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An Innovative Method for Titanium Production from Ilmenite using Microorganisms

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Abstract: Ilmenite ore is one of the most important sources of titanium dioxide production. An innovative method for titanium production from ilmenite ore was developed in this work. The method is based on the use of microorganisms for bioleaching of TiO_2 from ilmenite ores. The results obtained shows that the bioleaching process is very effective and efficient for producing TiO_2.. The TiO_2 content in the treated sample is 3.34 times the corresponding value in the ilmenite ore samples. The proposed method is a promising since it is new, cost effective, and it is an ecofriendly. It opens the door for the possibilities of Ti production from ilmenite ores at the industrial scale in Egypt.

Keywords: Ilmenite, Bioleaching, Titanium.

1 Introduction

Titanium (Ti) is a transition metal and it is the second most abundant element after iron and in the Earth's crust, it is the ninth most abundant element [1-6]. Ti is present in large quantities in ilmenite, rutile, anatase, titanite. perovskite and leucoxene minerals [1-6]. Since rutile contains the highest content of TiO_2, it is considered the most economical ore for titanium among other Ti- bearing minerals. Ilmenite ($FeTiO_3$) is the second economical ore for titanium and it a promising ore for titanium metal. Other economical Ti-bearing minerals are perovskite ($CaTiO_3$) and leucoxene (plus rutile mixture, weathered ilmenite). Due to the high cost of processing for production of Ti from pyrophanite ($MnTiO_3$) and sphene ($CaTiSiO_5$), these ores are not considered economical ones. 95% of the titanium in the form of TiO_2 is found in nature [2]. The Earth and oceanic crusts contain approximately 2.3 % of TiO_2. Since Ti is characterized with high strength to weight ratio, it can used as an alloy with some metals including vanadium, aluminum, molybdenum,….etc. Ti-based alloys can be used in military and aerospace industry, medical and many other industrial applications [2,7,8]. TiO_2 is well known for its photocatalytic activity [1.2,9,10,11] including water splitting for the production of H_2 (clean fuel) and degradation of organic molecules (textile dyes, pesticides, pharmaceuticals) present as pollutants mainly in wastewater in the presence of UV and/or visible light [1.2,9,10,11]. It is promising in photovoltaic cells [1,12], and it is used as the anode material in lithium ion batteries in electric vehicles, mobile electronics etc [1,13] . Since TiO_2 in the rutile phase has a high refractive index, it is the best candidate as a white pigment in coatings, paints, plastics and inks [14,15].

There are large ilmenite deposits in the South Eastern desert of Egypt. Abu Ghalaga region is considered one of the most promising sites containing large reserves of ilmenite ore. It was estimated that the reserves in this area to be about 50 million tons [16-18].

Extraction of Ti from its ores can be carried out using various methods as reported in literature by many authors [1,3,4,6]. Among these methods, there are only two commercial methods for Extraction of Ti which are attributed to Kroll and Hunter [1,6]. The Kroll method is based on the use magnesium metal for the reduction of $TiCl_4$ while in the Hunter method, sodium is used. Limitations of these methods are mainly attributed to the corrosion of reactor vessels resulting from the use of high concentration of acids for digestion, the huge amounts of solid and acid wastes created, and high costs related to the high amount of required energy and chemicals [1,6].

An innovative green technology and/ or method is urgently needed for Ti-extraction from its ore because of the limitations of the methods used for Ti- extraction and the availability of a large ilmenite deposits in Egypt. The proposed method should employ biological resources such

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as fungi, bacteria, algae, and viruses as more environmentally friendly and also cost effective ways to extract Ti from its ores.

Titanium concentration was found to up to 33,700 ppm in the marine species, Karenia brevis, of dinoflagellates [2]. The concentration of Ti in in the whole organism of Diatoms was reported to be 940 ppm, however it can reach 1254 ppm in its frustule [2]. Some microorganisms may have a selectivity mechanism toward Ti minerals. Evidences of such hypothesis can be found in the species of foraminifera (Bathysiphon argenteus), isolated from sedimentary rocks, which is composed of TiO_2 in rutile form [2, 19]. 10% of the shell of Ammobaculites balkwilli is composed of TiO_2 in anatase form [2,20]. Titanium in the ilmenite form was found in tests of Textularia hauerii [21]. 27% TiO2 and 11% ilmenite were found in test of Psammophaga zirconia [22]. Strong as well as selective adhesive between cells of some gram positive bacteria and TiO_2 in the anatase and rutile mineral forms was observed, where more than 85% of the cells adsorb to TiO_2 within a minute [2]. Biosorption and agglomeration interaction processes of TiO_2 nanoparticles were observed in some bacteria. Such processes can be attributed siderophores and polysaccharides found on the cell surface [2, 23,24]

To the authors best knowledge, microorganisms were not used before for production Ti from its bearing minerals. There were only some studies devoted for biosynthesis of nano TiO_2 [25-29]. In this work, some microorganisms grown on ilmenite samples collected form Abu Ghalaga region, were isolated. They were was used together with some additional agents to extract Ti from its bearing mineral. Ti and other elements present in the extracted samples were determined using XRF.

2 Material and methods

2.1 Fungal isolation

Sampling: the ilmenite samples were collected from Abu Ghalaga region, Aswan , Egypt, from different depths (1-50 cm). 25 samples were collected superficially from about 1 Km^2 and mixed in five samples. Each sample (100 gm) was moistened with 20 ml of demineralized water.

Preparation of samples: samples wetted by demineralized water to activate the growth of microorganisms present in the samples powder sieved with sieve set and the fine powder was used in the experiment.

Media: different solid media were used in the cultivation of very fine, sieved ilmenite samples as (PDA) Potato dextrose media Czpack's. Agar media, Dox's agar media. The solidified culture plates were inoculated with 1 gm from the fine powder of ilmenite and other from the serial dilution of 1 gm powder.

Cultivation and purification: four fungal isolates were the most abundant with high growth rate and repeated in all cultures were used to test its selectivity with enriched titanium dioxide culture.

Selectivity : the fungal isolates were cultivated in enriched Dox's media liquid and solid with different concentrations of titanium dioxide suspended with Tween 80 in liquid media only at different temperatures from 10 – 50 ^{0}C for different incubation periods (3-21 d) with different stirring velocities (25-150 rpm).

2.2 Fungal growth and titanium extraction:

- 500 gm of crude ilmenite were grinded to a very fine powder in 2 liters conical flask

- Immersed in one liter of modified liquid Dox's media and the PH was adjusted at certain PH value.

- Inoculated with 10 ml of spore suspension of the most dominant and has a good capability for the production siderophores in the presence of high concentration of iron.

After sterilization with a U.V. lamb for two hours with stirring at 150 pm.

- The culture was fed by air supply with certain intensity for 15 days at 30^{0}C.

- The PH was readjusted through the experiment.

- All steps were compared with the control samples.

2.3 Titanium organic matter extraction:

- The semi-reactor flask liquid layer was filtrated to separate the biomass which was washed by demineralized water and the filtrate was examined to the presence of titanium and iron but was not contained with valuable amounts.

- Then heavy precipitate was washed with demineralized water and the fine suspended white layer was decanted and separated from the heavy brownish precipitate layer.

- This physical flotation method repeated until all fine white, insoluble suspension was separated from the remainder of the crude sample.

- The white suspension was filtrated by Puchner filter and dried for five days at 105 ^{0}C until fixed weight is obtained. The dry samples were subjected to XRF.

3 Results and Discussion

The dried samples, white samples obtained from microorganism treated ilmenite ore samples, as well as ilmenite ore samples were subjected chemical analysis using wavelength dispersive x-ray fluorescence (XRF). The results are listed in Table 1. For comparison purposes, results reported in literature for the same ilmenite ore are listed in Table 1. The TiO_2 and Fe_2O_3 contents in the ilmenite ore samples analyzed in this work are lower than the corresponding values reported in [16-18]. Additionally, these values are lower than reported values in literature. The treatment of the ilmenite ore yielded a white compound enriched with TiO_2. The TiO_2 content in the treated sample is 2.2 times the corresponding value in the ilmenite ore samples. if the loss of ignition of the treated sample (35.1 %) was taken into account, the real TiO_2 content would be 45.8%. Consequently, the TiO_2 content in the treated sample is 3.34 times the corresponding value in the ilmenite ore samples. This means that the TiO_2 enrichment is 234.5 %.This is a very important result. The reported enrichments in literature did not approach the enrichment value in this work. The result obtained due to the bio-mineralization of ilmenite ore to produce a Ti- rich compound is interesting and is of a great value. The method used can be upgraded at the commercial scale for production of Ti-rich compounds.

Some samples were analyzed using short time neutron activation analysis (NAA). These samples were collected from surface of Abu Ghalaga region. The pneumatic rabbit neutron irradiation system installed at the second Egyptian research reactor was used for irradiating the samples for short times. The irradiated samples were measured using a HPGe detector. The k_0 standardization method was used to analyze acquired spectra- details of the k_0 is beyond the scope of the present paper. The results are listed in table 2. As one can see the concentration are different from those listed in Table 1, since the samples were collected from surface. Interestingly, the Ti-content in the treated samples is `~ 4.9 times that in the ore sample. These results credit the method developed for enrichment of ilmenite ores. Further discussion of the results obtained will be reported in a forthcoming paper.

Table 1: Chemical composition of ilmenite ores from Abu Ghalaga region analyzed in this work and published results.

Compound (%)	This work	Treated sample	[16]	[17]	[18]
TiO_2(%)	13.7	30.2	41.1	40.91	36.78
FeO	-	-	24.4	-	25.85
Fe_2O_3	23.0	5.02	28.6	51.9	29.86
SiO_2	31.3	7.27	2.43	1.97	4.46
Al_2O_3	10.5	15.2	0.63	1.1	0.72
Cr_2O_3	-	-	0.36	0.071	0.21
MnO	0.113	-	0.36	0.25	0.36
CaO	5.23	3.3	0.15	0.33	0.15
MgO	5.13	2.43	0.64	3.38	0.81
P_2O_5	0.207	1.94	0.02	0.05	0.03
V_2O_5	=	-	0.4	-	0.38
SO_3	-	-	0.11	-	0.21
CO_2	-	-	0.65	-	-
Na_2O	1.34	-	-	0.07	-
K_2O	0.129	0.136	-	< 0.01	-
Cl	0.039	0.015	-	-	-
S	1.34	0.3	-	-	-
Ni	0.098	0.016	-	-	-
Zn	0.025	0.014	-	-	-
Sr	0.061	0.015	-	-	-
Zr	0.007	-	-	-	-
Cu	0.21	0.036	-	-	-
Cr	0.11	-	-	-	-
L.O.I	1.47	35.1	-	-	-

Table 2. Elemental concentrations in ppm of treated and ore samples analyzed using k_0-NAA.

Element	Treated sample	Ore sample
Ti	12.01	2.45
Mg	2.22	0.35
Mn	0.14	0.003
Mg	2.22	0.43
Cu	0.14	0.06
Na	0.35	0.086
V	0.11	0.003
K	6.60	0.33
Cl	0.18	0.0002
Al	4.16	0.38
Mn	0.15	0.003
Na	0.39	0.088
Ca	1.50	0.20
Na	0.40	0.090

4 Conclusions

Based on the above results as well as according to reported values of TiO_2 content in ilmenite ores in literature, one would expect that high purity TiO_2 samples could be obtained using the method developed in this work. The present study is based on simple procedures. It may encourage and pay the attention of the decision makers and governmental authorities to commercially implement the method developed in this work. Bioreactors, inexpensive chemicals and less amount of energy are required items for implementing the developed method.

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