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RESEARCH ARTICLE

Characterization of different types of petroleum refinery spent catalyst followed by microbial mediated leaching of metal values

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Abstract: The present study aims for characterization and classification of five different spent petroleum refinery catalysts followed by metal recovery via bioleaching. The nomenclature given to the different spent catalyst (SC) is SC1, SC2, SC3, SC4 and SC5 collected from an Indian petroleum refinery. All spent catalysts were crushed and ground prior to their characterization by X-Ray Fluorescence for chemical composition followed by X-Ray Diffraction and Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy for their mineralogy. Metal recovery from the spent catalysts was carried out by bioleaching by a mixed microbial consortium of iron and sulphur oxidizing microorganisms. Most of the spent catalysts showed very significant metal recovery with respect to Ni, Cu, Cr, Mo, Zn, Sr and Ti. The study provides a possible metal recovery route via bioleaching for further testing and scaling up.

Keywords: X-Ray fluorescence, X-Ray diffraction, scanning electron microscopy, metal, mineralogy, bioleaching

1 Introduction

The rising need for clean energy has led to an increase in the demand for efficient catalysts in the petrochemical industries. The global demand for petroleum catalyst is increasing by 3.6% every year [1, 2]. The scope of petroleum catalysts includes the production of diesel, gasoline, jet fuel, heavy hydrocarbons and petrochemicals [3]. Different types of catalysts with a different chemical composition are employed for different reactions during petroleum refining. For examples, Hydrodesulphurization (HDS) catalysts used for eliminating sulphur from organic components of petroleum is composed of bimetallic catalysts based on Mo/V, promoted by Ni/Co and supported on Al_2O_3 matrix and Fluid Catalytic Cracking (FCC) catalysts responsible for the conversion of heavy feed-stocks (gas oils) into lighter, more valuable products such as liquefied petroleum gases (LPG) and cracked naphtha consists a mixture of an inert matrix (kaolin), an active matrix (alumina), a binder (silica or silica-alumina) and a rare earth exchanged Y-zeolite [3]. The extensive exploitation of catalyst to meet the consumer demand and poor quality of feedstock leads to inactivation of the petroleum catalyst. The dead catalyst is finally termed as 'spent' after several cycles of regeneration and reuse. This waste product of petroleum refining industry is considered to be hazardous in nature due to the presence heavy metals like nickel, molybdenum, cobalt, vanadium, chromium, copper and zinc which could pollute the environment if not land-filled properly. Reclaiming the rich metal values of the spent catalyst before landfilling will not only contribute to economic benefits but also combat the environmental challenges.

There are conventional approaches like pyrometallurgy, hydrometallurgy along with the greener and equally potent bioleaching route to extract the valuable metals from spent catalyst. Though bioleaching is more preferred by the researchers owing to the eco-friendly and cost-effective line of action to leach out metals into the solution by the attack of bio-oxidized ferric ion and protons as lixiviant yet it's scope is limited by its metal selective approach [4]. Many researchers have attempted the use of pure acids (H_2SO_4, HCl) and alkali (NaOH, Na_2CO_3, NH_4OH, NH_4Cl, $(NH_4)_2CO_3$ [5–7]. Owing to the presence of refractory Mo and Ni, which are easily soluble in alkali and acidic medium respectively, several studies have reported two-step leaching process. These two step leaching process could be bioleaching-bioleaching, bioleaching-alkali leaching, alkali leaching-alkali leaching *etc*. [4, 8]. It is noteworthy here that the majority of bioleaching studies have been conducted on hydrodesulfurization, hydrotreating and fluid catalytic cracking catalyst but several other type of spent catalysts from the petroleum refinery with recoverable metal values remain unexplored. A complete knowledge of both

physical and chemical properties of petroleum refinery spent catalysts is a prerequisite for designing any leaching process for metal extraction. A pre-treatment step before characterization is utterly important, which includes comminution of coarse spent catalysts into fine size fractions by crushing and grinding. Fine and homogeneous particles of spent catalyst will increase the accuracy and precision of the characterization technique. Comminuting will not only increase the surface area of the spent catalyst particles but also help in the liberation of the inbound refractory metals like Mo from the alumina or aluminum silicate matrix, ultimately increasing the reactant and solid interaction leading to enhanced metal recovery and leaching kinetics [9–11]. Further characterization of the pre-treated spent catalyst will give an insight into elemental composition, morphology, and mineralogy to understand the chemistry and nature of spent catalyst according to which leaching experiment can be designed. It will also help in unveiling the role of the spent catalyst in the refinery prior to its dumping off.

Therefore, the present work encompasses the collection, pre-treatment, characterization, and classification of 5 different spent catalyst samples followed by metal leaching from them via biological route. The five different petroleum refinery spent catalysts were collected from the dumping yard of a petroleum refinery, characterized to understand their chemical composition and mineralogy and henceforth classify them. The utility of iron and sulphur oxidizing microorganism was found most suitable for bioleaching of the spent catalyst to harness their metal content. This study would also help future research on spent catalysts to select the material based on the lixiviant priority and metal of interest for leaching and other applications.

2 Materials and methods

2.1 Sample collection and physical characteristics

The five different samples of spent petroleum refinery catalyst were obtained from the Petroleum refinery of Indian Oil Corporation Limited (IOCL), Mathura, India. The samples were coded as SC1, SC2, SC3, SC4, and SC5 where SC stands for Spent Catalyst. The physical appearance of the spent petroleum catalysts received was self-distinguishing from each other without any difficulty. Some of them had round bead like structures together grain like structures mixed into them. Some were heterogeneous in structure and property, while few of them were having homogenous structure and property (Figure 1)

Figure 1 **(a)** Physical appearance of the six different Petroleum refinery spent catalyst; **(b)** Ground samples of the six different Petroleum refinery spent catalyst.

The spent catalyst with sample code SC1 had round small dark and light brown colored circular structures with brown transparent crystals, SC2 and SC3 had dark brown colored balls and crystals, SC4 had black cylindrical grains with pale yellow colored transparent crystals and SC5 had black cylindrical grains only.

2.2 Pre- treatment and characterization of the petroleum refinery spent catalysts

Crushing and grinding to pre-treat all the six samples of spent catalyst was achieved by rod milling at the Department of Mineral Process Technology, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar, India. A fine particle size with an 80% passing (d_{80}) of

below 100μ was obtained. All the ground samples were further mixed and divided by coning and quartering method to ensure homogeneity (see supplementary Figure 1(b)).

The morphological and elemental analysis of the spent catalyst samples was performed with SEM- EDX (Nova Nano FESEM 450(FEI)). The powdered samples were mounted on the stubs with the assistance of a carbon tape. The samples were gold coated by a sputter to avoid their surface charging and reduce the noise in the SEM data. The images were obtained in the voltage range of 15 kV - 30 kV. The major, minor and trace elements present in the samples along with their mass% (w/w) were confirmed by the XRF (Bruker) analysis. XRD (PANalytical) was done for mineralogical study by measuring the diffraction patterns at angles between 5º to 90º and step size 0.013 angles/second.

2.3 Bioleaching experiments

The five different spent catalysts samples were bioleached for the metal recovery after characterization. The bioleaching experiments were performed with the mixed culture of iron and sulphur oxidizing microorganisms grown in modified 9K medium supplemented with 22 g/L ferrous sulphate heptahydrate as iron source and 2 mM of potassium tetrathionate as sulphur source. The highly activated inoculum with redox potential $>$ 700 mV (presence of biooxidized ferric ion) and cell count $\sim 10^8$ cells/mL was employed for bioleaching. The bioleaching experiments were carried out in 2.5 L baffled bioreactor at a working volume of 1L. A pulp density (PD) of 10% (w/v) of spent catalyst was subjected to 1 L of modified 9K medium containing 20% (v/v) inoculum and no iron and sulphur source. The microorganisms were motivated to derive nutrition and energy from the spent catalyst. The optimum temperature (30 ºC $\pm$5) and homogeneous mixing (220 rpm) of the pulp in the reactor was strictly maintained by a hotplate placed beneath the reactor and an impeller with four blades placed at right angle to the axis. The pH of culture, media and bioleaching solution was maintained at 1.5 to avoid iron precipitation and support the growth of these Fe and S oxidizing acidophilic microbiota. The pH and redox potential (Eutech) was measured on regular basis. The acid demand was fulfilled by the addition of 2 M/5 M H_2SO_4. The total acid consumption during bioleaching was calculated in terms of Kg concentrated H_2SO_4 consumed/ ton of spent catalyst. The evaporative loss of water was compensated by the addition of deionized water. All the analytical parameters during the tests were examined on a regular note. The cell counting to calculate cells/ mL in the culture and bioleach solution were done by diluting the samples and counting the viable cells on a neubauer haemocytometer under a bright field microscope at 100x objective and 10x ocular lens magnification. On completion the experiments were terminated for solid/ liquid separation by filtration assembly assisted by a vacuum filtration pump or aspirator (Lab companion). The oven dried residues obtained were crushed, ground and thoroughly homogenized before their analysis by XRF for the metal content. The metal recovery (%) in all the samples was calculated by the following formula (Equation 1-3).

$$M_f = M\% * w_f \tag{1}$$

$$M_{br} = M\% * w_{br} \tag{2}$$

$$L_Y(\%) = \left(1 - \frac{M_{br}}{M_f}\right) \times 100 \tag{3}$$

Where, M_f= metal content in the feed; M_{br}= metal content in bioleached residue; w_f= feed weight; w_{br} = bioleach residue weight; $M\%$ = Metal percentage; $L_Y(\%)$ = leaching yield percentage.

3 Results and discussion

3.1 Characterization of spent catalysts

The elemental composition of all the spent petroleum catalysts samples was obtained in mass percentage by the X-Ray Fluorescence analyzer (XRF) (Table 1).

The SC1 sample was rich in Al, Si and Cl with minor content of P, Ca, Fe, S *etc*. (Table 1). The samples of SC2 and SC3 were similar with high content of Si and Al and minor content of P, S, Ca *etc*., with traces of Cr, K, Zr, Zn *etc*. Major content of SC4 was Si, Fe, Ca, S and Al with low content of P, Cl, Mg *etc*. (Table 1). The sample SC5 sample was rich in Fe and Ca with minor contents of Si, Al, S and P and also had the trace elements similar to others (Table 1). The amount of aluminum and silica was found to be high in all the spent catalyst samples.

Table 1 Elements and their mass % (w/w) in the spent catalyst samples (SC1- SC5) and their bioleached residues (rSC1- rSC5)

Elements	SC1	rSC1	SC2	rSC2	SC3	rSC3	SC4	rSC4	SC5	rSC5
Aluminium (Al)	49.6	16.66	10.1	2.34	11	2.7	4.62	0.91	9.87	0.31
Bromine (Br)	ND	ND	0.009	ND	ND	ND	ND	ND	ND	ND
Calcium (Ca)	0.464	0.02	0.55	0.01	0.539	0.01	13.4	0.02	21.2	0.03
Chlorine (Cl)	10.7	ND	3.42	ND	2.73	ND	1.05	ND	0.393	ND
Chromium (Cr)	ND	ND	0.039	0.01	ND	ND	0.11	0.01	ND	ND
Copper (Cu)	0.008	0.03	ND	ND	ND	ND	0.13	0.01	0.266	0.01
Gallium (Ga)	0.012	ND	ND	ND	ND	ND	ND	ND	ND	ND
Iron (Fe)	0.144	0.09	0.146	0.03	0.169	0.03	13.7	0.24	37.7	0.33
Magnesium (Mg)	ND	ND	ND	ND	ND	ND	0.89	0.02	2.15	0.03
Manganese (Mn)	ND	ND	ND	ND	ND	ND	0.16	0.01	0.396	0.01
Molybdenum (Mo)	ND	ND	0.01	ND	ND	ND	ND	ND	ND	ND
Nickel (Ni)	0.011	ND	ND	ND	ND	ND	0.075	0.01	0.228	0.01
Phosphorous (P)	1.12	NA	1.46	NA	1.49	NA	2.31	NA	2.43	NA
Potassium (K)	ND	ND	0.024	ND	ND	ND	0.57	0.01	1.01	0.01
Silica (Si)	37.8	NA	84.0	NA	83.7	NA	54.2	NA	12.8	NA
Strontium (Sr)	0.005	ND	0.009	ND	0.012	ND	0.27	ND	1.19	ND
Sulphur (S)	0.107	NA	0.25	NA	0.188	NA	7.83	NA	9.11	NA
Titanium (Ti)	ND	ND	ND	ND	0.149	0.02	0.73	0.02	1.26	0.02
Zinc (Zn)	0.026	0.01	0.01	ND	ND	ND	ND	ND	ND	ND
Zirconium (Zr)	0.006	NA	0.017	NA	0.011	NA	ND	NA	ND	NA

Unit: Mass% (w/w); NA - Not Analyzed, ND - Not detecte

Metals like nickel, molybdenum, copper, zinc, gallium, strontium were present less than 0.2% in all the spent catalyst samples.

The Powder-X-ray Diffractogram patterns and mineralogical phases identified in all the five spent petroleum catalyst samples are stated in Figure S2-S6. The sample SC1 contained quartz (SiO_2) as a major mineral phase, while other minor phases contained oxides, phosphates, chlorides *etc.* of Ni, Ga, Zn *etc*. (Figure 2). The SC2 sample showed the presence of silicates and phosphates of K, Al, *etc*., while quartz was one of the major phase in it (Figure 3)

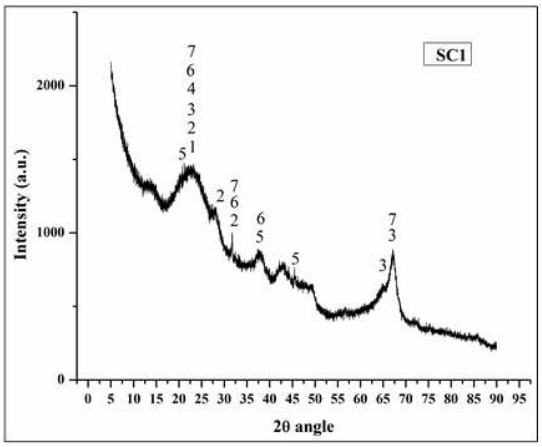

Figure 2 X-Ray Diffractogram of Petroleum refinery spent catalyst SC1

SC3 sample also showed the presence of similar mineral phases as observed in SC2 but were not exactly the same mineralogy (Figure 4).

Major XRD peaks in spent catalyst sample SC4 were manganese phosphate (MnP_4O_{11}), quartz (SiO_2), aluminum phosphate ($AlPO_4$) and a sodium aluminum silicate phase containing chloride and bromide ($Al_6Br_{1.74}Cl_{0.26}Na_8O_{24}Si_6$) (see supplementary Figure S5).

The SC5 sample revealed the presence of muscovite ($Al_3H_2KO_{12}Si_3$), quartz (SiO_2), titanium phosphate ($Ti_3P_9O_{27}$) and graphite (C) (Figure 6).

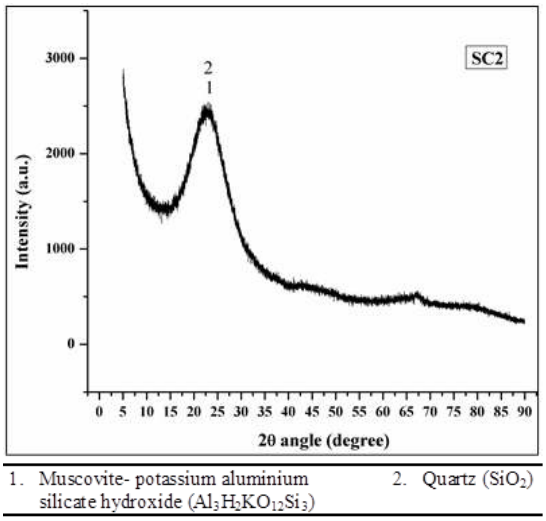

Figure 3 X-Ray Diffractogram of Petroleum refinery spent catalyst SC2

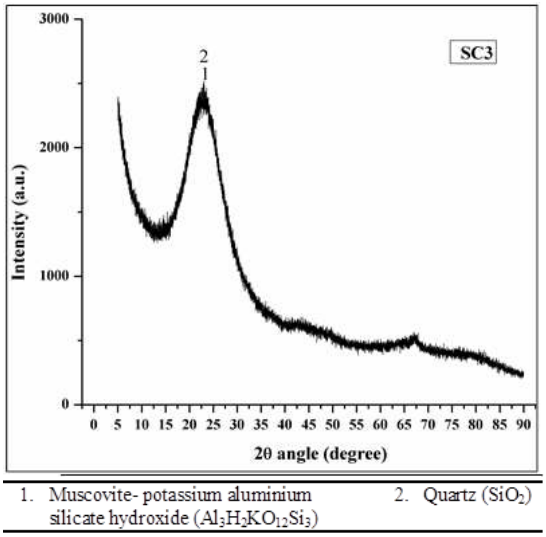

Figure 4 X-Ray Diffractogram of Petroleum refinery spent catalyst SC3

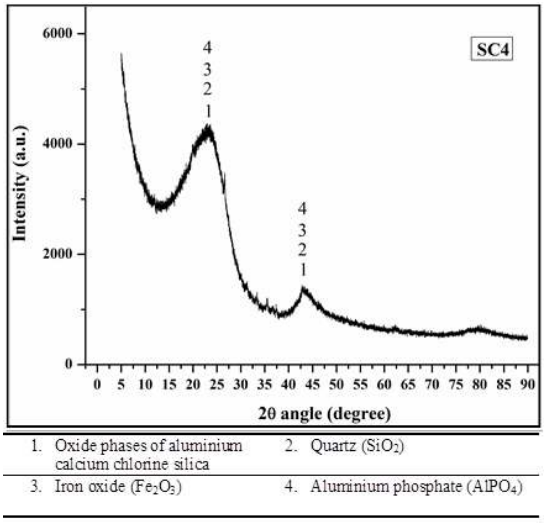

Figure 5 X-Ray Diffractogram of Petroleum refinery spent catalyst SC4

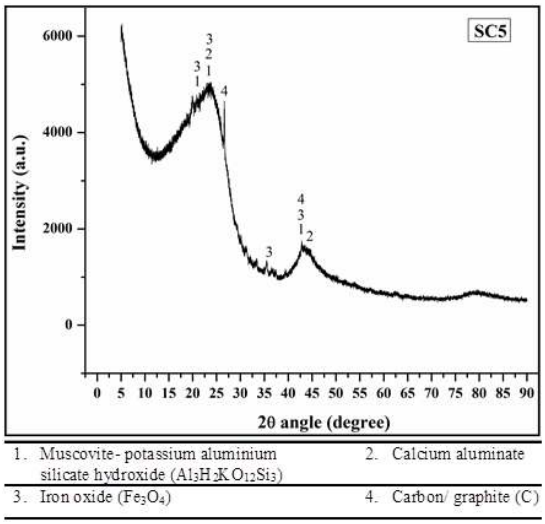

Figure 6 X-Ray Diffractogram of Petroleum refinery spent catalyst SC5

Quartz and aluminum silicates of sodium, potassium were found as major peaks in the XRD profiles of all the spent catalyst samples. It is observed that no phases of metals detected by XRF i.e. nickel, molybdenum, zinc could be analyzed in the XRD peaks due to the presence of high amount of silicon oxides and aluminum silicates.

The Scanning electron microscopy- Electron dispersive X-ray spectroscopy (SEM-EDX) profiles of all the spent catalyst samples marked few common peaks of elements like aluminum, silica, oxygen, and carbon. As discussed in the XRF and XRD analysis section, aluminum and silica were the major elements with prominent phases in all the samples. Apart from these elements, EDX of SC1 also showed peaks of chlorine whose mass percentage was found to be high (10% (w/w)) (Table 1, Figure 7).

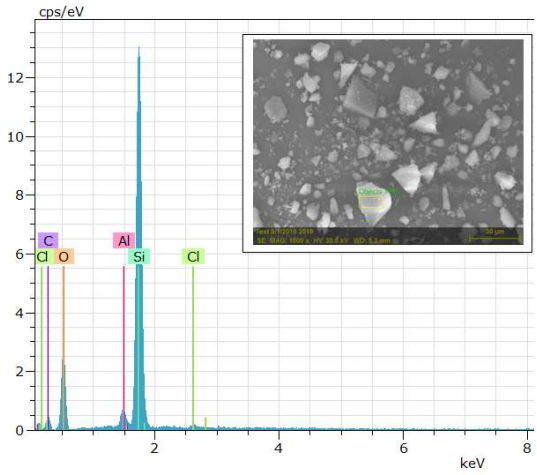

Figure 7 SEM micrograph and EDX analysis of Petroleum refinery spent catalyst SC1

The SEM micrograph shows sharp crystalline structures at 1000x magnification. In SC2, the point EDX scan of SEM micrograph at 1500x magnification show peaks of molybdenum, potassium, nickel, phosphorous and sulfur (Figure 2).

Only aluminum, silica, carbon, oxygen were present in EDX point scan profile of 500x and 10000x magnification SEM micrograph of SC3 and SC4 respectively (Figure 3 and 4).

In SC3 and SC4, EDX peaks of other elements like sulfur, chromium, nickel, titanium, strontium *etc*. that were detected in traces by XRF analysis were absent due to their low percentage. In spent catalyst sample code SC5 peaks of molybdenum, sulfur, calcium, iron, and magnesium were observed in the EDX graph of the point scan of SEM image at 2500x magnification (Figure 11).

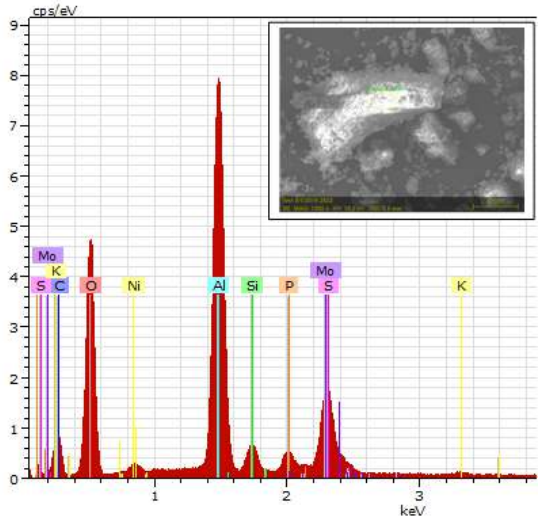

Figure 8 SEM micrograph and EDX analysis of Petroleum refinery spent catalyst SC2

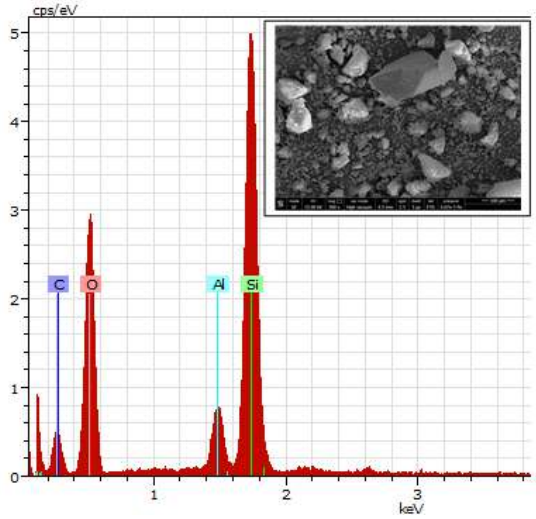

Figure 9 SEM micrograph and EDX analysis of Petroleum refinery spent catalyst SC3

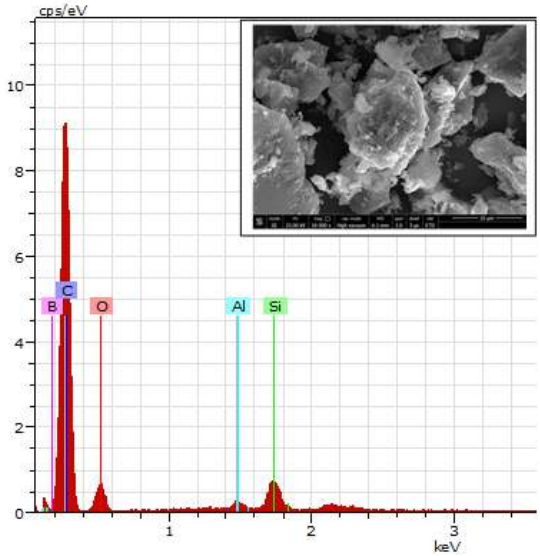

Figure 10 SEM micrograph and EDX analysis of Petroleum refinery spent catalyst SC4

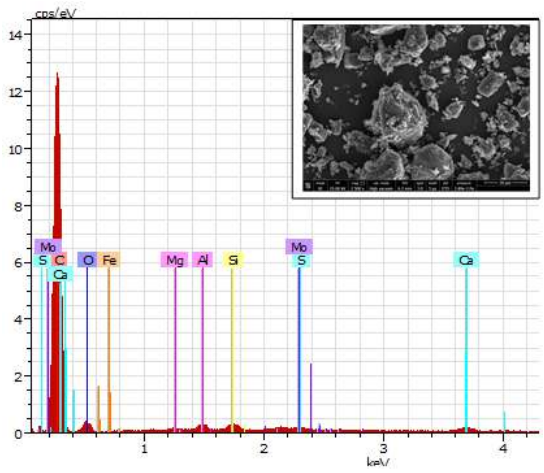

Figure 11 SEM micrograph and EDX analysis of Petroleum refinery spent catalyst SC5

The characterization of the five pre-treated spent catalyst samples disclosed their role in the refinery processes and recoverable metal content in them (Table 2).

Table 2 Classification of petroleum refinery spent catalyst samples

Sample	Name	Type	Reaction	Role
SC1	Isom-catalyst	Cl/ amorphous alumina silica	Isomerisation	low octane hydrocarbon to high octane hydrocarbon
SC2	Isom-catalyst	Cl/ amorphous alumina silica	Isomerisation	low octane hydrocarbon to high octane hydrocarbon
SC3	Isom-catalyst	Cl/ amorphous alumina silica	Isomerisation	low octane hydrocarbon to high octane hydrocarbon
SC4	HGU* catalyst	Ni/ alumina/ zeolite	Steam reforming	Hydrogen generation
SC5	HGU catalyst	Ni/ alumina/ zeolite	Steam reforming	Hydrogen generation

Note:*HGU- Hydrogen Generation Unit

Due to the presence of relatively high chlorine content (2- 10%) along with an amorphous aluminium silicate support in SC1, SC2 and SC3 were identified as isomerization catalysts involved in the isomerization reactions taking place in the petroleum refinery, for an instance, butane to iso-butane (Liquefied Petroleum Gas) isomerization. Due to the presence of Ni on a zeolite framework, SC4 and SC5 were considered to be HGU (hydrogen generation unit) catalyst involved in the hydrogen production for the refinery operations by steam reformation. The presence of other elements in these catalysts might be the result of metal fouling.

3.2 Bioleaching of spent catalysts

The presence of a good percentage of iron and sulfur content in the samples suggested that a bioleaching process using iron and sulfur-oxidizing microorganisms can be a potential strategy to recover their metal values. The samples had recoverable metal values but in less amount. According to the mineralogical studies recoverable metals are present in both oxidic and sulphidic phases. Metal oxides can be directly attacked by biogenic protons whereas Fe^{3+} produced by bio-oxidation of ferrous (from spent catalyst) and protons produced by sulfur oxidation together lead to metal sulfide oxidation.

The spent catalysts SC1, SC2 and SC3 were similar in properties (chemical and mineralogical) and were designated as isom- catalysts contains high amount of chloride i.e. 10.7%, 3.42% and 2.73% respectively. Despite of the presence of high chloride content in the sample, the microorganisms showed resilience. The all three samples had ~0.15% of Fe and 0.1- 0.2% S for contributing as the energy source for the microbes. A surplus amount of ferric ion was present in the medium throughout the experiments and therefore the redox potential in all the bioleaching experiments was high (470- 520 mV) (Figure 12).

The cell count in all the three experiment was consistent. There were fewer variations and the viable planktonic cells were calculated to be in the range of 10^6-10^7 cells/ mL (Figure 13(a)).

This shows that the microbial community inside the reactors were unaffected by the proximity of chloride containing sample. This might be due to the presence of chloride in non-soluble form

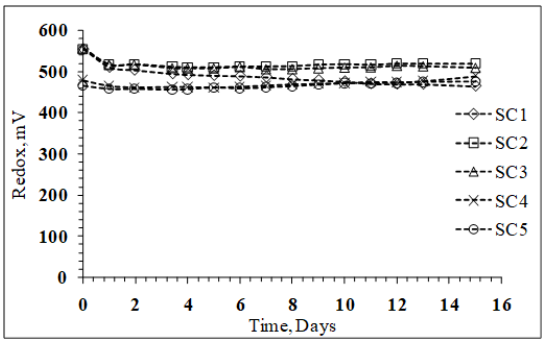

Figure 12 The redox potential profile (mV) in batch bioleaching of spent catalyst samples SC1, SC2, SC3, SC4 and SC5

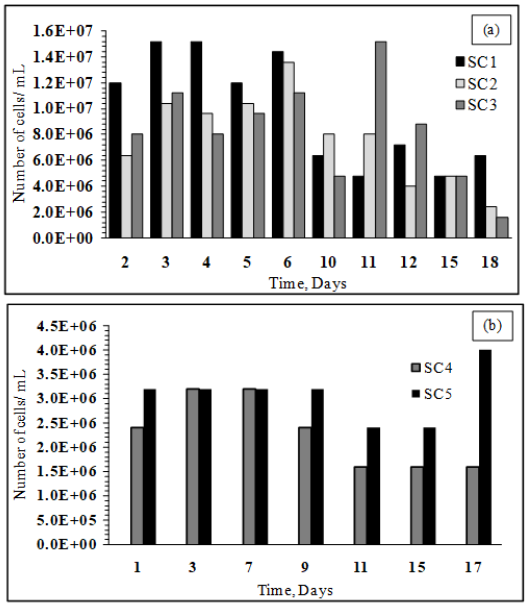

Figure 13 The viable cell count profile (number of cell/ mL) in batch bioleaching of spent catalyst samples **(a)** SC1, SC2 and SC3 and **(b)** SC4 and SC5 utilizing Fe & S oxidizing mixed culture

which made the microorganism sustain in the system with 10- 2% (w/w) chloride containing compounds. Apart from this, the experiments consumed very less acid as the acid demand was majorly compensated by the sulphur oxidizers during sulphur oxidation (Table 3).

Table 3 Summary table of all the batch bioleaching experiments (SC 1, 2, 3, 4 and 5)

	SC1	SC2	SC3	SC4	SC5
Feed weight, g	100	100	100	100	100
Bioleach residue, g	90.65	95.85	95.21	94.98	95,63
Acid Consumption, kg Conc. H_2SO_4/ ton spent catalyst	41.54	25.5	26.97	53.45	39.23

All the three experiments yielded in high recoveries of the metal values. The bioleaching of spent catalyst sample SC1 resulted in 100% recovery of Zn and Mo and 75% recovery of Cr. Sample SC2 yielded 100% and 65% recovery of Ni and Zn respectively. The leaching yield (%) of Ti in SC3 was 87% (Figure 14(a)).

The spent catalyst SC4 and SC5 similar type of catalysts, designated as HGU catalysts were having recoverable metal values like Ni, Cr, Cu and Sr which were targeted during their bioleaching. The ferric oxidant was high during both studied like in SC1, 2 and 3. The redox profile (Figure 12) having high potential values shows the abundance of ferric ion in the system. The high iron content in both of them was well utilized in the iron biooxidation process by the microorganisms as only 0.24% and 0.33% (w/w) total iron remained in the residue (due to precipitation) in SC4 and SC5 respectively (Table 1). Though the samples had chloride content

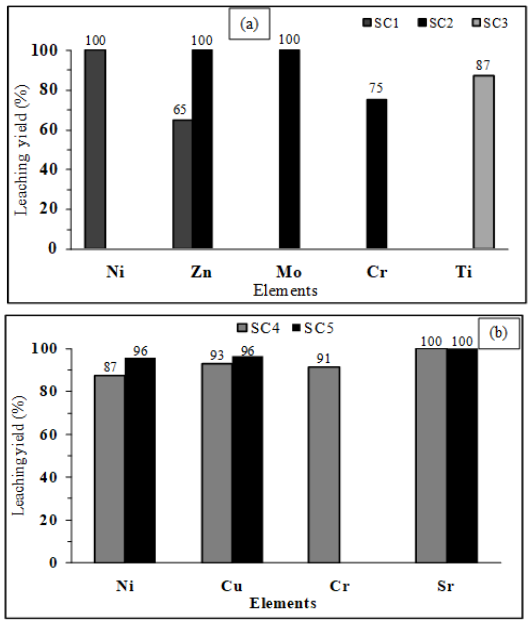

Figure 14 Leaching yield (%) of nickel (Ni), zinc (Zn), molybdenum (Mo), chromium (Cr), copper (Cu), strontium (Sr) and titanium (Ti) in batch bioleaching of spent catalyst samples (a) SC1, SC2 and SC3 and (b) SC4 and SC5 utilizing Fe & S oxidizing mixed culture

in them too yet no negative effect on cell count was observed during study. The null effect of chloride might be due to its presence in insoluble form. The consistent cell count depicts the same (Figure 13(b)). The bioleaching of SC4 and SC5 also witnessed less acid consumption relates with the good activity of sulphur oxidizers (Table 3). In SC4, the leaching yield of metals Ni, Cu, Cr and Sr was calculated as 87, 93, 91, and 100% respectively whereas in SC5, the recovery of Ni, Cu and Sr was 96, 96 and 100% respectively (Figure 13(b)). The good recovery of metal values also confirms good microbial activity in the bioleaching mediums.

4 Conclusions

The characterization of all the five samples of spent petroleum catalyst by XRF, XRD, and SEM-EDX improved the understanding of their physic-chemical properties to develop an eco-friendly as well as economical process to exploit its metal content. After having complete knowledge about the chemical composition, mineralogical phases, and morphology, it can be concluded that all the spent catalyst samples have similar elements but in different percentages. Aluminum and silica were the major phases in all the samples. In SC1, SC2, and SC3, their percentage was relatively higher i.e. aluminum and silica both contributed to 84-90% mass of the samples, rest 10-16% comprised of 3-10% chlorine and 6-13% other elements like zinc, sulfur, iron, potassium, phosphorous, magnesium, molybdenum, chromium, nickel *etc*. Charcterization not only paved way for the following bioleaching studies but also gave a clear picture of the role and reaction performed by these catalysts in the petroleum refinery. On the basis of the elemental and mineralogical analysis, SC1, SC2 and SC3 were revealed to be isomerization catalysts and SC4 and SC5 were found out to be hydrogen generation unit catalyst. All the samples conceived good iron and sulfur content in them which motivated the further bioleaching studies on the samples using iron and sulfur-oxidizing microorganisms. The samples had recoverable metal values but in less amount. Therefore, bioleaching being a potential metal extraction method for recovery of metals from low grade ores was successfully applied to these samples for harnessing their metal values. The high concentrations of elements like Ni, Mo, Cr, Cu, Zn, Ti and Sr from their respective sample sources were mobilized into the solution.

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