



Kinetics study for lateritic Chromite overburden leaching by organic (oxalic) acid

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ABSTRACT

The kinetics of nickel leaching from lateritic Chromite overburden (COB) by organic (Oxalic) acid has been investigated. In this context, the effects of oxalic acid concentration and temperature upon the rate of nickel extraction from COB were evaluated. The leaching kinetics study was also performed for nickel extraction from thermally pre-treated COB, since nickel extraction was improved by the thermal pre-treatment of the COB. Well established shrinking core models were applied to study the kinetics of nickel extraction from raw and pre-treated COB. The experimental outcomes evident that, rates of nickel extraction from raw as well as the pre-treated COB were controlled by diffusion controlled shrinking core rate kinetics model. Further, apparent activation energies for extraction of nickel from raw and pre-treated COB were estimated to be 14.31 kJ/mol and 14.56 kJ/mol respectively.

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Introduction

Lateritic minerals deposited in the earth crust have occupied the most abundant reserves (>70%) of nickel (Simate, *et al.*, 2010). Indeed, these lateritic deposits are representing bulk portion of nickel bearing minerals, still the sulphide nickel minerals have been contributing for major portion of global nickel production. Usually, nickel minerals are broadly classified into two types *i.e.* (i) sulphide and (ii) lateritic (oxidic) type.

Presently the sulphidic minerals are the prime sources for nickel extraction in the world. Since nickel present in lateritic minerals is in very complex form as well as the nickel content is poor, hence lateritic minerals have been neglected for nickel extraction. However the extensively exploited sulphidic minerals are depleting in alarming rate and as a consequent the laterites are gaining importance as an alternative resource of nickel production.

Though India is a mineral rich country but there is no known deposit for sulphide mineral of nickel. The majority of national nickel requirement is fulfilled by external import only. On the other hand the Sukinda valley, Odisha which is one of the major chromite reservoirs of the world and is known for lateritic form of nickel deposits (Murthy, *et al.*, 2010). Chromite mining at Sukinda valley annually generates around 6 to 7 million tonnes of lateritic overburdens containing nickel (0.5 to 1.0%) (Swain, *et al.*, 2007). Weathering of these abandoned mineral wastes also crating threat to environment. So, it becomes inevitable for utilization of these lateritic minerals to extract metal values.

The extraction of metal values from laterites/Chromite overburdens through the conventional pyrometallurgy and hydrometallurgical technologies have not been so far accepted due the involvement of larger capital costs in their processing for metal recovery (Valix, *et al.*, 2001). However applications of

microorganisms have been studied extensively for extraction of metals through microbes-minerals interactions.

Furthermore, by applying microorganisms such as species of *Aspergillus*, *Penicillium*, *Acidithiobacillus*, *Leptosporillium* etc. it is possible to recover valuable metals from low grade minerals like laterites (Das, *et al.*, 2011). Use of *Acidithiobacillus* bacterial strain for extraction of metals is a well-established phenomenon for treatment of low-grade sulphide ores. As the laterites lake energy sources for supporting the chemo-autotrophic mode of life style of *Acidithiobacillus*, hence the heterotrophic fungal species like *Aspergillus* and *Penicillium* have been studied more elaborately for processing of laterites. These heterotrophic microbes perform the leaching of metals through the secretion of metal chelating organic acids (citric and oxalic acids) (Bosecker, 1997; Behera *et al.*, 2011). Amongst different organic acids, oxalic acid has been reported to be more effective in leaching of lateritic COB (Sukla, *et al.*, 1993).

Leaching kinetics study is an inevitable factor to justify the reaction mechanisms in metals extraction process. The leaching rate kinetics plays the most important parameter for designing of batch experiments. Subsequently, it is necessary to study the leaching of metals depending upon time under variation in experimental parameters. In this regard, the present study deals with the kinetics of nickel leaching from lateritic COB by using oxalic acid solutions with a view to elucidate reaction mechanism involved in nickel extraction. The kinetic analysis for nickel leaching was performed based on well established shrinking core model. Activation energy for nickel leaching was also determined in addition to kinetics study to further support the kinetic models involve in the process. The effects important parameters like temperature and thermal pre-treatment of lateritic COB were also investigated in this paper.

Materials and methods

Lateritic Chromite overburdens (COB)

The COB samples were collected from the mining sites of Sukinda, Odisha, India and brought to the laboratory for further processing. The COB samples were crushed and sieved to obtain a particle size of $\sim 500 \mu\text{m}$. Along with the raw COB leaching experiments were also conducted with thermally pre-treated COB. Thermal pre-treatment of COB was done in muffle furnace at 600°C for 3hrs. The metal composition of the lateritic COBs has been presented in Table 1.

Organic acids

Analytical grade of oxalic acid was taken throughout the experiments for nickel leaching from COB.

Analytical methods

The samples of COB were air dried and the metal concentrations were determined after acid digestion. Nickel concentration in samples drawn at regular interval was done by atomic absorption spectrophotometer (AAS) (Perkin Elmer-AA200, USA).

Mineralogical analysis of original and leached residues were carried out by means of X-Ray diffraction study (Phillips Diffractometer - PW3710) with a radiation operating at 40 kV and 30 mA to identify major and minor minerals.

COB leaching by oxalic acid

The leaching kinetics experiments were performed for both raw and pre-treated COB having average particle size of $\sim 500 \mu\text{m}$ in 1L Erlenmeyer flasks. Leaching experiments at room temperature were performed by using oxalic acid concentrations of 0.125, 0.25 and 0.5M/L. Further experiments were carried out in oxalic acid (0.5M/L) at temperatures 323K, 333K and 343K under atmospheric pressure for estimation of activation energy in nickel leaching. Prior to the experiments each flask containing 500 ml of oxalic acid solution was submerged in hot water bath maintained at constant temperature. After reaching to the desired temperature, 10g of COB was added and agitation was started with a mechanical stirrer. The agitation rate was maintained at 600 ± 10 rpm. The experiments were performed for 150 min, during which samples (5 ml) from the leach slurry were taken periodically (10, 20, 30, 60, 90, 120 and 150 min). The samples drawn from leaching vessel were filtered out using membrane filter ($0.22 \mu\text{m}$) for determination of the nickel concentration by atomic absorption spectrophotometer.

Results and discussion

Mineralogical analysis

X-ray diffraction study of COB elucidates the crystal structure, chemical composition of the COB. The X-ray diffraction spectrum (Fig. 1) of the COB indicated the presence of goethite as major iron mineral phase in COB. The nickel present in the COB occurs in an absorbed state within the goethite matrix (Behera *et al.*, 2011). The X-ray diffraction spectra showed that, goethite mineral phase which was initially present in raw COB changes to the hematite by the thermal pre-treatment. Furthermore, the transmission electron microscopic (TEM) study (Fig. 2) of raw and pre-treated COB samples revealed that thermal pre-treatment increased the porosity in COB as a result of with the surface area of ore particles were increased.

Nickel extraction

Oxalic acid is a prominent metabolic by product generated by several heterotrophic fungal strains used in bioleaching studies (Castro, *et al.*, 2000). In the present study oxalic acid was used for nickel leaching from lateritic COB, since the oxalic

acid has been reported as a favourable leaching agent for dissolution of nickel as well as iron from laterites (Sukla, and Panchanadikar, 1993). The higher leaching efficiency of oxalic acid in compare to other organic acids like citric acid gluconic acid, acetic acid is attributed to its higher acidic nature, as well as chelating and complex forming property (Ambikadevi, and Lalithambika, 2000).

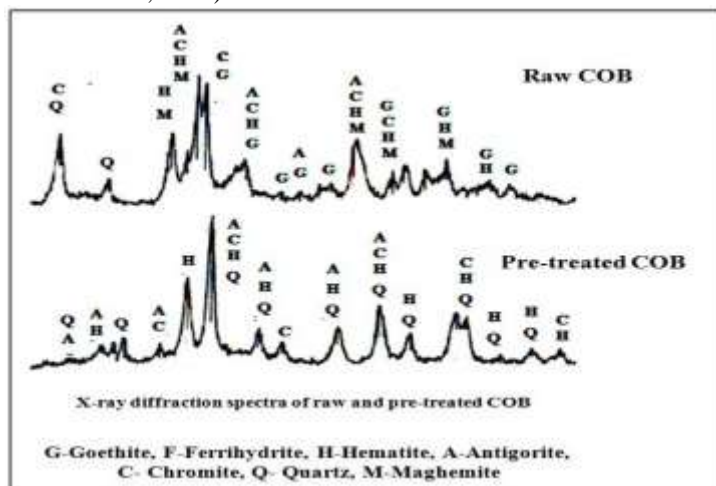


Fig. 1: X-ray diffraction spectrum of the raw and pre-treated Chromite overburdens

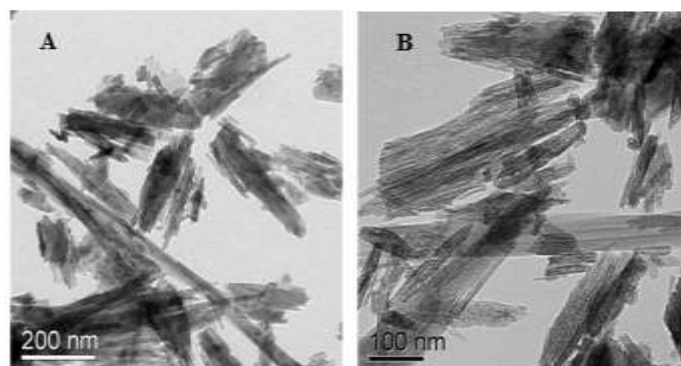


Fig. 2: Transmission electron microscopic study for Chromite overburdens (A) raw COB and (B) pre-treated COB

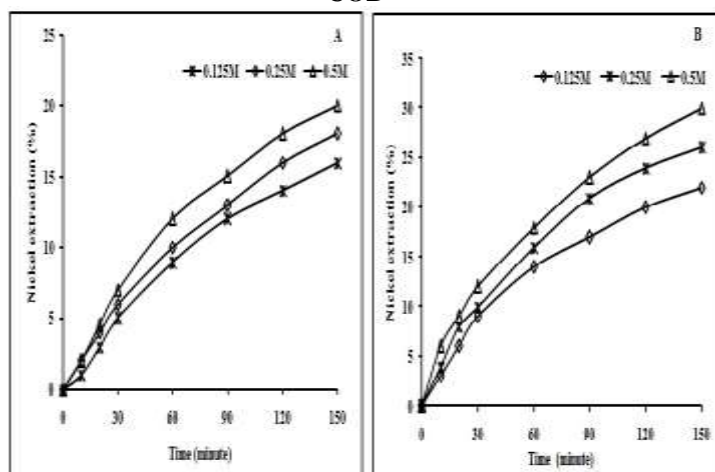
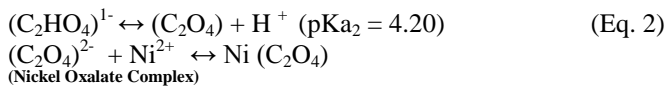
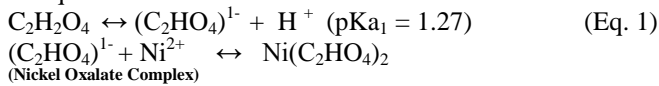


Fig. 3: The Plot showing nickel extraction (%) as a function of time from Chromite overburdens (COB) by using different concentrations of oxalic acid (A) nickel extraction from raw COB (B) nickel extraction from pre-treated COB

Fig. 3(A & B) represents the extraction of nickel from raw and thermally pre-treated COB in different concentration of oxalic acid. It was observed that, the nickel extraction from COBs was increased with increase in oxalic acid concentration. Also the nickel extraction from pre-treated COB was comparably higher in compare to raw COB. About 30% nickel was extracted from pre-treated COB whereas in case of raw COB only 20% nickel was extracted by leaching conducted at 2% pulp density by using 0.5M/L oxalic acid under atmospheric pressure and room temperature. From the X-ray diffraction and TEM study it was evident that the thermal pre-treatment of the COB altered its mineralogical composition along with it also increased its porosity and surface area. Thus pre-treatment of COB made it more amenable to leaching by lixiviates and hence the nickel extraction was more from pre-treated COB. Nickel content of COB was solubilised by the oxalic acid as mentioned in Eq. 1 and 2.



To elucidate the reaction mechanism involved in the nickel leaching by oxalic acid, the leaching data represented in Fig. 3(A & B) are subjected to analysis under different models of reaction kinetics. Further to rationalize the reaction mechanisms involved in the process the activation energy during the processes were estimated by conducting the leaching experiments in different temperatures. Figure 4 (A & B) presenting the nickel leaching from raw and pre-treated COB data over the time in different temperatures (323K, 333K and 343K).

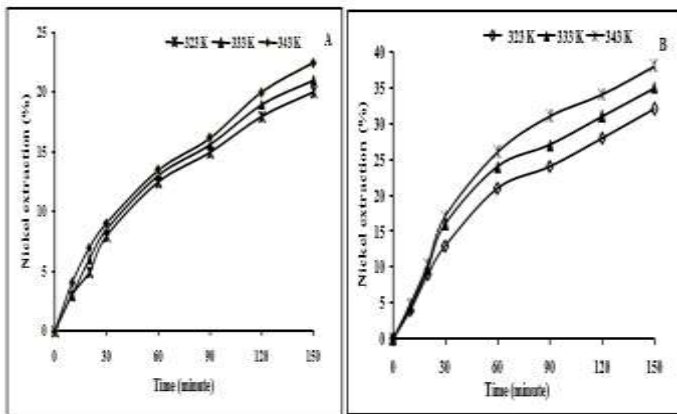


Fig. 4: The Plot showing nickel extraction (%) as a function of time from Chromite overburdens (COB) in different temperatures by of oxalic acid (0.5M/L) (A) nickel extraction from raw COB (B) nickel extraction from pre-treated COB Kinetics of nickel extraction

Kinetics studies for the extraction of nickel from both raw and pre-treated laterite COB were conducted basing upon the amount of nickel extraction with respect to time. Separate kinetics studies were conducted for the rate of nickel leaching from raw and pre-treated COB in different concentrations of oxalic acid at room temperature (Fig. 5). For estimation of

activation energy the kinetics studies were conducted in different temperatures (323°K, 333°K and 343°K) at 0.5M/L oxalic acid concentration (Fig. 6).

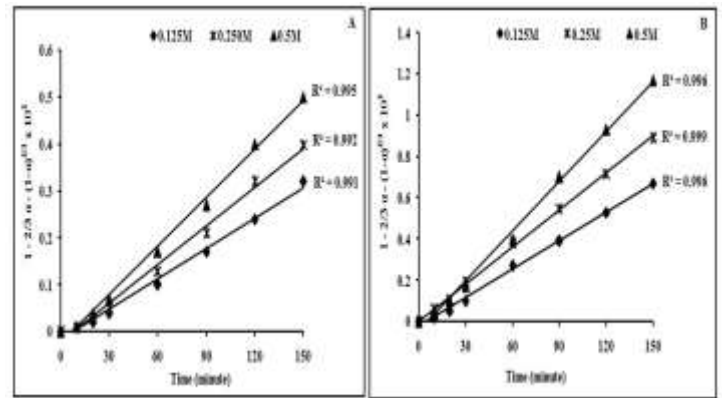


Fig. 5: Application of diffusion shrinking core model ($k_2t = 1 - 2/3\alpha - (1 - \alpha)^{2/3}$) for extraction of nickel from raw and pre-treated COB by different concentration of oxalic acid

The kinetics of solid-liquid interactions in mineral processing involved three established shrinking core models such as (i) chemical reaction model *i.e.* reaction at the particle surface, (ii) diffusion through the product layer model and (iii) combination of both chemical control and diffusion model. For the nickel leaching kinetics, two established shrinking core models represented by the following equations (Eq.3 and 4) were studied (Habasi, 1069; Olanipekun, 2000).

$$k_1t = 1 - (1 - \alpha)^{1/3} \quad (Eq. 3)$$

$$k_2t = 1 - 2/3\alpha - (1 - \alpha)^{2/3} \quad (Eq. 4)$$

Where α is fraction of nickel extraction at time t and k_1 and k_2 are the rate constants of Eq. 3 and Eq. 4, respectively.

Eq. 3 assumes the nickel extraction rate from COB was controlled by the chemical reaction taking place on the surface of the mineral, and Eq. 4 assumes the controlling step for nickel extraction was diffusion through the product layer by considering shape of the ore particle as spherical.

Only the Eq. (4) fits for the extraction of nickel from both raw and pre-treated COB by leaching conducted in concentrations of oxalic acid solutions (Fig. 5). Thus, the kinetics of nickel extraction from lateritic COB by oxalic acid leaching obeyed the diffusion process of shrinking core model. Similarly Senanayake and Das reported that the iron extraction from limonitic laterite was followed by shrinking core models (Senanayake, and Das, 2004). Also nickel associated with the iron matrix of limonitic laterite was also concurrently leached and followed similar type of kinetics rate.

Correspondingly the rate of nickel extraction during leaching conducted by oxalic acid (0.5M/L) at different temperatures obeyed the diffusion shrinking core model of kinetics (Fig.6). The aforesaid observations inferred that during leaching process nickel was diffused from the COB matrix by metal chelating and solubilising oxalic acid. To validate aforesaid observations the authors have estimated the activation energy.

Table 1: Metal composition of raw and pre-treated chromate overburden

Types of Chromite Overburden	Ni %	Co %	Fe %	Cr %	Mn %
Pre treated	1.02	0.04	50.85	3.65	0.35
Raw	0.99	0.03	48.88	2.59	0.21

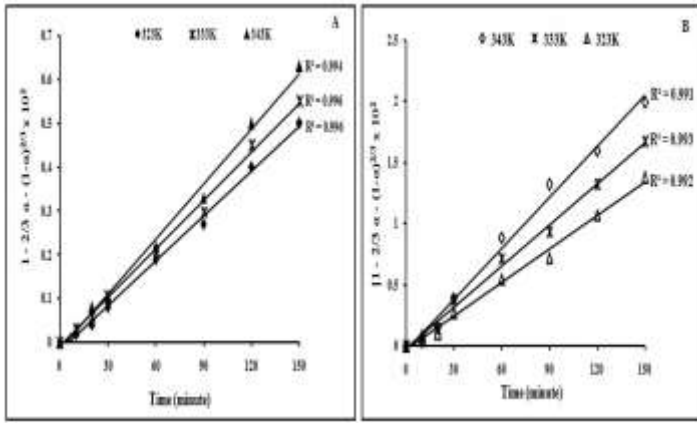


Fig. 6: Application of diffusion shrinking core model ($k_2t = 1-2/3\alpha-(1-\alpha)^{2/3}$) for extraction of nickel from raw and pre-treated COB in different temperatures (K) by oxalic acid (0.5M/L)

The apparent rate constants calculated from data mentioned in Fig. 5 & 6 were used for the determination of the activation energy for the extraction of nickel from raw and pre-treated COB respectively. The temperature dependent Arrhenius equation (Eq. 5) was used for the estimation of activation energy in the leaching process.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (\text{Eq. 5})$$

Where k is the overall rate constant, A is the frequency factor E_a is the activation energy, R is universal gas constant and T is the reaction temperature in Kelvin.

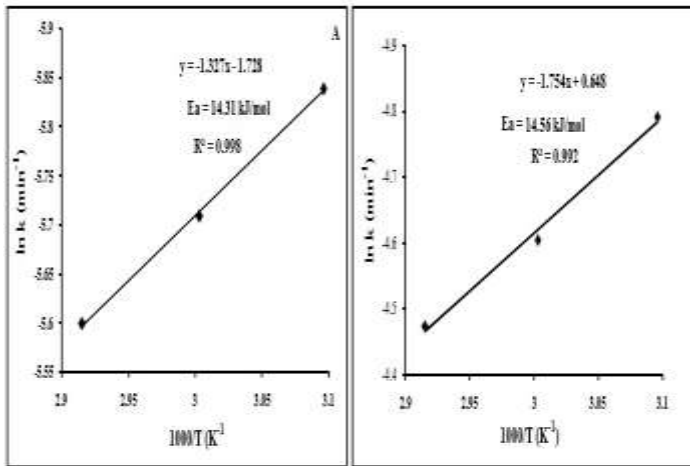


Fig. 7: Arrhenius plot for extraction of nickel from COB (A) raw COB (B) pre-treated COB

The activation energies for nickel extraction from raw and pre-treated COB were estimated from Arrhenius plot of $\ln k$ vs. T^{-1} (Fig. 7). The apparent activation energy for raw and pre-treated COB was 14.31 and 14.56 (kJ/mol.) respectively. As the diffusion model is least dependent upon the temperature, hence the activation energy for diffusion controlled process is comparably low (4 and 12 kJ/mol), whereas, for a chemical controlled process, the activation energy is generally greater than 40 kJ/mol (Habasi, 1069; Abdel-Aal, 2000). The cumulatively corroborate of the calculated apparent activation energy with the Eq. 4 of rate kinetics for mineral processing, supported diffusion process of shrinking core model involve in nickel extraction from COB.

Conclusions

The aforesaid discussion was concluded that the nickel extraction by oxalic acid was favoured by thermal pre-treatment of COB. The kinetic study indicates that the leaching of nickel was controlled by diffusion of nickel from COB matrix during the leaching processes. The activation energy was calculated to be for raw COB was about 14.31kJ/mol and for pre-treated COB it was 14.56 kJ/mol, these findings are consistent with the values of activation energies reported for the diffusion-controlled reactions.

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