each trial was conducted continuously for 1 h duration. Terminalia chebula is added to the process circuit at identified location by using different flow rates of T. chebula solution (obtained by mixing dry T. chebula with water) having concentration of 1 and 3 w/v%. The results for Cr(VI) removal are shown in Fig. 10. It is observed that, 1 w/v% T. chebula solution results in maximum Cr(VI) removal of 96%, which corresponds to the decrease of Cr(VI) content in chromite concentrates to 0.15 mg-Cr/kg, at higher flow rate of 40 L/min. Although the flow rate of 1 w/v% T. chebula solution is increased further to 50 L/min, there is no significant improvement in Cr(VI) removal. However, in the case of 3 w/v% T. chebula in solution, it is seen that at an optimum flow rate of 15 L/min almost 99.5% Cr(VI) removal is obtained. The reason for higher degree of Cr(VI) removal not obtained in case of 1 w/v% solution even at higher flow rates (50 L/min) can be explained as follows: since with higher increase in flow rate an excessive dilution of T. chebula resulted in improper contact between T. chebula and solids in the process stream.

5.2.2. T. Chebula and Water Consumption Estimation

The dry T. chebula consumption and the corresponding water consumption during the plant trials are then calculated and shown in Fig. 11. It can be seen that at an optimum flow rate (15 L/min) of 3 w/v% T. chebula in solution, the dry T. chebula consumption is 540 g/1000 kg with an additional (required to prepare the 3 w/v% strength T. chebula solution) water consumption of 18 L/1000 kg. However, in the case of 1 w/v% strength at similar degree (600 g/1000 kg) of T. chebula consumption the additional water requirement is almost three times greater (60 L/1000 kg) and with lower Cr(VI) removal efficiency of about 96%. Since the objective of this study is to minimize the Cr(VI) concentration in chromite concentrates to traces, 3 w/v% concentration of T. chebula in solution with specific dry T. chebula consumption of 540 g/1000 kg concentrate is recommended to the plant.

5.3. Advantages of T. Chebula for Cr(VI) Removal

Apart from being environmental friendly due to organic nature of the T. chebula, this method requires negligible (18 L) amount of additional water compared to large quantities (about 200 L) required for one ton concentrate treatment in conventional (FeSO₄) method. Also, in contrast to the conventional method, T. chebula does not create any secondary pollution like sulphur impurities both in water and concentrate product. The little consumption (540 g/ton) of T. chebula required for Cr(VI) removal in chromite concentrates makes this method a cost effective option over the conventional approach. Therefore, this method is implemented at chrome ore beneficiation plant Sukinda, Tata Steel.

6. Conclusions

The use of T. chebula which is an organic product was explored for Cr(VI) removal in chromite concentrates. The critical Cr(VI) removal process parameters such as T. chebula dosages, contact time and water requirements were
established and used at plant scale. It was found that 540 g of *T. chebula* and contact time of 120 s is required for one ton concentrate treatment at plant for minimizing Cr(VI) to trace levels (0.02 mg-Cr/kg). It was also observed that the water requirements in this process are insignificant compared to conventional method. In essence, the application of *T. chebula* for removing Cr(VI) in chromite concentrate was found to be suitable for removing Cr(VI) in chromite concentrates and therefore used in continuous production process of chromite concentrates at plant.

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