

## BIO-DISSOLUTION OF METALS FROM ACTIVATED NODULES OF INDIAN OCEAN

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### Abstract

The biodissolution of valuable metals from ferro-manganese nodules of Indian Ocean in presence of *Aspergillus niger* is a slow process. In order to improve the kinetics of bioleaching, the sea nodules were activated in high energy attrition mill thereby changing the granulometry and surface charge characteristics of the particles. The zeta potential, particle size distribution and surface area of the activated material were recorded and bioleaching was carried out by *A.niger* in the pH range 4.0-5.5. The mechano-chemical activation of the mixed particles ( $\leq 75 \mu\text{m}$ ) of nodules in 10 min reduced almost 86 % material to  $\leq 10 \mu\text{m}$  size with a change in zeta potential from -18 to -34 mV. Bioleaching of metals from the activated nodules was compared with that of the dissolution pattern of metals in presence of *A.niger* without any pretreatment as well as those under the chemical leaching conditions. The results showed the bio-recovery of more than 95% copper, nickel and cobalt each in 15 days time when the nodules activated for 10 min was leached at 5 % (w/v) pulp density, 4.5 pH and 35 °C temperature. Bio-leaching of these metals was observed to be similar from the nodules activated for 30 min. The non-activated nodules showed  $\geq 89\%$  metal recovery in 25 days under the above conditions. The mechano-chemical activation of sea nodules has thus been found to improve the kinetics of the process and has also resulted in to the availability of wider pH in the range of 4-5 for the processing.

### Introduction

Bioprocessing of the polymetallic manganese nodules of Pacific and Atlantic Oceans for extraction of non-ferrous metals has been reported by several investigators [1-8]. Some reports are also available on bio-dissolution of metals from Indian Ocean Nodules [9-16]. By using *Acidithiobacillus ferrooxidans* (At.f) [12,13] and microbial isolate from the nodules [10,11,14-16], the bioleaching of metals from sea nodules has been described. The microbial metal dissolution process from ocean nodules is generally a slow process taking a few days to months. The kinetics of metal bioleaching may be enhanced with the help of transferring energy to the ore particles through pre-treatment such as those involving ultrasonics, microwave, mechanochemical activation (MA) etc. The application of ultrasonics [9] as pretreatment in the bioleaching of laterite nickel by *A. niger* showed improved nickel extraction. The MA leads to structural and physicochemical changes in the solids by deformation, disintegration and/dispersion [17-20], while changing the surface charge and creating defects in the lattice by stored of energy [18,19]. The use of mechanochemical activation as a pre-treatment prior to the bioleaching of ocean nodules has not been investigated in detail [21]

and therefore, worth exploring with the aim of improving the kinetics/extent of metal extraction using *Aspergillus niger*. The results are reported in the present paper.

### Materials and Methods

*Aspergillus niger* (MTCC 281) was obtained from the culture bank of Institute of Microbial Technology (IMTECH), Chandigarh (India) and was revived at 35 °C using Czapek Dox Medium. The culture of *A. niger* in Liquid Czapek Dox Medium was grown on 5% (w/v) sea nodules of  $< 75 \mu\text{m}$  size to adapt fungi on the substrate and the adapted strain (four times) was used for the bioleaching of metals.

The air dried sea nodule sample obtained from National Institute of Oceanography (NIO), Goa (India) was characterised for the phases by XRD and was found to have todorokite, birnesite, and lithiophorite as major Mn(IV) minerals and goethite, maghemite and ferrihydrite as the major iron minerals. Copper, nickel and cobalt were a part of manganese and iron oxyhydroxide phases. The size of sea nodule sample was less than 300  $\mu\text{m}$  and the analysis of the representative sample by atomic absorption spectroscopy (AAS) showed 0.89 % Cu, 0.96 % Ni, 0.12 % Co, 18.31 % Mn and 6.4 % Fe.

A 150 g nodule of  $< 75 \mu\text{m}$  size was activated in an attrition mill (Model: PE 075, NETZSCH-Feinmahltechnik GmbH, Germany) under the following conditions: 500 ml volume, 2 kg SS balls of 2 mm diameter (86% of volume filled up), 250 ml water, 25 °C temperature and activation for desired period (5–30 min) at 1000 rpm.

Bioleaching of sea nodules was carried out in conical flasks of 250 ml in an orbital motion incubator shaker as described elsewhere [21] inoculating the adapted culture in the Czapek Dox medium (Sucrose-30 g/L,  $\text{NaNO}_3$ -3 g/L,  $\text{K}_2\text{HPO}_4$ - 1 g/L,  $\text{MgSO}_4$ -0.5 g/L, KCl-0.5 g/L and  $\text{FeSO}_4$ -0.01g/L). Different parameters such as pH, particle size of nodules, time etc were optimised for the activated material and those without any pre-treatment. Metal recovery was calculated by analyzing the supernatant by AAS. Redox potential against SCE and pH were measured/maintained on alternate days. The metal adsorbed on the fungal biomass was also determined from the leach residue and the biomass by thoroughly washing with dilute sulphuric acid (pH : 1) and then centrifuging [21]. The particle size distribution and specific surface area (SSA) were determined by laser particle size analyser (Model: Mastersizer, Malven, UK) and zeta potential by zeta meter (Model: 501 PENKEM Inc, USA).

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## Results and Discussion

The effect of activation of the ocean nodules with time has resulted in change in particle size distribution, surface charge potential and surface area etc; data on  $d_{50}$ , the median diameter, and increase in specific surface area (SSA) and zeta potential are given in Table 1. The milling for 5 min represented the particle behaviour typically that of Rittinger stage where excessive breakage occurred and surface area increased proportionately to the energy input. It was in the next stage of milling between 5-20 min that limited breakage of the particles still continued but the increase in surface area was proportional and the input energy was consumed to activate the material by way of energy storage and creating plastic deformation, defects and transformation to a certain extent. Beyond 20 min, some breakage occurred with the increase in SSA.

**Table1.** Size reduction and surface area during activation of sea nodules

Time of Activation (min)	Average particle size ( $d_{50}$ ) $\mu\text{m}$	Specific Surface Area ( $\text{m}^2/\text{g}$ )	Zeta Potential (-mV)
0	18.53	0.607	18
5	5.85	1.641	20
10	5	1.8	34
15	4.3	1.9653	48
20	3.4	2.2	51
25	1.05	3.424	54
30	0.95	3.53	55.5

A look at the surface charge characteristics of particles, in terms of zeta potential (Table 1), shows gradual decrease in the value -18 mV for non-activated sea nodules to -34 mV after 10 min and -48 mV after 15 min of activation. The zeta potential did not change much after 5 min of activation. Increase in zeta potential with time of activation indicated the accumulation of the similar charge on the surface and higher electrophoretic mobility of the activated particles in the leaching medium. The activated particles thus acquired so less gravitational force that they remained dispersed in bulk medium offering better contact for a reaction to proceed.

Fig. 1 and 2 shows the particle size distribution with the time of milling. The activation milling of the nodules for 10 min reduced the size of the particles to  $< 38.5 \mu\text{m}$ , whereas the activation in 20 min and 30 min brought the particles to  $< 28.7 \mu\text{m}$  and  $< 11.9 \mu\text{m}$  size. The sea nodules ground for 45 min in a planetary mill reduced about 95 % of the particles to below  $42.45 \mu\text{m}$ . Fig. 2 show that most of the activated materials from 10-30min milling lie in the range  $0.5\text{--}10 \mu\text{m}$  and only 4-7 % particles were of  $20\text{--}30 \mu\text{m}$  size. The activated material with higher surface area could be more reactive for chemical-microbial interaction. The bio-leaching experiments were carried out for the activated material on 5-30 min milling.

Results summarized in Table 2 show the bio-recovery of more than 95 % Cu, Ni and Co with *A. niger* in 15 days for the activated nodules of 10 min milling. The recovery was almost similar for the three metals with non-activated (planetary mill

product) sample in 25 days time. The optimum pH was 4.5 for the non-activated material but in case of 10 min activated sea nodules, even leaching at 4 and 5 pH resulted in good metal recovery. Thus, the kinetics of bio-leaching improved significantly along with a high metal recovery and even providing a broader pH range i.e., 4 to 5 for biodissolution. The milling/activation for 5 min did not have much impact on metal biodissolution. The longer time of milling (30 min) has yielded the similar metal bio-dissolution.

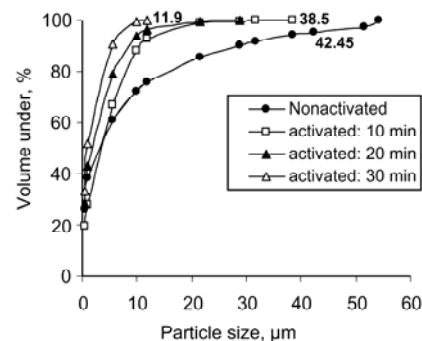


Figure1. Particle size distribution - Cumulative volume (%)

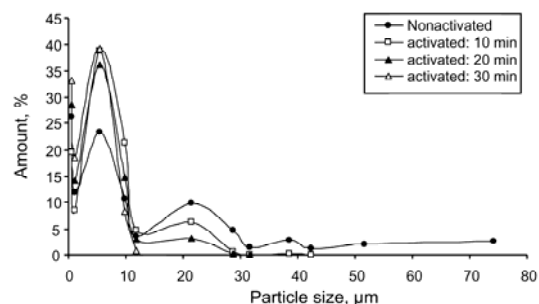


Figure 2. Particle size distribution during milling of sea nodules

**Table 2.** Metal recovery from sea nodules\* by *A. niger* at 35 °C, 5% PD while varying pH and activation time

Time of activation (min)	pH	Metal recovery (%) in 15 days									
		Control leaching					Bioleaching (with acid wash)				
		Cu	Ni	Co	Mn	Fe	Cu	Ni	Co	Mn	Fe
0	4	3.3	8.8	13	0	4.6	61	55	73	75	5.9
	4.5	2	9	4	0.8	0.4	63	62	36	57	6.1
5	4.5	11.6	15.3	11.6	17.5	5	78	64	50	63	7.0
	5	10.7	9.8	5.9	7.1	0.5	74	73	41	58	7.2
10	4	25	37	42	40	0.2	Recovery more than 95 % Cu, Ni, Co				
	4.5	31.2	28	46	30	1					
	5	35	21	58	23	2					
30	4.5	67	59.5	42.9	7.7	1.4	Recovery more than 97 % Cu, Ni, and 94% Co				

\* Bio-recovery in 25 days at 4.5 pH without activation: 89.2% Cu, 93.5% Ni, 93% Co & 79% Mn.

At 4.5 pH and 35°C temperature, the variation of pH prior to adjustment and corresponding redox potential during bioleaching of activated nodules (for 10 min) are presented in Fig. 3. In 15 days, pH and  $E_{SCE}$  became almost stable at 3.3 and 380 mV respectively. This indicated that the bio-leaching of metals reached to the optimum level in this period. It may be mentioned that the size of non-activated particles ranged from 5-75  $\mu\text{m}$  whereas it was 2-38.5 $\mu\text{m}$  for the 10 min activated particles. The improved kinetics of biodissolution in activated material could be the results of finer particle size available and use of the stored energy and surface charge due to the milling.

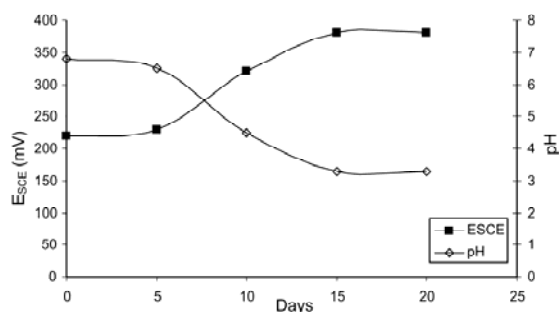


Figure3. The pH profile and redox potential during bioleaching by *Aspergillus niger* in 20 days at 35 °C temperature

Experiments were also carried out for the bioleaching of activated (attrition milling) and non-activated sea nodule (from ball milling) particles both of  $\leq 38.5 \mu\text{m}$  and results are presented in Fig. 4(a) and 4(b). It may be seen that the final recovery of copper and nickel was almost similar in 20 days of leaching, but copper bio-recovery after acid wash increased from 49.8 % on day 5 to 98 % on day 10 and nickel recovery also reached to 98% on day 15, this kind of rise was not observed in case of non-activated nodules. Kinetics of cobalt recovery also improved with mechanochemical activation as about 95 % cobalt bio-dissolution was observed in 15 days time as compared to 44 % Co recovery from the ball milled material. The metal recovery was 7–10 % higher in control experiments for activated (10 min) nodules over non-activated material. Activation of nodules may unlock the host lattice facilitated by stress/defects induced by milling thus improving the kinetics of bioleaching.

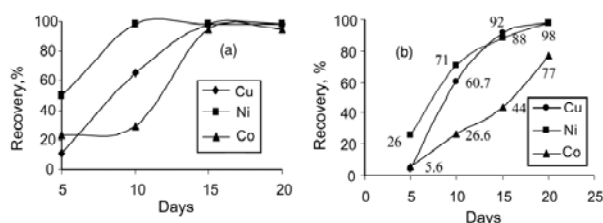


Figure 4. Comparison of bioleaching using (a) activated and (b) non-activated (ball milled) sea nodules of  $\leq 38.5 \mu\text{m}$  particles, at 4.5 pH, 35°C temperature and 5% PD [Recovery of metals after acid wash]

The XRD phase identification of bio-leach residue from 10 min activation at pH 4.5 is shown in Table 3. Apart from the manganese phases such as birnesite, lithiophorite and silica, formation of hydronium jarosite at pH 4.5 as a major phase was an interesting feature. Besides, some amount of  $\gamma\text{-Mn}_2\text{O}_3$  and goethite were also observed as minor phases in leach residue. Formation of the phases comprising of mixed and lower oxidation states of manganese and iron clearly indicated microbial attack of host lattice and release of metals associated with the lattice. The SEM of the bio-leach residue at pH 4.5 (Fig. 5 (a) and 5(b)) confirmed the formation of ferric hydroxide which covered mostly the corroded surface of the manganese and iron phase of the nodules. This has also resulted in increased size of the residue particles as compared to the original particles.

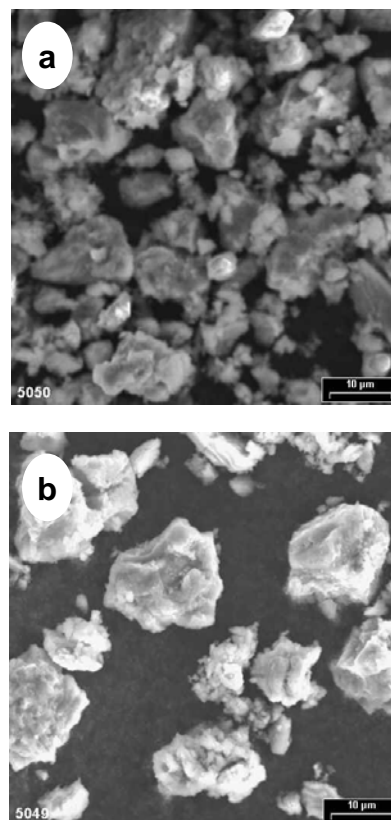
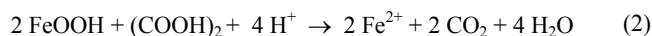
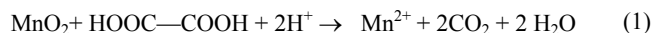


Figure 5. SEM of sea nodules : (a) after activation, (b) bioleach residue obtained from the activated nodules (at 4.5 pH)

Table 3. XRD phase identification of sea nodules before and after bioleaching at 35°C in 15 days

Sample	Mineral phase
Sea nodules	<i>Major:</i> Todorokite, birnesite, lithiophorite, silica
	<i>Minor:</i> Maghemite, goethite, alumina
Bioleach residue at pH 4.5	<i>Major:</i> Birnesite, lithiophorite, silica, $\text{Fe}(\text{OH})_3$
	<i>Minor:</i> $\gamma\text{-Mn}_2\text{O}_3$ , goethite, alumina

Bioleaching of metals with *A. niger* appears to follow the indirect mechanism releasing acids viz., oxalic and citric (Eq. 1 and 2) which in turn converts Fe (III) to Fe (II) and Mn (IV) to Mn (II).



The valuable metals viz., Cu, Ni & Co are thus released and get dissolved, besides even forming soluble metal complexes. Some of the metals are in turn adsorbed on fungal cell wall and easily desorbed again by acid wash (AW) of the biomass at 1.0 pH.

### Conclusions

1. Mechano-chemical activation of sea nodules displays reduction in particle size and increase in surface charge. In 10 min of milling,  $\approx 86\%$  particles are of  $\leq 10\ \mu\text{m}$  size whereas the same size is obtained almost quantitatively (99 %) in 30 min of milling. The zeta potential increases from -18 mV to -34 mV in 10 min of activation and becomes -48 mV in 15 min of activation, with marginal increase in milling duration.
2. Activation of nodules improves the bioleaching kinetics with *A. niger* and provides larger pH range (4-5 pH) for metal recovery. Above 95 % Cu, Ni, Co and Mn are recovered within 15 days of bioleaching at 35 °C and 5 % PD with 10 min activated particles as compared to 25 days time required for the non-activated material. Activation milling develops shear stress, accumulates charge and defect in the nodules, besides storing some energy thereby improving the kinetics of leaching.
3. Improved metal recovery in activated material of similar size range ( $\leq 38.5\ \mu\text{m}$ ) is obtained than that from ball milling. The metal bio-dissolution follows indirect leaching mechanism. The formation of ferric hydroxide in the bio-leach residue is observed by XRD phase identification whereas covering the particles by porous  $\text{Fe}(\text{OH})_3$  is reflected from SEM pictures.

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