Chapter IV

Aqueous leaching of high sulphur coal and overburden from Ledo colliery and their physico-chemical and elemental analysis

4.0 Introduction

Coal is a heterogeneous mixture of different types of organic and inorganic materials. Majority of inorganic materials are occurred in mineral forms. The minerals present in coal consist of several metals and nonmetals especially Si, S, Ca, Mg, Fe, Al etc. (Tomeczec and Palugniok, 2002; Mukherjee and Borthakur, 2003). The common minerals found in coal and OB are quartz (SiO_2), pyrite (FeS_2), hematite, marcasite, and kaolinite. Coal is composed of different elements, metals, and non- metals as a long biological and physical alteration process taken place during the formation of the coal (Swine, 1990; Singh and Singh, 1995). Before mining these elements are in an immobile state, but during and after mining they have a tendency to disperse into the surrounding areas (Equeenuddin, 2015). Most of these elements are found in trace amount which are toxic in nature beyond their threshold limit. Trace elements are those whose concentrations are lower than 0.1% in the coal (Swaine, 2000; Singh et al., 2012a). The study of these trace elements is very important due to their complex changes, inability to decompose in natural processes like weathering and high toxicity to the environment followed by their release and dispersal to the atmosphere, soil, and water through the pathways of leaching and weathering (Zhou et al., 2014; Querol et al., 2008; Dai et al., 2005; Chen et al., 2013). Leaching is one of the primary pathways for trace elements to enter into the ecosystem (Yang et al., 2016, Baruah et al., 2004). Swaine (2000) proposed the possibility of the presence of twenty six trace elements in coal that have potential environmental impacts, including As, Cr, Cd, Hg, Pb, Se, B, Mn, Ni, Cu, V, Zn, Co, Sn, Cl, F, Br, Mo, P, Th, U, Ba, Ra, Sb and Tl. Out of these elements As, Cd, Hg, Pb, Cr and Se are of greater environmental importance (Swaine, 2000; Prachiti et al., 2011; Singh et al., 2015a, b). Most of the Se in coal is associated with organic constituents; however, some of the Se is also associated with the sulfide minerals of coal, mainly pyrite (Swaine, 1990). In coal, Cd is predominantly associated with sphalerite (ZnS) (Alper et al., 2008). Lead (Pb) occurs in coal mainly as the sulphide mineral galena (PbS) which is the most common form of lead in coal (Finkelman, 1994; Swaine, 1990). These trace elements present in coal and its mine rejects/overburden enter into the environment through different processes including leaching of coal and oxidation of pyrite (Equeenuddin, 2015). Coal dumps are also an important factor in the environmental degradation because the potentially toxic elements are directly released to the environment through the leaching and oxidation of pyrite. To understand the release of potential hazardous elements (PHEs) from coal and coal mine rejects in potential environmental and ecological conditions, the study on the leaching behavior of coal and mine rejects in open cast coal mining is important. Although AMD generation and metal leaching processes from coal and mine OB are natural processes, these processes are accelerated by intensification of mining operations (Banerjee, 2014). Such mining activities have a detrimental effect on the local environment as well as on the ecology (Kimmel, 1983; Johnson, 1987; Kaeser and Sharpe, 2001).

The metals in coal and coal wastes, which are mineral, associated with the coal structure, are easily dissolved in highly acidic AMD. Thus, the AMD (pH 2.0-3.0) has a strong leaching potential for releasing a large number of potentially PHE's into the aquatic environment (Baruah et al., 2006; Dowarah et al., 2009). In addition to the AMD formation, under different atmospheric conditions, pyrite (FeS_2) in coal is often found in association with the hazardous elements such as As, Cd, Cu, Co, Pb, Hg, and Zn (Monterroso and Macias, 1998; Singh et al., 2016). The formation of elemental sulphur takes place during depyritization of coal by leaching of coal wastes (Schippers et al., 1996). The leachates generated from OB dumps are rich in heavy metals, especially Fe, Cu, Mn and Ni (Tiwari, 2001). The leaching property of different elements depends on several factors like specific element solubility and availability or release potential (Moyo et al., 2011). Also the other factors that enhance the metal leaching include swiftly weathering metal containing minerals and the mine drainage conditions that can increase the solubility and flow rates through the contaminated minerals (Banerjee, 2014). The sulphur present in Northeastern (NER) Indian coal is mainly in three forms-sulphate sulphur, pyritic sulphur, and organic sulphur (Baruah and Gogoi, 1998). The major part of the inorganic sulphur present in coal is in pyrite (FeS_2). The Northeastern Indian coals are rich in sulphur (2%–11%) (Chabukdhara and Singh, 2016; Singh et al., 2012b, 2013). The sulphate formed from pyritic sulphur in coal by atmospheric oxygen is not only responsible factor for AMD generation but the oxidation of Fe(II) ion to Fe(III) ion during the process of weathering of pyrite can produce a noticeable amount of AMD (Baruah et al., 2006). Equeenuddin (2015) reported that coal dumps cause environmental degradation due to the release of potentially hazardous elements through the process of leaching of pyrite. The amount of impact of waste and coal containing contaminants in a form of toxic elements on the environment depend not only on the type and concentrations of these elements, but mainly on their mobility. The mobility of pollutants contained in the waste is expressed as the potentiality of them to leach in water (Kalembkiewicz and Palczak, 2015). Leaching methods are classified into two types depending upon whether the leaching liquid is added at a single instance (static) or it is renewed (dynamic) (Moyo et al., 2011). The potential to produce acidity of drainage from mine water and mine wastes can be predicted by both geochemical methods in static and kinetic leaching processes (Ferguson and Erickson, 1998). The static methods are further classified into two classes, batch leaching where a specific amount of sample is placed in a given amount of leachant solution (US DOE, 2005; Hesbach et al., 2005; Kim et al., 2003) and column leaching. Thus, the quality of surface and ground water in the streams, drains, well, contaminated with AMD water and leachates of coal and overburden was also analyzed to study the possible impact of coal mining on the nearby water resources. During leaching, the elements present in coal and OB dissolve or undergo some chemical and physical reactions and as a result they transfer into the leaching solution (Fotoupoulou et al., 2010; Wang et al., 1999). In the present chapter, the static aqueous leaching experiments are mainly carried out to evaluate the potential of release of selected metals. The aqueous leaching experiments of different coal and overburden samples, from the Ledo colliery are carried out and the results are also compared with those of field data.

4.1 Experimental section

4.1.1 Sampling and aqueous leaching

Freshly mined representative coal samples (LC-20A, LC-60A) and overburden samples (LOB-15A, LOB-15B) (dump sites) were collected from the Ledo colliery (India) using the standard methods given in chapter II. The coal and overburden samples were ground into 72 BS (0.211 mm) size, preserved in a desiccator for subsequent experiments. Mine water samples (LW-15A, LW-15B, LW-15C, LW-15D, LW-15E, and LW-15F) were also collected from the AMD source and from different points within the 5 km radius from the mining source of the Ledo colliery as shown in Figure 4.1

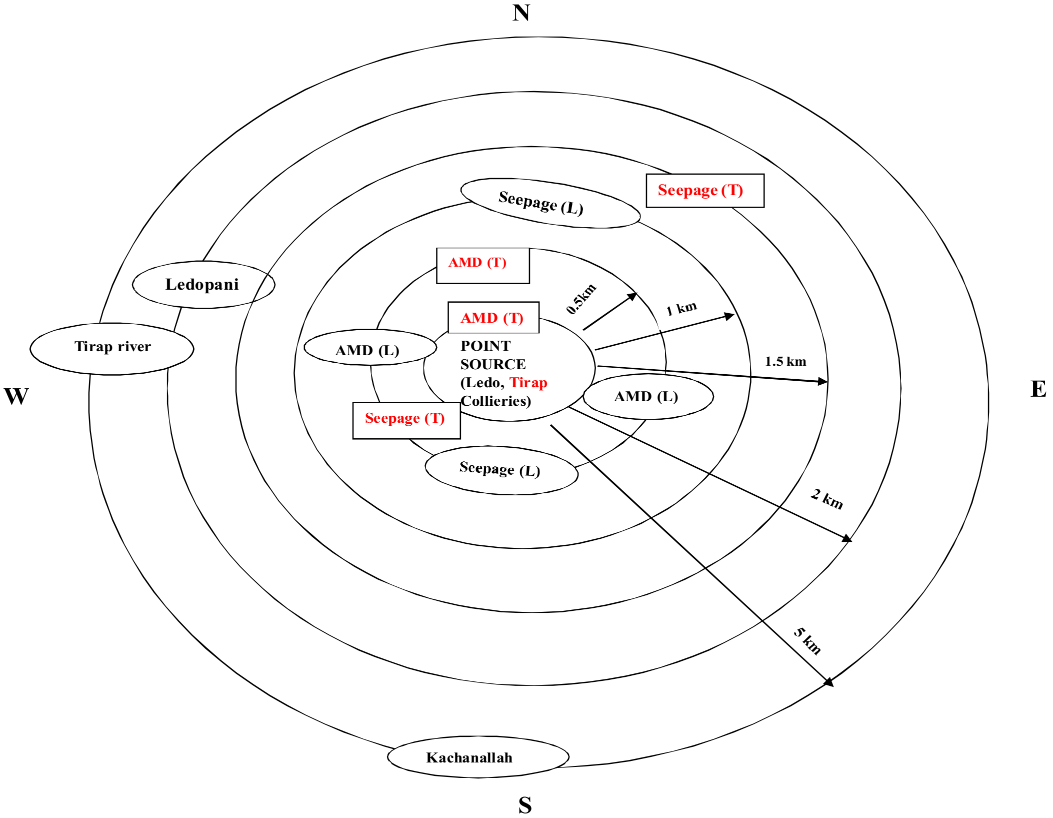

Figure 4.1: Schematic diagram showing the actual sampling locations in around Ledo colliery

100 g of each finely ground sample was mixed with distilled water (300 ml)

separately in 500 ml beakers, for 1hr, 3hrs, 5hrs, and 8 hrs. Then the mixture was mechanically stirred in an electronic shaker (VELP, Scintifica JLT6) for the time periods 1hr, 3hrs, 5hrs, and 8 hrs at a stirring rate of 250 rpm at 25º C, 45º C, 65º C, and 90° C respectively. The supernatant liquid was filtered from the solid phase by a Whatmann-1 filter paper. The filtrate (i.e. the leachates) were collected and used for different physical, chemical, and elemental analyses. The residues of the leached samples were also subjected to selected chemical analyses as mentioned in later part.

4.1.2 Physico-chemical analyses of aqueous leachates

The aqueous leachates of the coal and overburden (OB) samples obtained were subjected to pH, TDS (total dissolved solid), and EC (electrical conductivity) analysis by using a EUTECH PC700 pH/EC/TDS meter.

4.1.3 Chemical analyses of aqueous leachates

The aqueous leachates of coal and overburden samples at different time and temperatures were subjected to ion chromatographic analysis to determine the concentrations of different cations and anions (in ppm). The trace elements present in leachates were determined by using ICP-OES, AAS, FAAS, and GFAAS analytical techniques. Accordingly, the presence of different minerals, different functional groups, including sulphur containing groups and the microscopic information (along with mapping analysis) in leached samples were done by using XRD, FTIR and FE-SEM analytical techniques respectively. The details of the methods used for the study are discussed in chapter II.

4.2 Results and discussions

4.2.1 Physico-chemical characteristics of aqueous leachates

The physico-chemical parameters including pH, EC, and TDS were determined for the aqueous leachates obtained at different time periods and temperatures. Table 4.1 shows that the pH values of the leachates of the samples decreased gradually from 1 hr of leaching to 5 hrs of leaching time at room temperature. The pH of the leachates however increased slightly at 8 hrs of leaching time. The leaching at 45º C for 1hr, 3hrs, 5hrs and 8hrs respectively demonstrate a gradual increase in pH values. The gradual increase in pH (decrease in acidity) values implies that the continuous rainfall at normal temperature for 5hrs can generate AMD at the coal mine site. Thus, AMD from coal and mine OB are highly acidic at the coalfield in the rainy season. The gradual increase in pH values of leachates at 45º C from 1 hr to 5 hrs indicates the low acidity of leachates with rise in leaching temperature. The Electrical conductivity (EC) of the aqueous leachates of the samples at room temperature (25º C) gradually increased from 1 hr to 8 hrs of leaching. Similarly, the TDS values were found to increase gradually with increase in time period of leaching and with increase in leaching temperature (from room temperature to 45^0 C). The high value of EC and TDS at a temperature higher than room temperature indicates the high mobility of ions present in the samples which were leached out of the sample as a result of leaching. Various physico-chemical properties of the aqueous leachates of coal and OB samples are given subsequently. The pH of the leachates (leached in different time periods at different temperature) from the Ledo coal is highly acidic (pH 2.5) while other OB samples release a nearly neutral discharge (4-7.4). In the cases of leaching at a temperature higher than room temperature (45^0 C), the pH increased up to 9.40. A high pH value of leachates may be attributed to the formation of $Ca(OH)_2$ from $CaCO_3$ present in overburden due to long time leaching (up to 8 hrs), since the pH of a solution is an important determinant for counting aquatic toxicity. The amount of toxicity tends to be higher at low pH or high pH situations than at an approximately neutral pH (near pH 7), since the dissolution of many metals can be considered as amphoteric, with a high tendency to dissolve and can form cations at low pH or anions at high pH values (Langmuir, 1997). For instance, $Al(OH)_3$ and different aluminosilicate minerals like kaolinite [$Al_2Si_2O_5(OH)_4$] have their minimum solubility at pH values 6-7 (Nordstrom and Ball, 1986; Bigham and Nordstrom, 2000) and even relatively low concentrations of dissolved Al can exert toxic effect to fish and other aquatic organisms (Baker and Schofield, 1982; Elder, 1988). The Environmental Protection Agency (EPA, 2000, 2002a, 2002b) recommends a pH 6.5-9.0 for protection of freshwater aquatic life and pH 6.5-8.5 for public drinking purposes. In the present study the maximum pH values for leachates of overburdens were found to have a pH 9.4.This indicates a lower contamination of water resources from overburden than for coal. It should however be noted that pH is not the only determining factor of metals dissolution. Comparing the physical parameters of aqueous leachates of coal and overburden with the mine waste water it was found that the elements from coal and overburden can leach easily under normal weathering processes.

4.2.2 Mine water characteristics and comparison with aqueous leachates

The aqueous leachates generated from coal and overburdens (OB) are compared with the AMD water collected from the coal mine. The parameters (pH, EC, TDS) are found to be similar as given in the Table 4.1 and Table 4.2 respectively. The increase of pH values in mine water samples in comparison with aqueous leachates may be due to dilution during raining as well as ground water contamination. The comparable data reveals the simulation experiment of AMD on a large scale.

Table 4.1: Physical analyses of aqueous leachates at room temperature at different leaching times

Sample type	Sample code	Leaching time	pH	TDS (ppm)	EC (µscm^{-1})
Coal	LC-20A	1hr	1.99	989	1912
	LC-60A		2.65	106	209
	LC-20A	3hrs	1.80	983	1970
	LC-60A		2.27	119	238
	LC-20A	5hrs	1.62	1003	2006
	LC-60A		3.52	106.9	210
	LC-20A	8hrs	2.10	790	313
	LC-60A		3.50	213	106
Overburden	LOB-15A	1hr	6.72	120	242
	LOB-15B		5.85	24.2	48.6
	LOB-15A	3hrs	4.76	129	129
	LOB-15B		6.92	89.2	89.2
	LOB-15A	5hrs	3.68	240	480
	LOB-15B		3.71	186	373
	LOB-15A	8hrs	5.36	139	278
	LOB-15B		6.30	69.5	129.5

Table 4.2: Geochemical analyses of mine water samples

Sample type	Distance from AMD source	pH	EC(µscm^{-1})	TDS (ppm)
LW-15A	**Sample point (source)**	**4.0**	**1226**	**927**
LW-15B	**0.5 km from sample point**	**4.1**	**1234**	**915**
LW-15C	**0.5 km from sample point**	**3.50**	**2290**	**1140**
LW-15D	**1 km from sample point**	**3.30**	**2490**	**1180**
LW-15E (Ledopani)	**2 km from sample point**	**4.4**	**936**	**0.0468**
LW-15F (Kachanallah)	**5 km from sample point**	**5.0**	**659**	**0.0328**

4.2.3 Ion- chromatographic analyses of aqueous leachates

The Ion-Chromatographic analyses were carried out for aqueous leachates of coal and overburden samples after leaching for 1hr, 3hrs, 5hrs, and 8hrs at 25^0 C, 45^0 C, and 65^{0}C respectively. The concentration of cations like Na^+, Mg^{2+}, Ca^{2+}, NH_4^+ and Li^+ ions in the leachates of coal and overburden decreased with an increase in leaching temperature (Figures 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, and 4.9). Also, these Figures show that the decrease in leaching of Li^+ ion with leaching duration. Since lithium is generally associated in coal and overburden as lithium silicate and decrease in concentration of Li^+ ion in leachates with leaching time is attributed to the production of orthosilicic acid (Li et al., 2017). The leaching of Ca^{2+} ion from Ledo coal is maximum at high temperature 65^0 C (Figures 4.8 and 4.9) which is an indication of maximum leaching of Ca^{2+} ion in monsoon season. The low concentration of Na^+, Mg^{2+}, NH_4^+ and Li^+ ions in the leachates of coal and overburden at high temperature indicates minimum leaching of these ions in monsoon season.

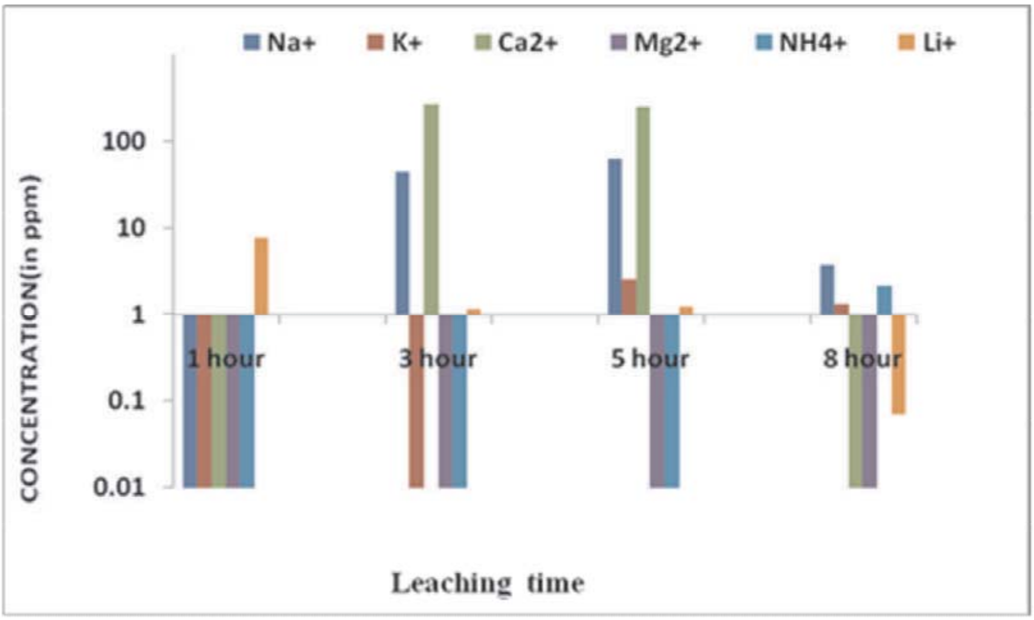

Figure 4.2: Change in concentration (in ppm) of cations in aqueous leachates of Ledo coal (LC-20A) with leaching time at 25^0 C

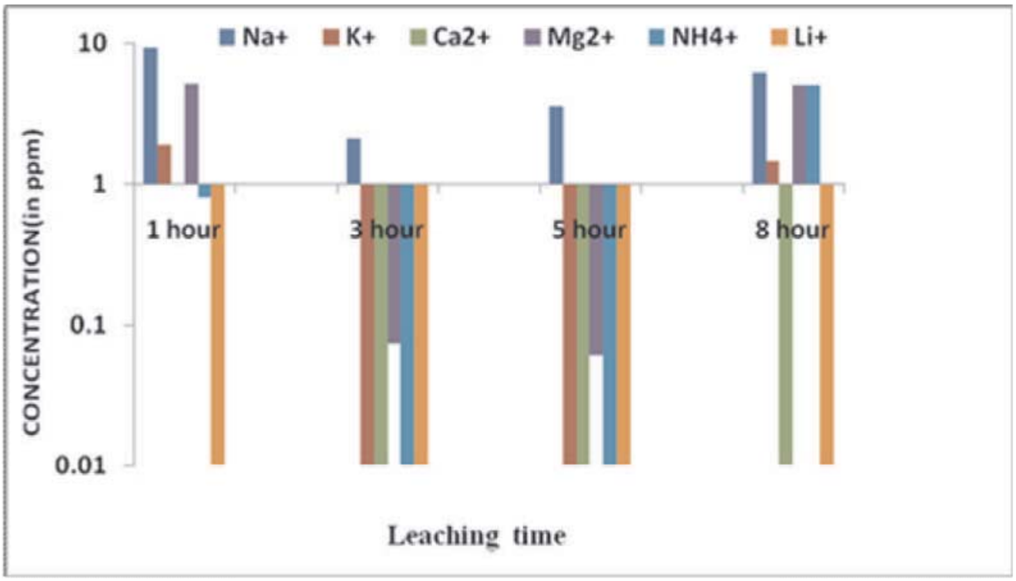

Figure 4.3: Change in concentration (in ppm) of cations in aqueous leachates of Ledo coal (LC-60A) with leaching time at 25º C

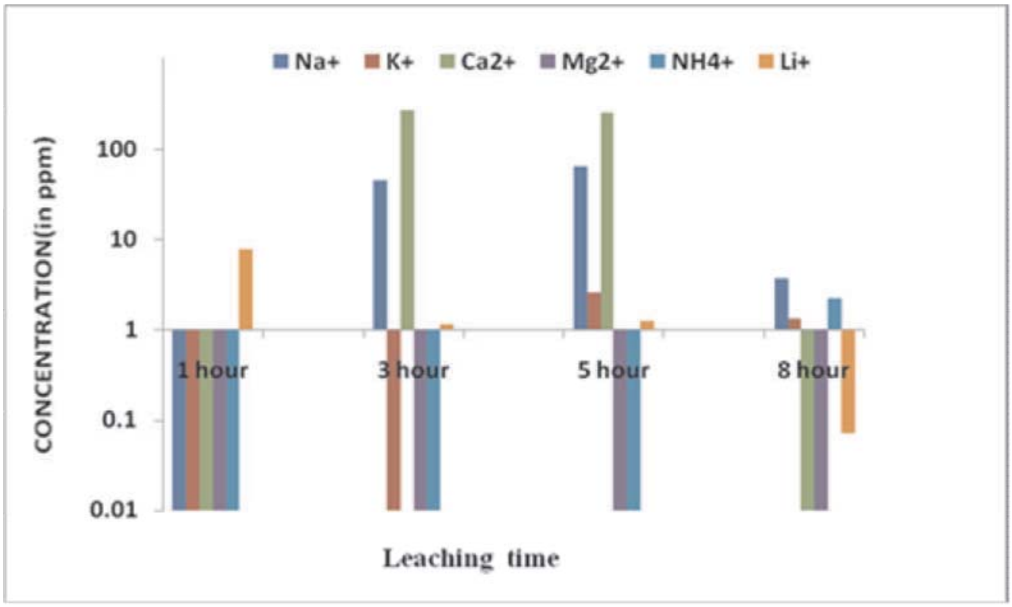

Figure 4.4: Change in concentration (in ppm) of cations in aqueous leachates with leaching time of Ledo overburden (LOB-15A) at 25º C

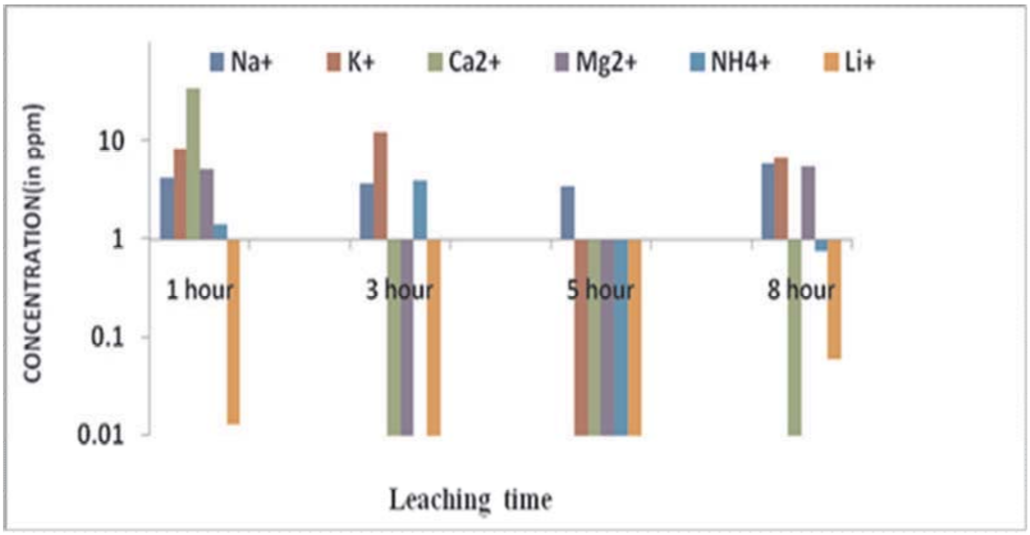

Figure 4.5: Change in concentration of cations (in ppm) in aqueous leachates of Ledo overburden (LOB-15B) with leaching time at 25º C

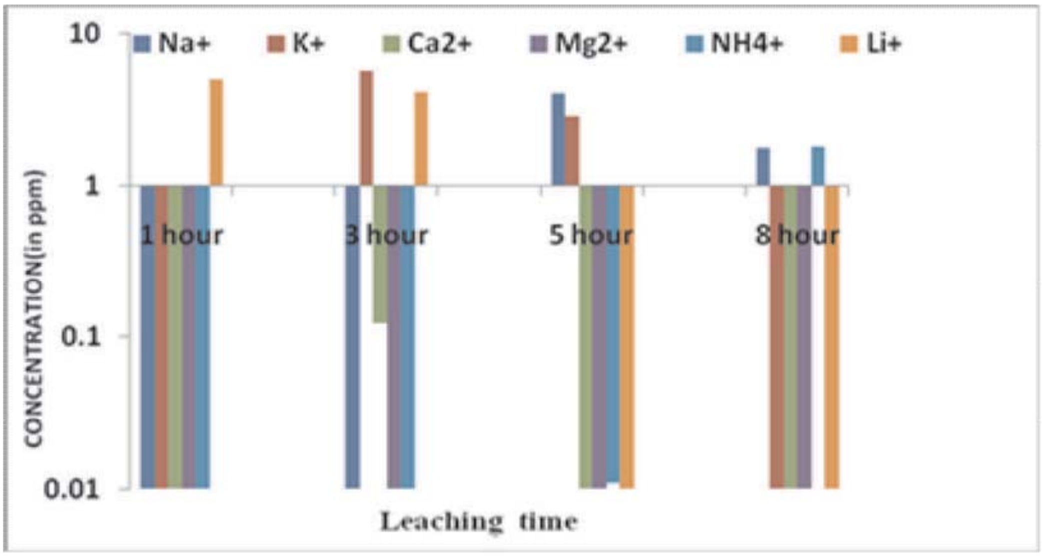

Figure 4.6: Change in concentration of cations (in ppm) in aqueous leachates of Ledo coal (LC-20A) with leaching time at 45º C

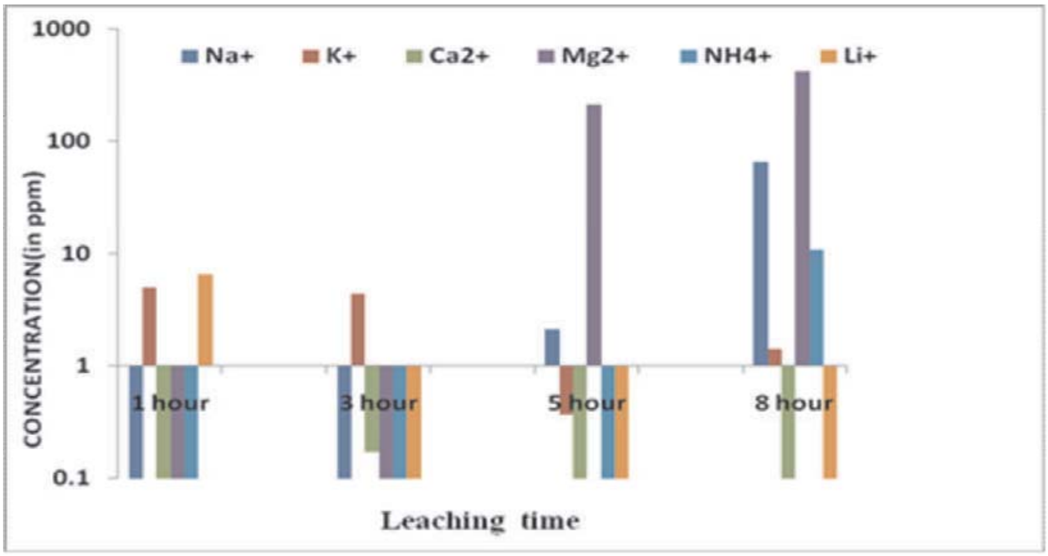

Figure 4.7: Change in concentration of cations (in ppm) in aqueous leachates of Ledo coal (LC-60A) with leaching time at 45º C

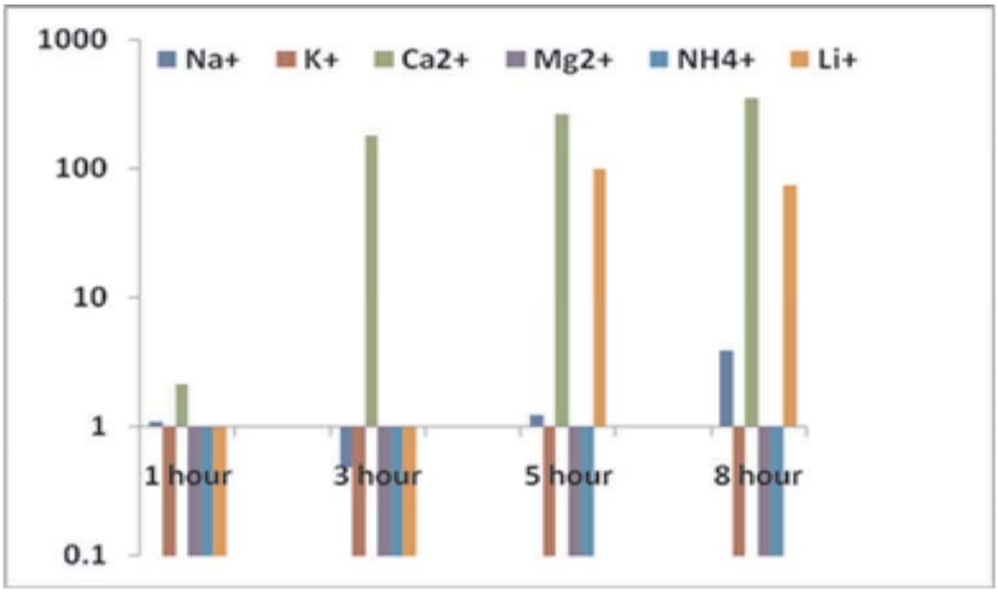

Figure 4.8: Change in concentration of cations (in ppm) in aqueous leachates of Ledo coal (LC-20A) with leaching time at 65º C

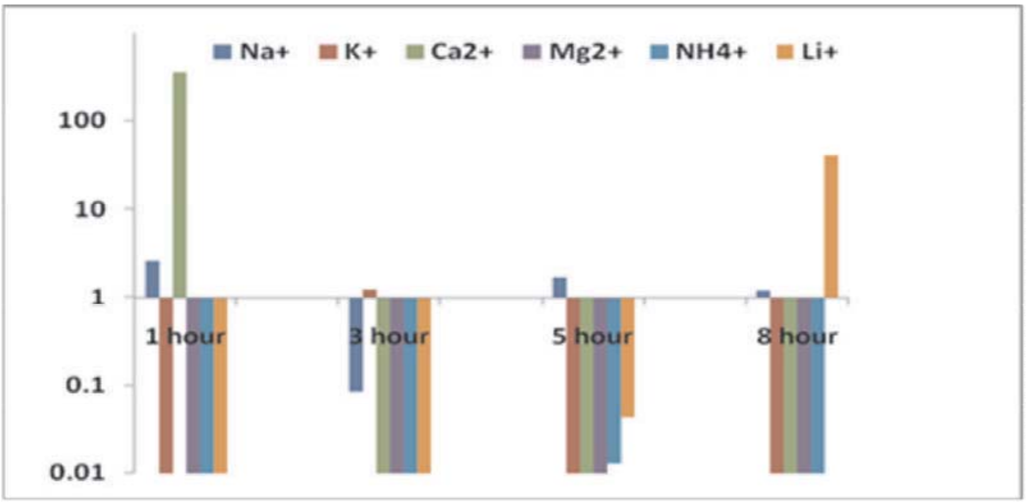

Figure 4.9: Change in concentration of cations in aqueous leachates of Ledo coal (LC-60A) with leaching time at 65^0 C

From Figures 4.10, 4.11, 4.12, and 4.13, it can be observed that the concentrations of F^-, Cl^- and SO_4^{2-} ions from the leachates of coal and overburden samples of Ledo colliery was increased with an increase in the leaching time at room temperature, because the leaching time is an important factor which determines the amount of elements leached from the raw coal (Moyo at el., 2011).

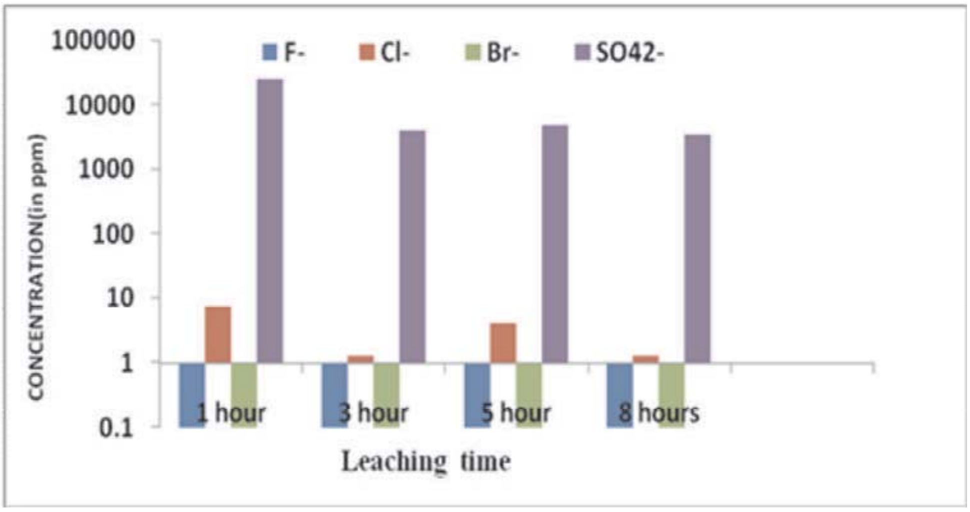

Figure 4.10: Change in concentration (in ppm) of anions in aqueous leachates of Ledo coal (LC-20A) with leaching time at 25^0 C

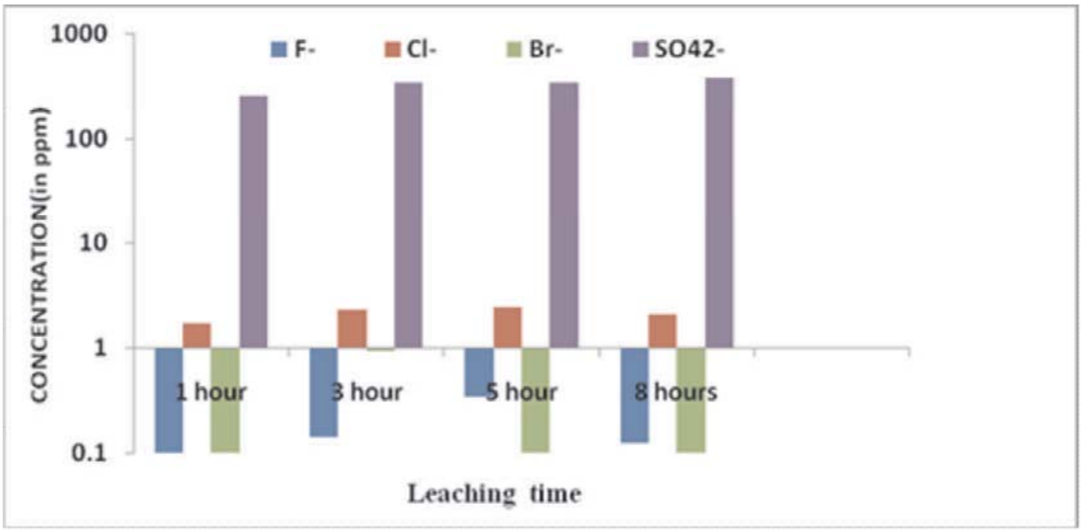

Figure 4.11: Change in concentration (in ppm) of anions in aqueous leachates of Ledo coal (LC-60A) with leaching time at 25º C

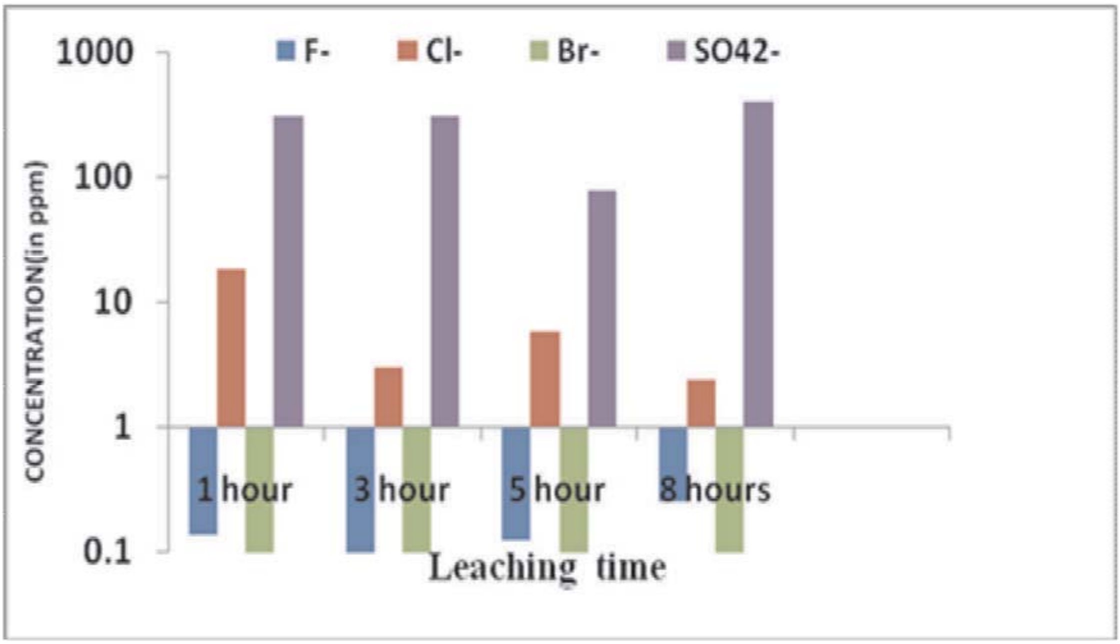

Figure 4.12: Change in concentration (in ppm) of anions in aqueous leachates of Ledo overburden (LOB-15A) with leaching time at 25º C

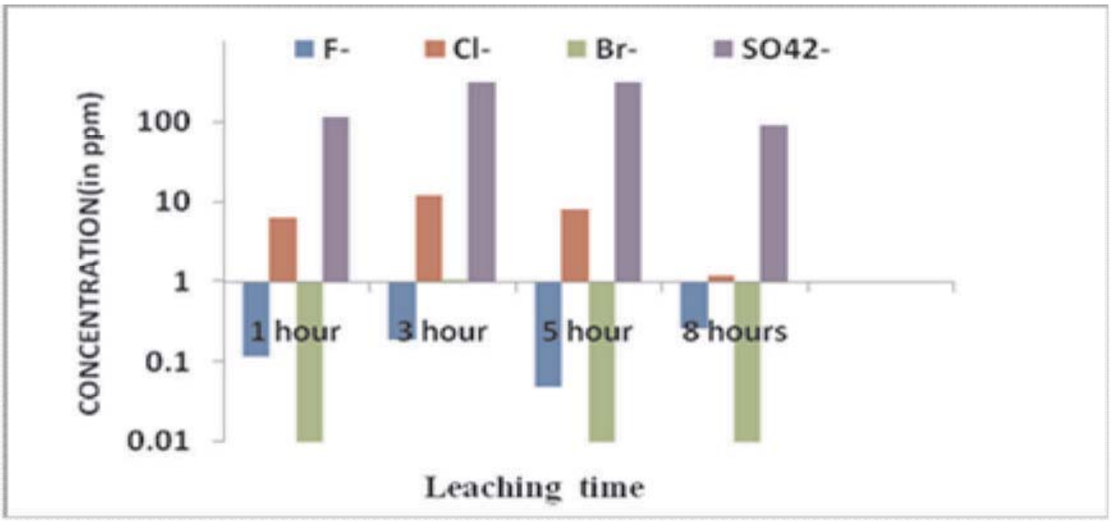

Figure 4.13: Change in concentration (in ppm) of anions in aqueous leachates of Ledo overburden (LOB-15B) with leaching time at 25º C

With the increase in leaching temperature from 25^0 C to 45^0 C however, the concentration of F^-, Cl^- became lower (Figures 4.14, 4.15, 4.16, and 4.17). The leaching of SO_4^{2-} ion from coal and overburden was increased with leaching temperature from 25^0 C to 65^0 C and time (shown in Figures 4.14, 4.15, 4.16, 4.17, 4.17, 4.17, 4.18, 4.19, and 4.20) which reveals the dependence of leaching of sulfate ion on leaching temperature and time.

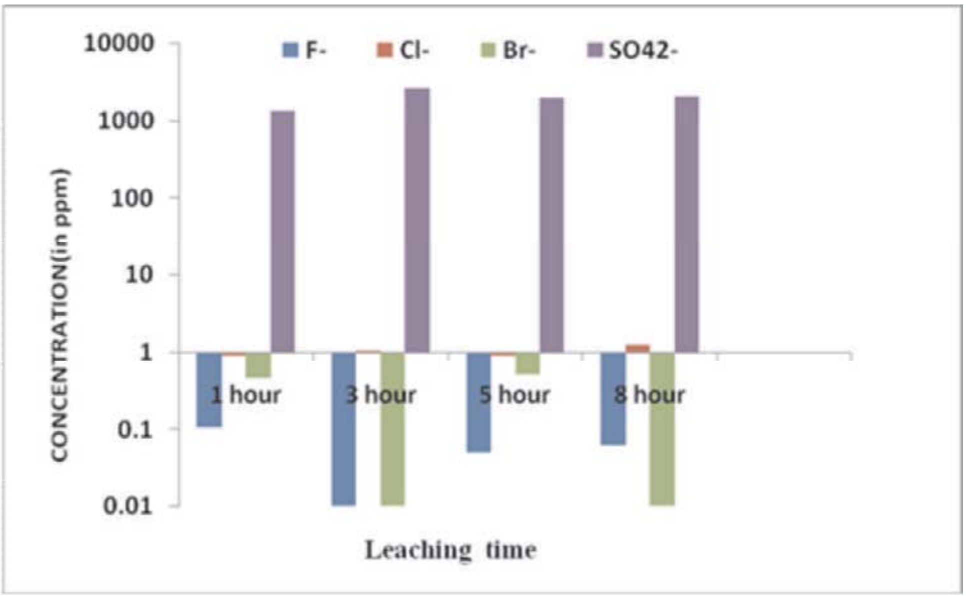

Figure 4.14: Change in concentration (in ppm) of anions in aqueous leachates of Ledo coal (LC-20A) with leaching time at 45^0 C

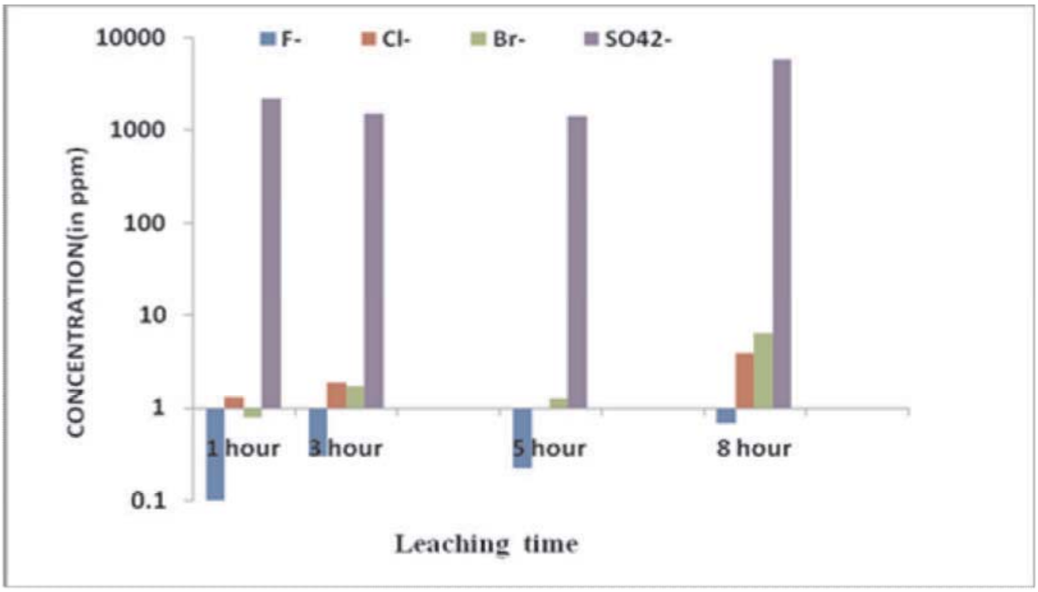

Figure 4.15: Change in concentration (in ppm) of anions in aqueous leachates of Ledo coal (LC-60A) with leaching time at 45^0 C

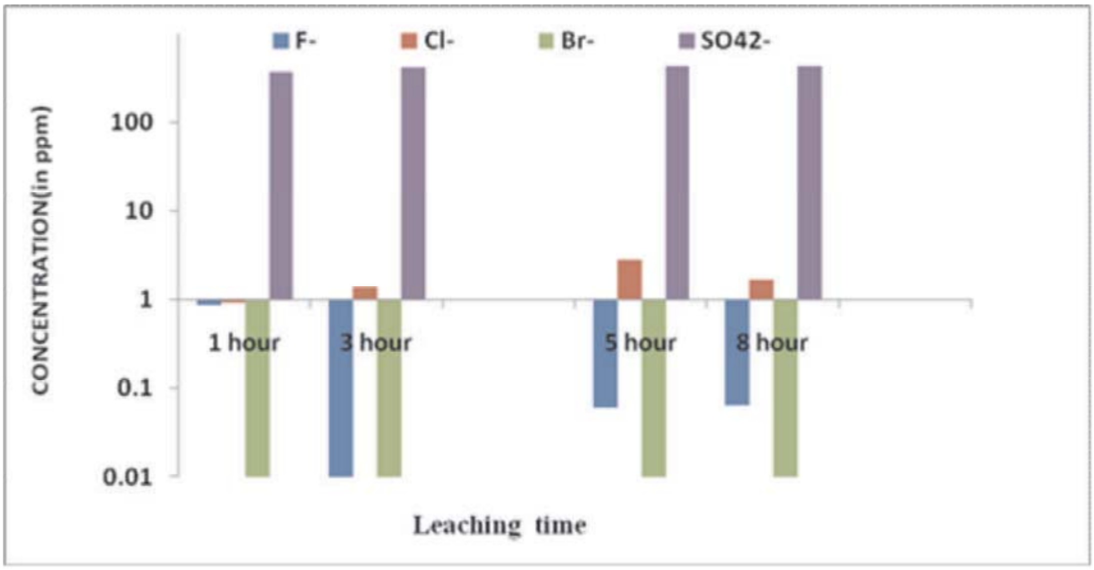

Figure 4.16: Change in concentration (in ppm) of anions in aqueous leachates of Ledo overburden (LOB-15A) with leaching time at 45^0 C

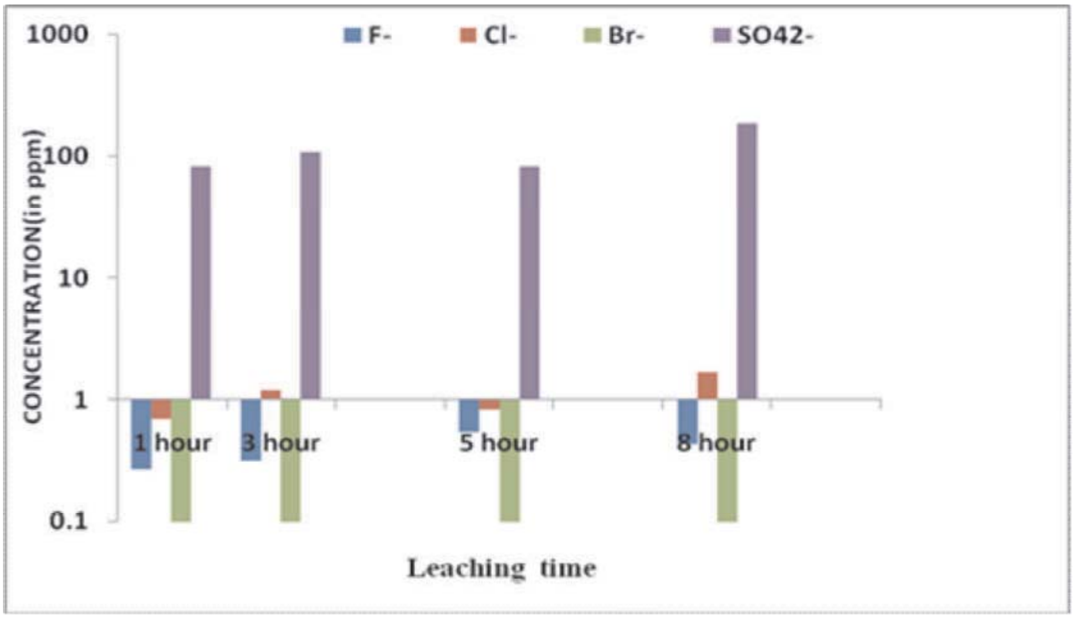

Figure 4.17: Change in concentration (in ppm) of anions in aqueous leachates of Ledo overburden (LOB-15B) with leaching time at 45^0 C

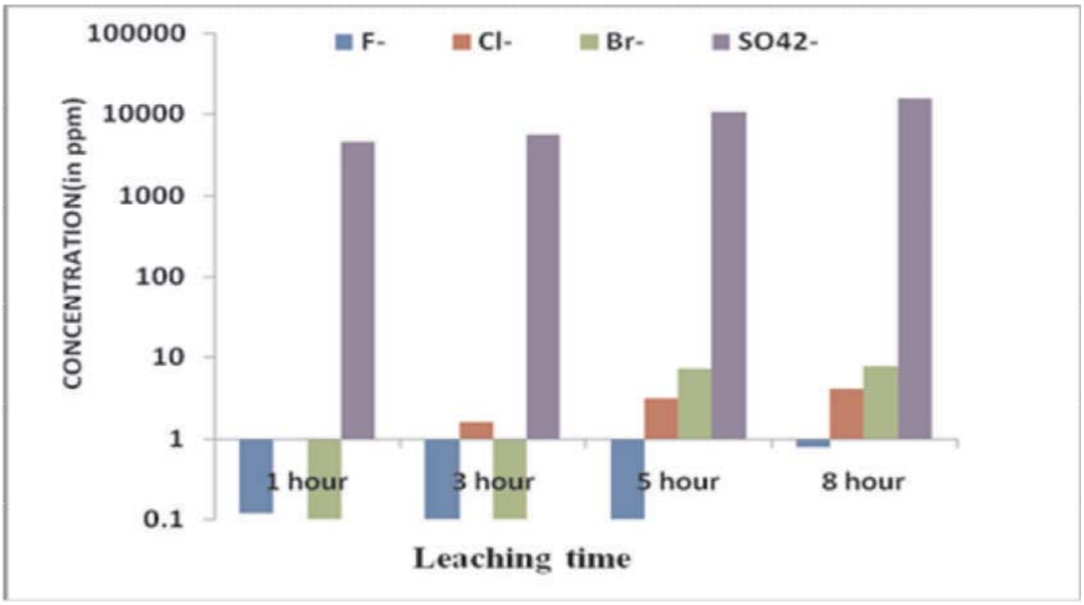

Figure 4.18: Change in concentration (in ppm) of anions in aqueous leachates of Ledo coal (LC-20A) with leaching time at 65^0 C

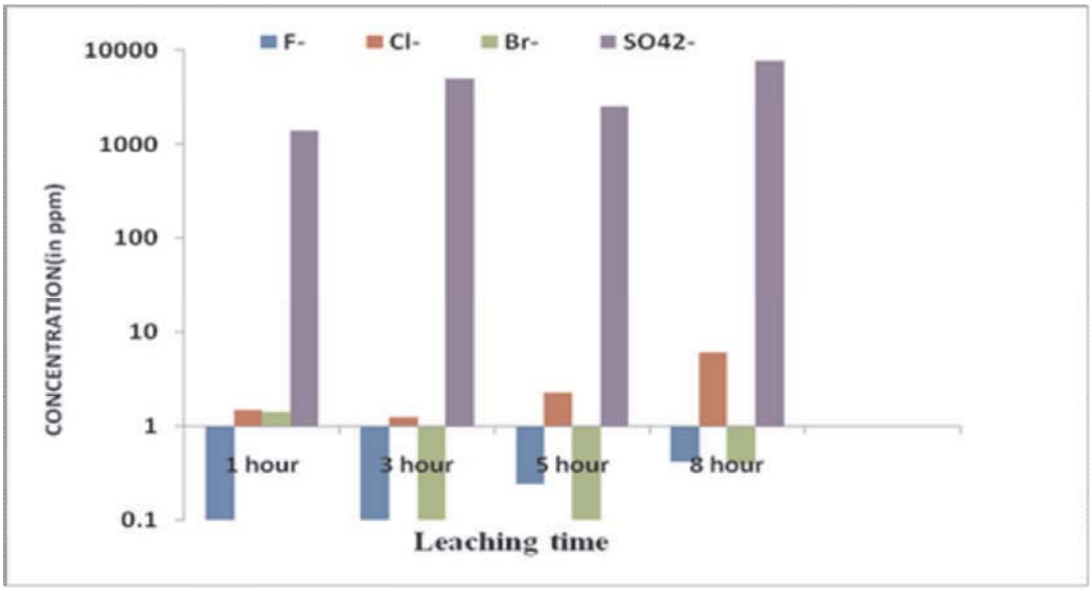

Figure 4.19: Change in concentration (in ppm) of anions in aqueous leachates of Ledo coal (LC-60A) with leaching time at 65^0 C

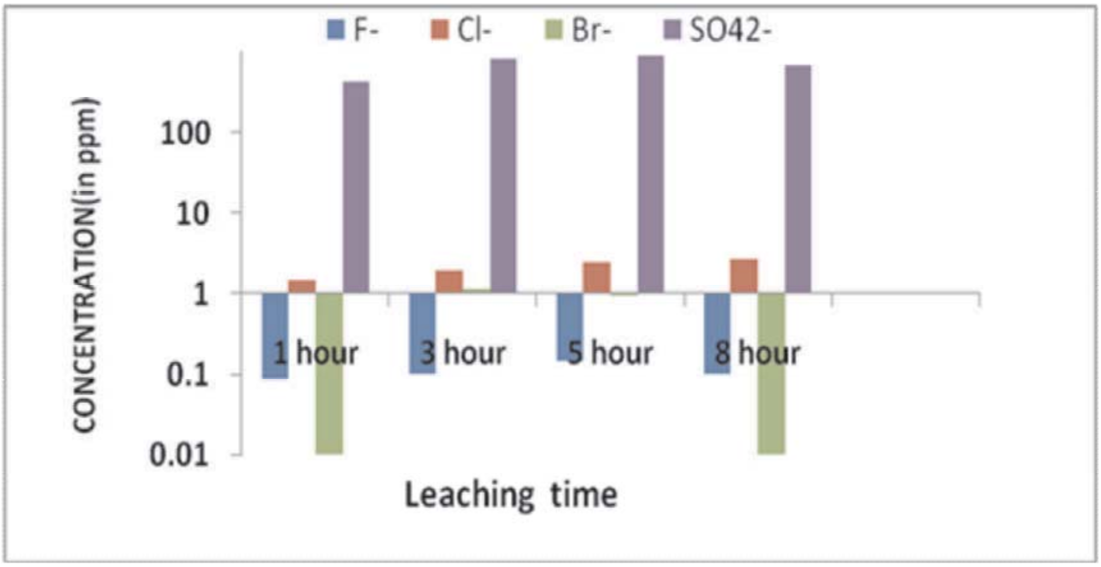

Figure 4.20: Change in concentration (in ppm) of anions in aqueous leachates of Ledo OB (LOB-15A) with leaching time at 65^0 C

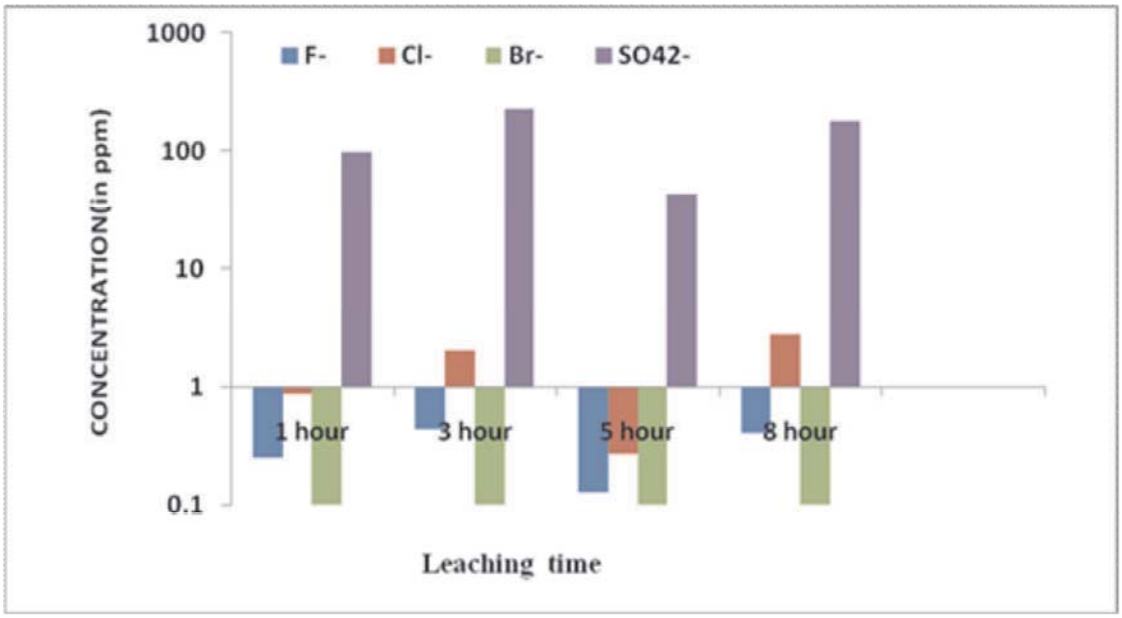

Figure 4.21: Change in concentration (in ppm) of anions in aqueous leachates of Ledo OB (LOB-15B) with leaching time at 65^0 C.

4.2.4 Elemental analyses (ICP-OES and AAS analysis)

The ICP-OES analysis of the aqueous leachates of the coal reveals that the concentration of different elements like Al, Ba, Co, Ni, Fe, Mn, Cu, and Zn increased with leaching time at room temperature (25^0 C) (Figures 4.22, 4.23, and 4.24). But after 5 hrs of leaching the concentration of these elements gradually decreased which implies that at 25^0 C most of the elements are released from the coal due to continuous raining of up to 5 hrs. The leaching property of Ni is temperature as well as leaching time dependent which are shown in Figures 4.22, 4.23, 4.24, 4.25, 4.26, and 4.27. Here the concentration of Ni in the aqueous leachates of coal is highest at leaching time of 8 hrs. In the case of Fe, Mn, Cu, Zn, Ca and Mg the concentration was found to increase with leaching time and temperature (Figures 4.22, 4.23, and 4.24). But when the temperature is low (25^0 C and 45^0 C), the concentrations of elements increase at maximum time of leaching 8 hrs (Figures 4.22, 4.23, and 4.24).

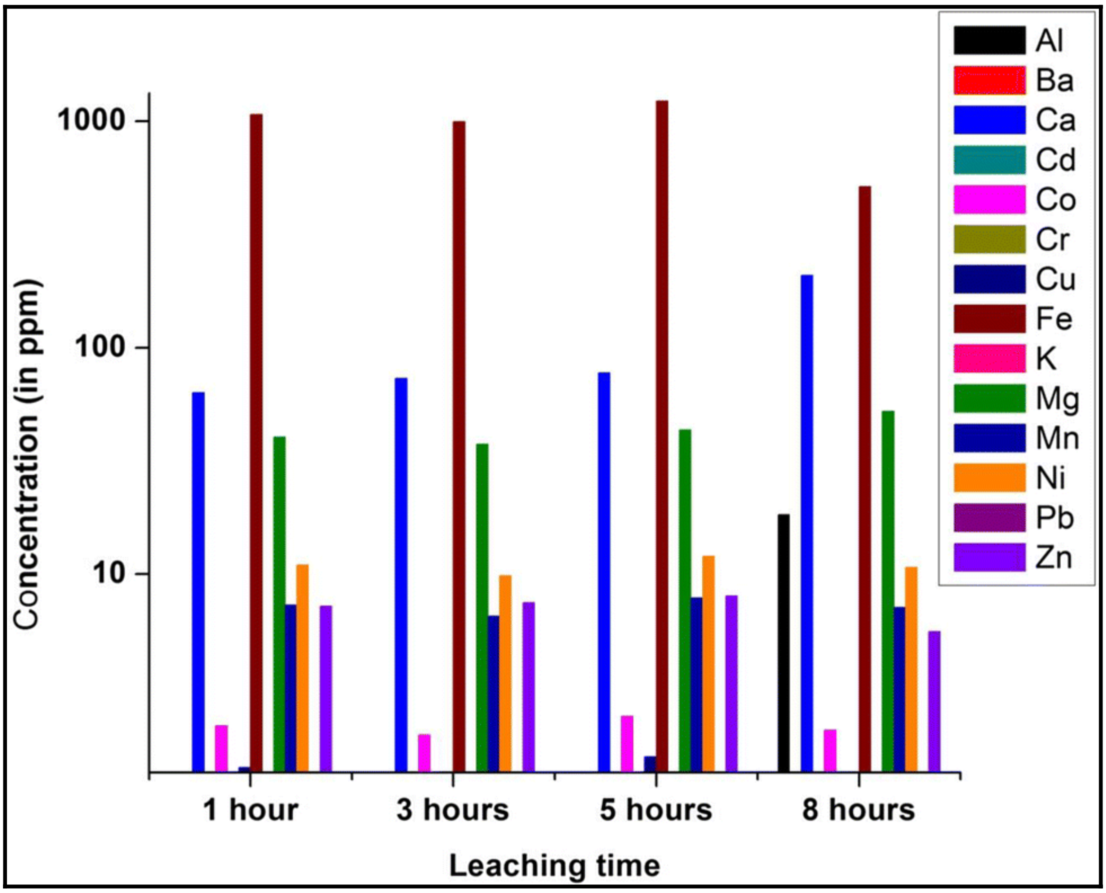

Figure 4.22: Change in elemental concentration (in ppm) in aqueous leachates of Ledo coal (LC-20A) with leaching time at 25^0 C

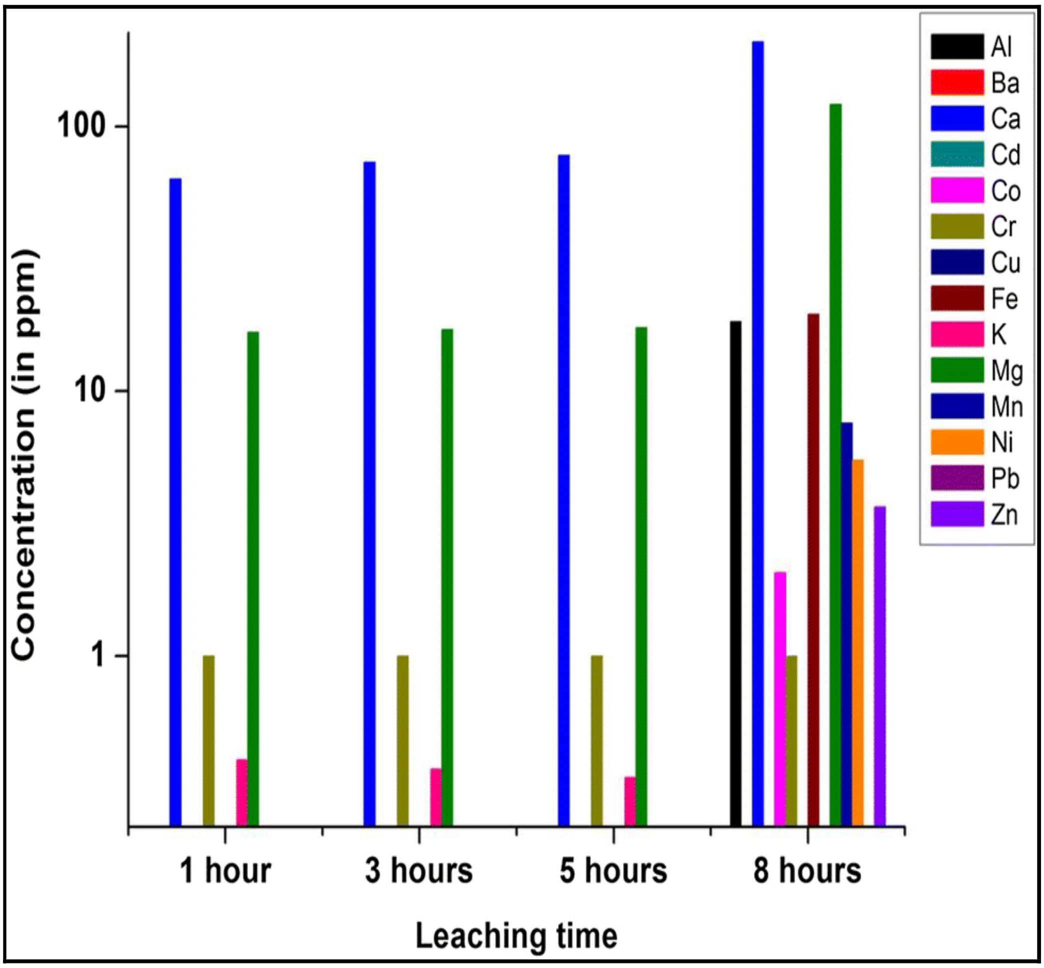

Figure 4.23: Change in elemental concentration (in ppm) in aqueous leachates of Ledo coal (LC-60A) with leaching time at 25^0 C

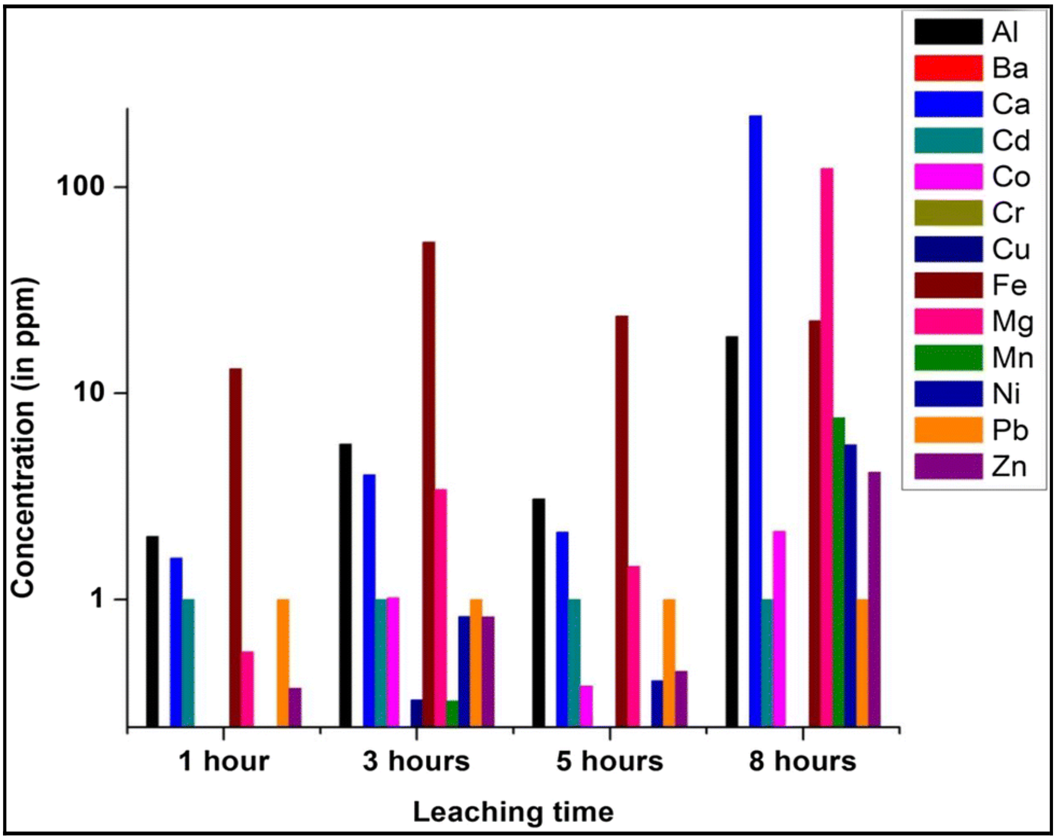

Figure 4.24: Change in elemental concentration (in ppm) in aqueous leachates of Ledo coal (LC-20A) with leaching time at 45^0 C

The release of Pb is highest at 45^0 C which is independent of leaching (Figure 4.24). This implies, the mining temperature (ranges from 25^0 C to 55^0 C) is favorable for release of Pb from coal as well as from overburden. The release of Cu, Co and Zn from the coal and overburden is temperature as well as the leaching time dependent (Figures 4.24, 4.25, 4.26, and 4.27) which can be interpreted from the ICP-OES results of the mine water collected in different seasons and the leachates of coal and overburden at different temperatures. The leaching of Al is fully leaching temperature dependent (Figures 4.24, 4.25, 4.26, and 4.27).

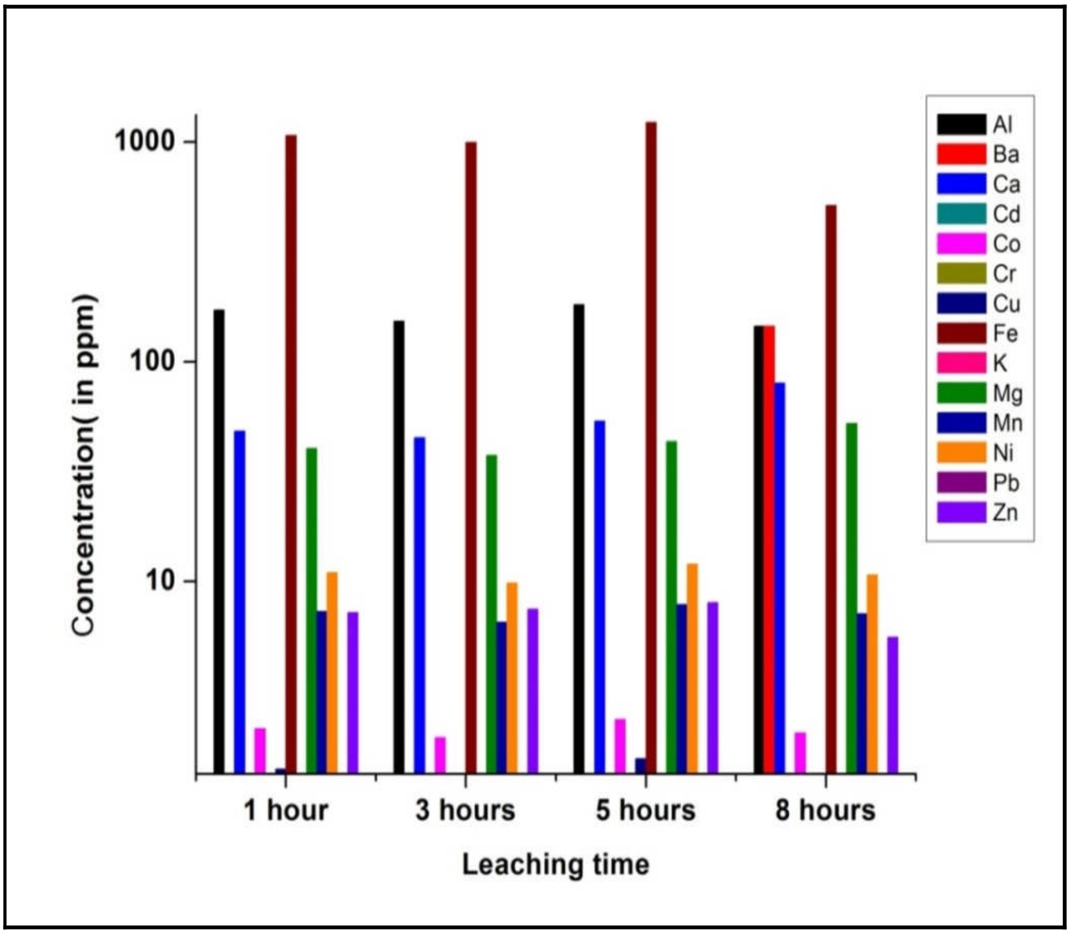

Figure 4.25: Change in elemental concentration (in ppm) in aqueous leachates of Ledo coal (LC-60A) with leaching time at 45^0 C

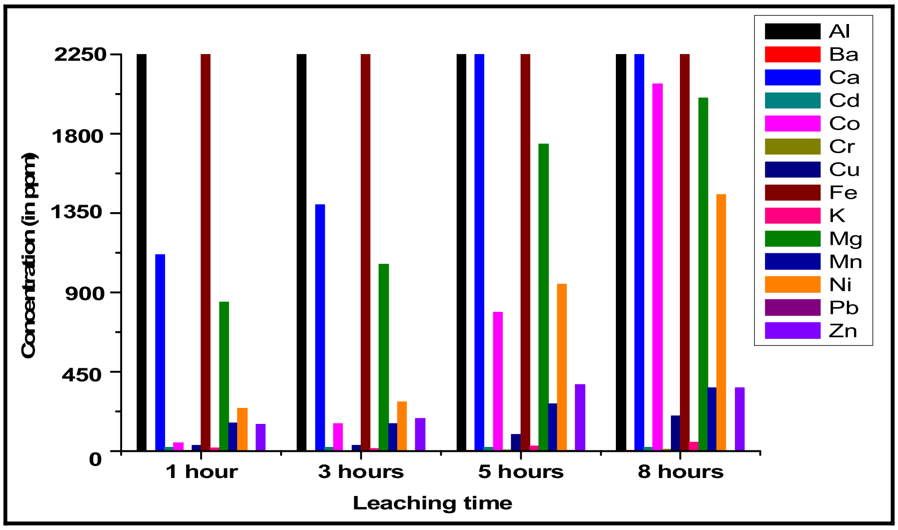

Figure 4.26: Change in elemental concentration (in ppm) in aqueous leachates of Ledo coal (LC-20A) with leaching time at 65^0 C

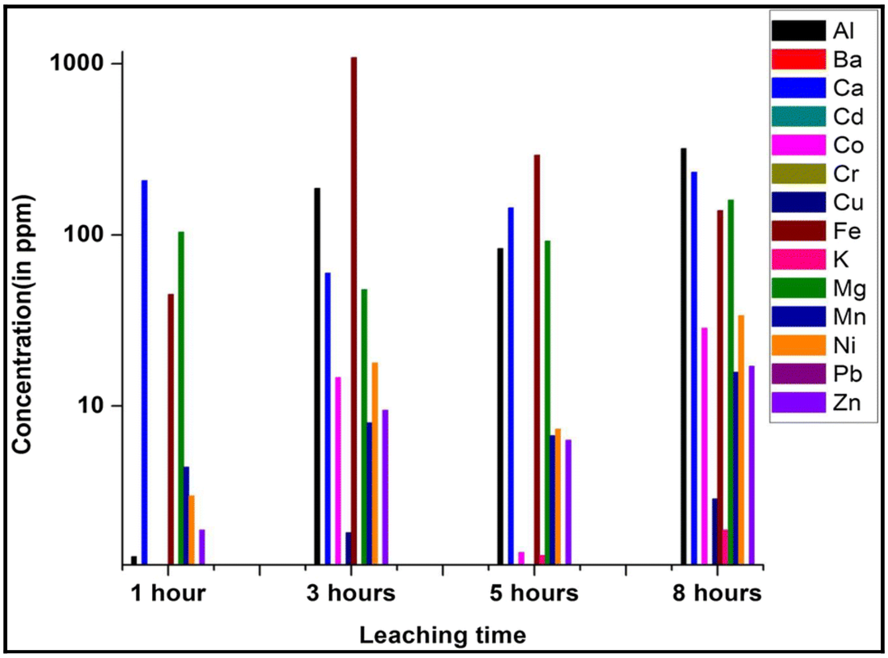

Figure 4.27: Change in elemental concentration (in ppm) in aqueous leachates of Ledo coal (LC-60A) with leaching time at 65^0 C

From the Figures 4.28 and 4.29 it can be summarized that at high temperature most of elements are leached from coal even at a short leaching time. In the case of Fe, the concentration is higher in leachates than in raw samples (the maximum Fe concentration in raw coal was 43.1 ppm and 2320 ppm in the leachates of the coal samples). This indicates that the maximum amount of Fe associated in coal can leach with rain water due to continuous raining. In the present work the leaching process has been done to compare the leaching type of different elements with the natural processes like weathering. The process was associated with continuous stirring of the water mixture of the samples for different time period (1hr, 3 hrs, 5 hrs and 8 hrs) at different temperatures (25^0 C, 45^0 C, 65^0 C and 90^0 C).

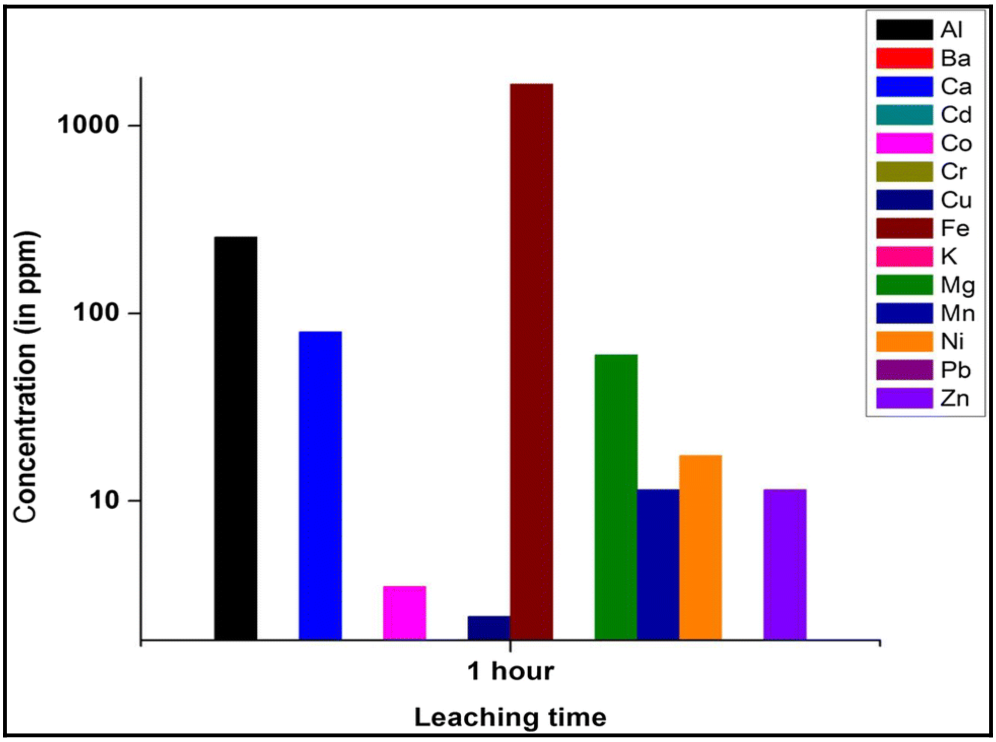

Figure 4.28: Change in elemental concentration (in ppm) in aqueous leachates of Ledo coal (LC-20A) leaching for 1 hour at 90^0 C

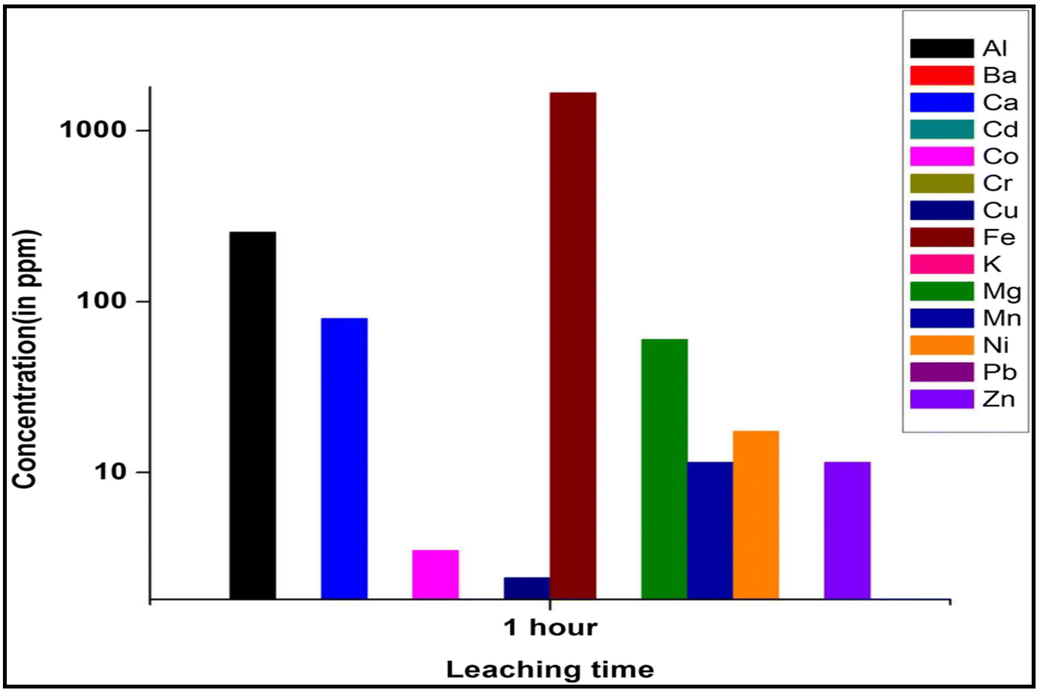

Figure 4.29: Change in elemental concentration (in ppm) in aqueous leachates of Ledo coal (LC-60A) leaching for 1 hour at 90^0 C

4.2.5 XRD and FTIR analyses of leached coals

From the XRD analyses, it is found that the minerals leached from coal and overburden (Figure 4.30) are absent after leaching. In raw samples of coal (Figure 4.31), the minerals quartz and hematite (d-values 3.3404 and 1.5789 respectively) were present but in leached samples hematite, pyrite, marcasite were not found. The minerals quartz, hematite, pyrite, marcasite (d-values 3.3404, 1.5789, 1.8252 respectively) were found in the overburden (OB) samples of Ledo colliery. On the contrary to this, the leached samples of the overburden contain only quartz. This may be an indication of leaching of different minerals which are associated with different elements that can be leached in natural processes, like weathering. These minerals are mainly associated with Fe. The absence of these minerals in the leached samples of coal and overburden indicates their easy leaching with rain water to form acid mine drainage (AMD).

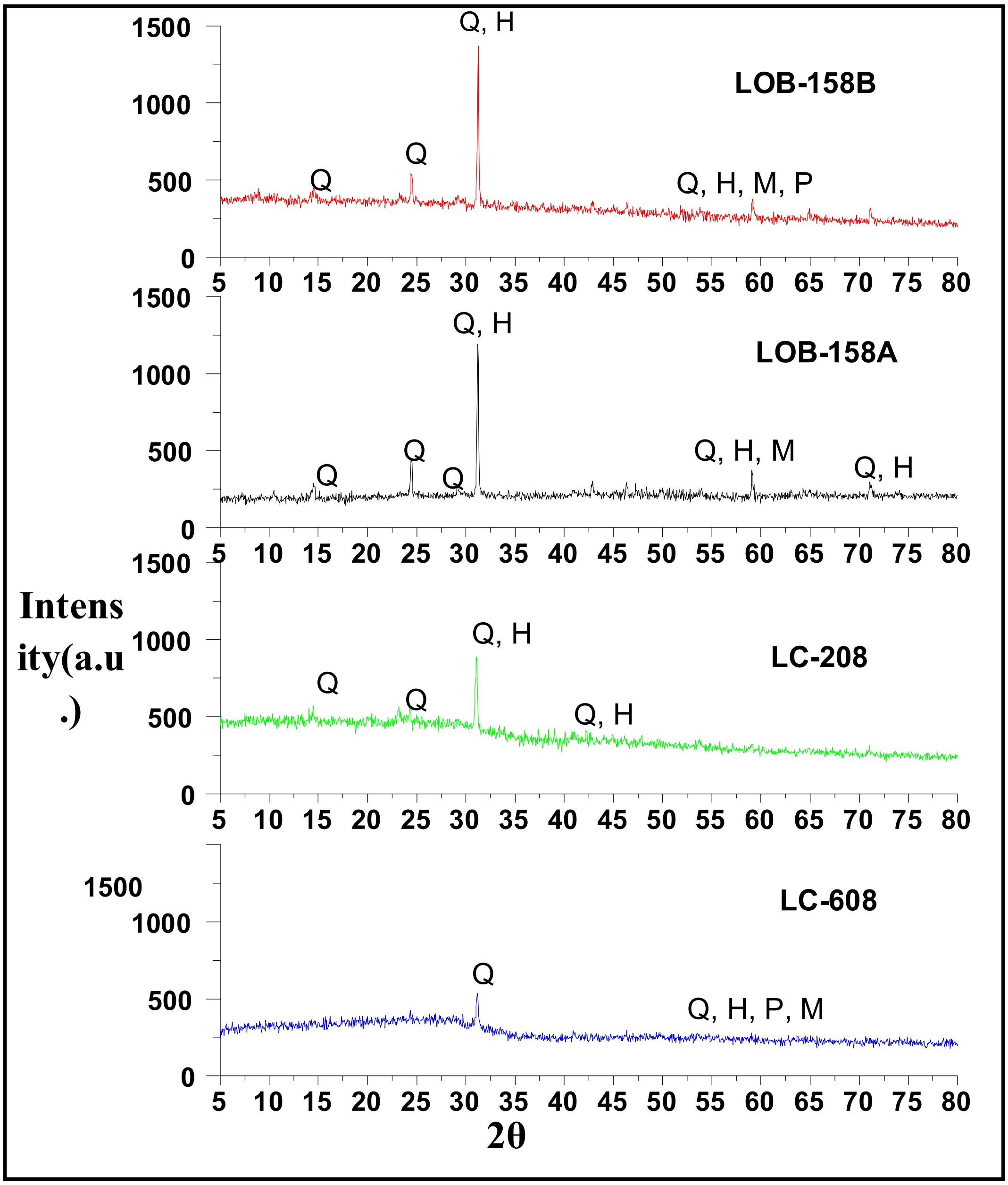

Figure 4.30: XRD pattern of raw coal and OB of Ledo colliery

(Q: Quartz, H: Hematite, M: Marcasite, P: Pyrite)

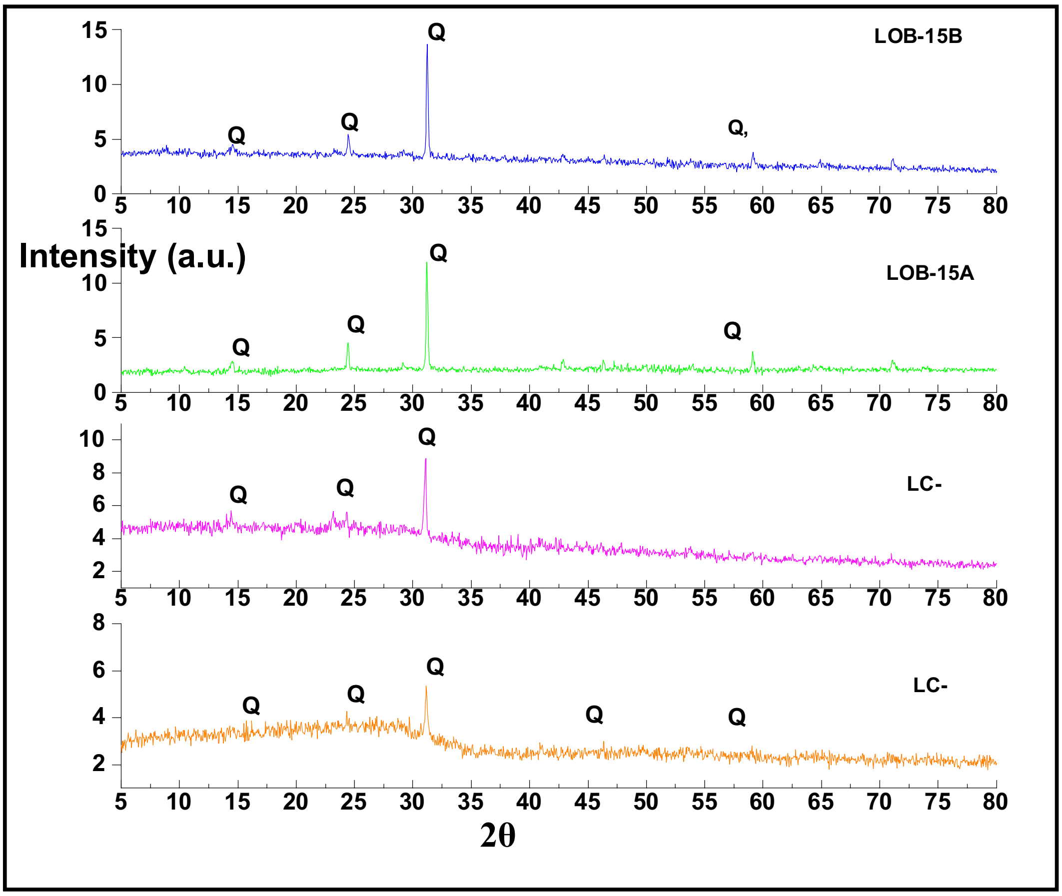

Figure 4.31: XRD graph for leached coal and OB of Ledo colliery (Q: Quartz, H: Hematite, M: Marcasite, P: Pyrite)

FTIR analysis of raw and leached coal and overburden of Ledo colliery (Figure 4.33 and Figure 4.32) revealed the absence of some of the leached components from the samples of coal and overburden. The absorption bands for CH, CH_2, CH_3 (al) are absent in the leached OB and the bands for both $-OH_{ar}$, $-OH_{al}$ are absent in both coal and OB. Although the absorption bands for C_{al}-O-$C_{al,}$ SO_4^{2-} etc. are present in both raw and leached samples of coal and OB but the intensity of these peaks in the FTIR spectra of the leached samples are weak. This is due to the leaching of these samples which causes a low carbon and sulphur contents in the leached samples.

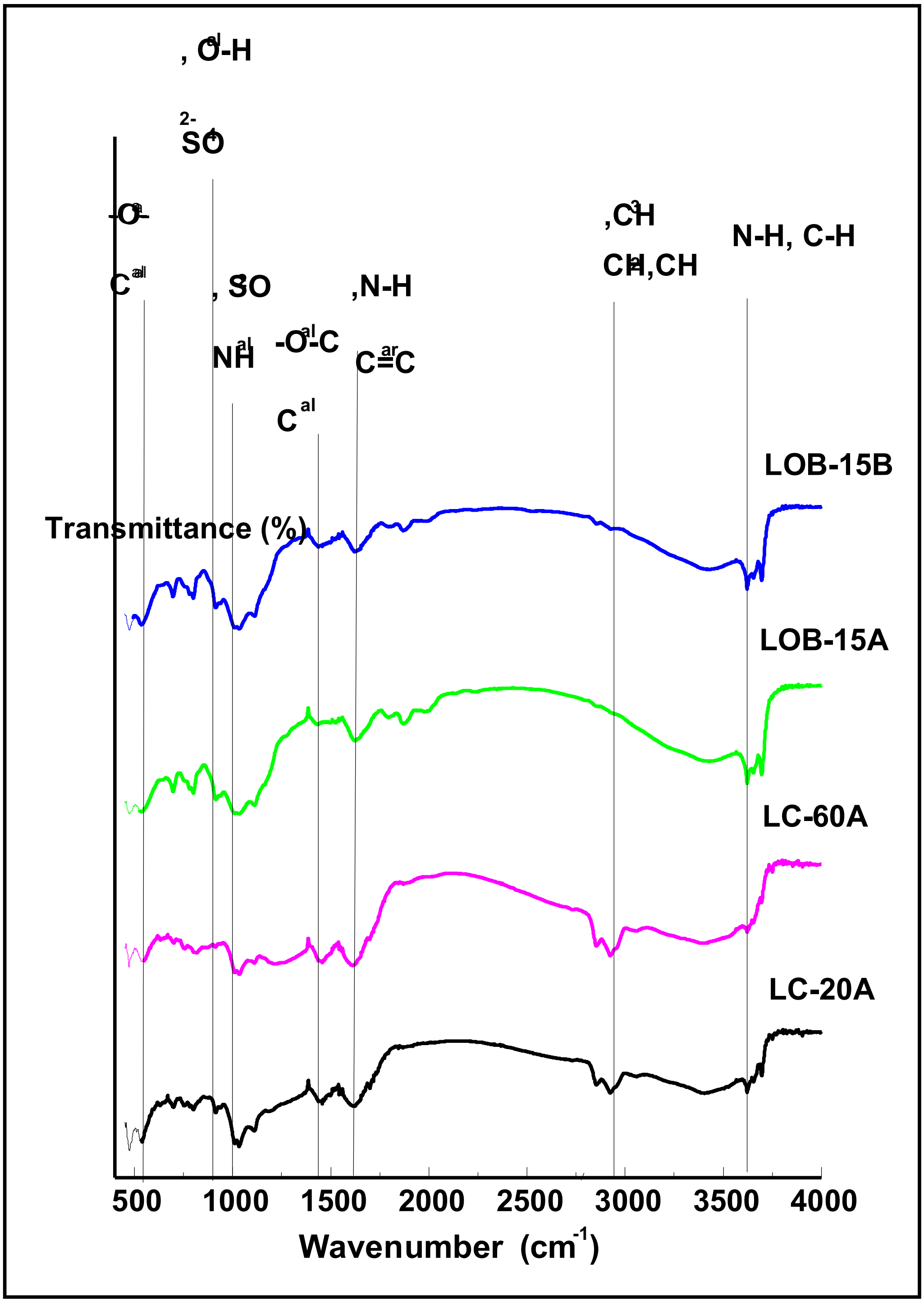

Figure 4.32: FT-IR spectra for leached coal and OB of Ledo colliery

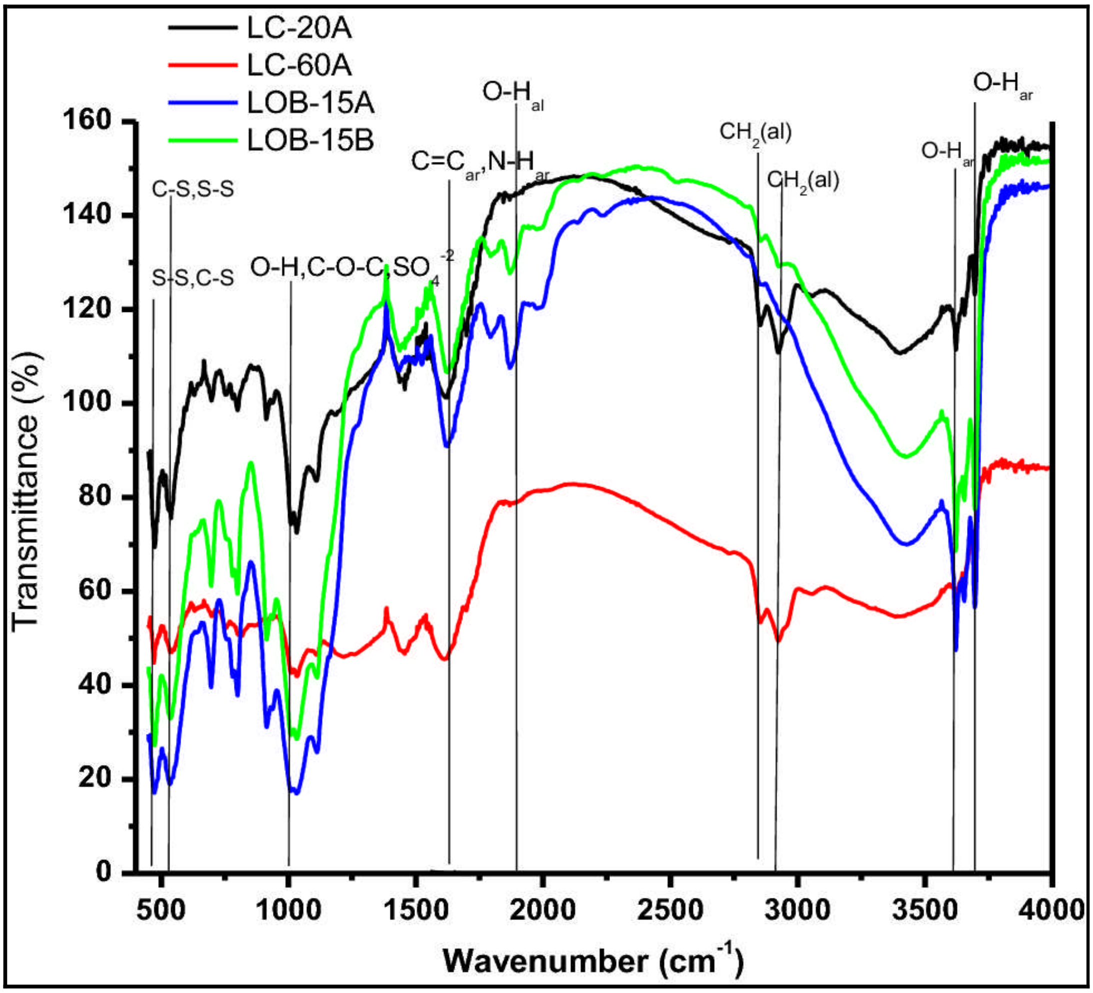

Figure 4.33: FT-IR spectra for the raw coal and OB of the Ledo colliery

The major minerals present in coal are quartz, kaolinite, illite, calcite, carbonate, dolomite and sulfide mineral like pyrite (Ward, 2002). From the XRD and FTIR analyses it was revealed that quartz, kaolinite and pyrite are the major minerals in the Ledo coal. Other Indian coals like Bokaro coal samples contain mostly kaolinite and quartz, but other minerals such as siderite and analcine are found as intermediate phases. In Neyeveli coal, dolomite and kaolinite are the major constituents with trace amounts of hematite and bassanite (Equeenuddin, 2015). From analytical data it was found that the aqueous leachates of the Ledo coal are highly acidic (pH range 1.99-

3.09). But the leachates of other Indian coals have the normal pH range (6.8-7.4) (Equeenuddin, 2015). The strong acidic nature of the leachates of Ledo coal is due to the leaching of pyrite which is present in high amounts in the Ledo coal. The high concentration of iron (1670 ppm) in the leachates is attributed to maximum leaching of pyrite. Low pH of aqueous leachates of Ledo coal leads to leach out most of the heavy metal from the coal.

4.2.6 Observation from field-emission-scanning-electron microscopic (FE-SEM) analyses

In the FE-SEM analysis of raw coal samples of the Ledo coal (Figure 4.34), it was found that barite ($BaSO_4$) and galena (PbS) were associated with pyrite (FeS_2). From the EDS analysis of the leached coal sample (Figure 4.35), it was found that there is no indication of the presence of both Pb and Ba. The association of these sulphur minerals is responsible for highly acidic leachates due to weathering under natural condition. From the literature it was found that Ba and Pb present in coal can easily be released from coal at a lower pH (Giere and Peter, 2004).

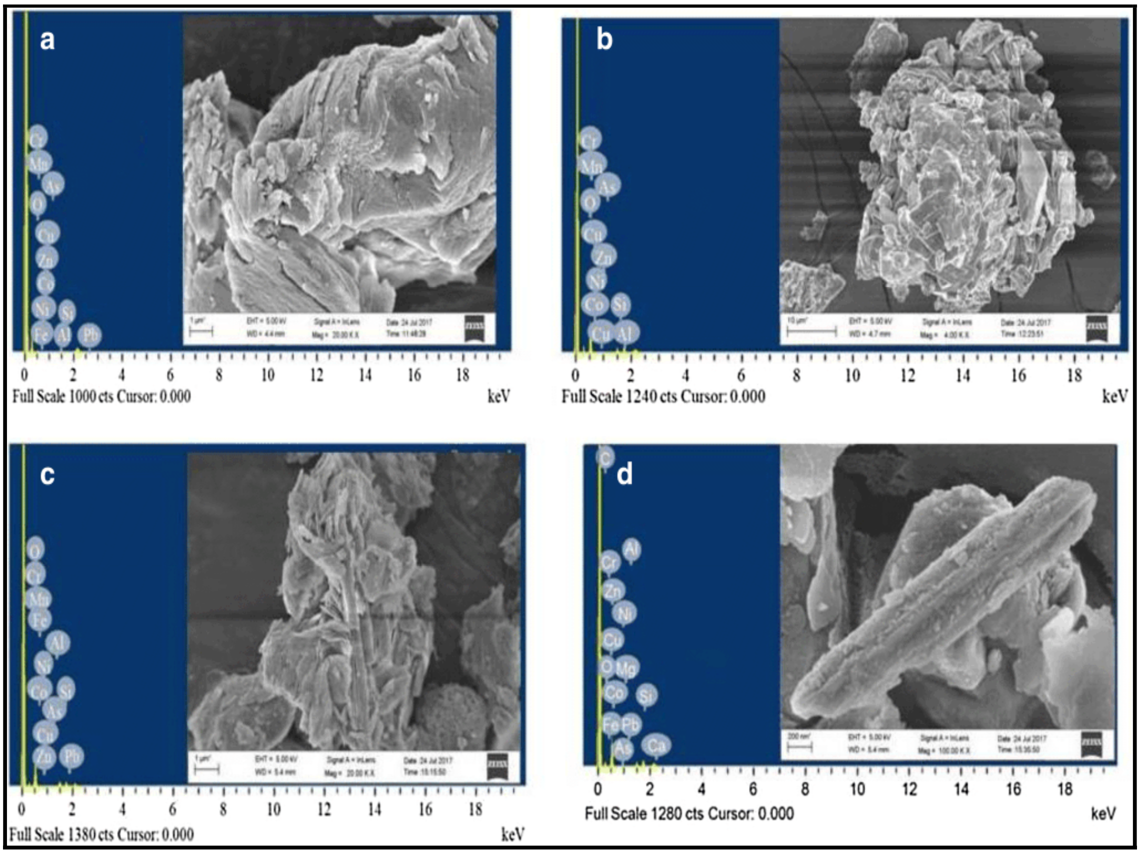

Figure 4.34: SEM-EDS micrographs of raw coal samples LC-20A (a), LC-60A (b) and OB samples LOB-15A (c), LOB-15B (d)

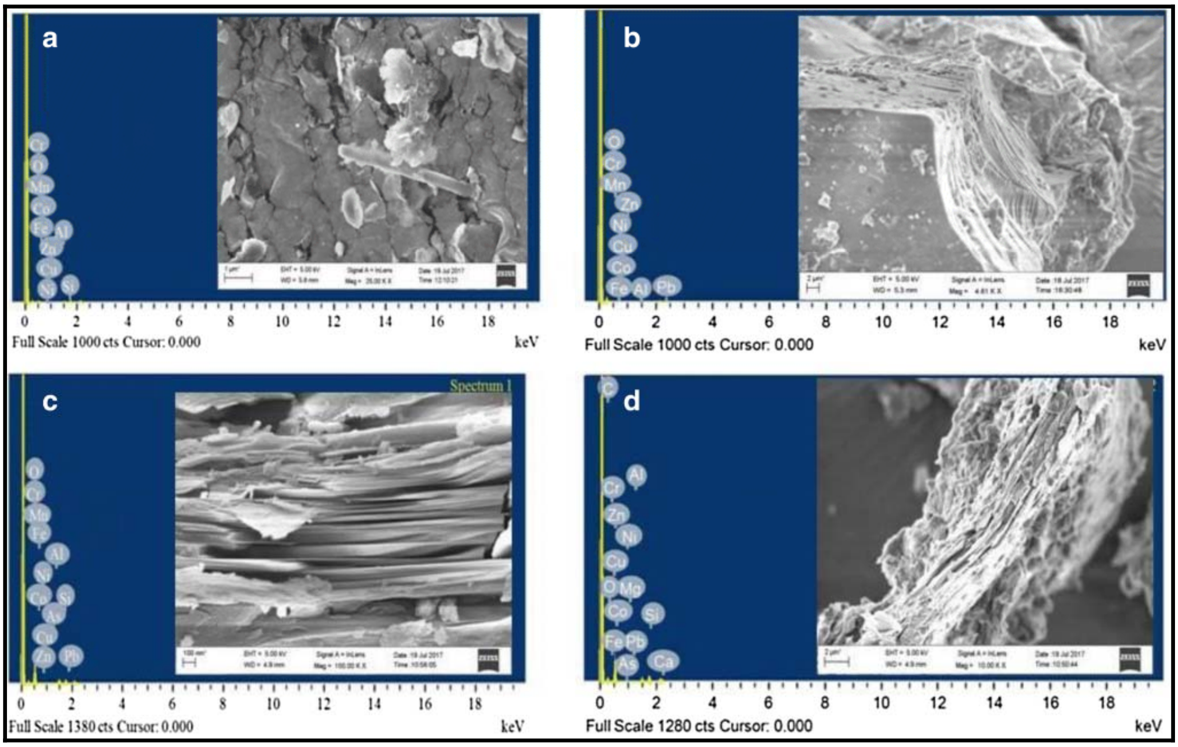

Figure 4.35: SEM-EDS of leached coal LC_L-20A (a), LC_L-60A (b) and OB samples LOB_L-15A (c), LOB_L-15B (d) (LC_L : leached coal, LOB_L: leached overburden)

Under the natural weathering condition, the coal associated with Pb and Ba undergoes leaching to release them and dissolve in AMD water, which was also confirmed by ICP-OES analysis of aqueous leachates of the Ledo coal at different time periods. From the FE-SEM/ EDS analyses of both the raw and leached samples, it was found that the atomic percentage of Fe in raw coal and overburden sample (LC-20A, LOB-15A) were 18.33 and 8.43% whereas in leached coal (LC_L-20A, LOB_L-15A) it was 7.84 and 4.80% respectively. During the leaching process, the coal samples lost their structural behavior by increasing porosity which may be due to release of inorganic minerals from their surface (Manoj et al., 2009).

The SEM-EDS analysis of leached coal and OB of the Ledo coal mine were carried out to find the approximate concentration of metals in the residues of leached samples. From this analysis it was found that in Ledo coals, namely LC-20A and LC-60A, the concentration of Cd, Cr and Ba were found in very low concentrations which resembles with the ICP-OES analysis of aqueous leachates of coal. On the other hand both analyses reported the excess concentrations of the elements Ni, Co, Zn, Cu, Fe (more than regulatory level). The FE-SEM/EDS results of leached samples can be integrated with the ICP-OES analytical data of aqueous leachates. The aqueous leachates of coal and OB at different leaching times and temperatures revealed maximum concentrations of Fe (1670 ppm), Cr (0.62 ppm), Cd (0.002 ppm), Co (92.5 ppm), Ni (64.7 ppm), Pb (0.181 ppm), Ba (0.213 ppm), Cu (9.02 ppm), and Zn (17.1 ppm). A high concentration of these elements in the leachates indicates their transfer from coal and OB under different chemical processes to the aqueous medium. After completing all the probable analyses of the aqueous leachates of Ledo coal and overburden, the data found can be used for relating the characteristics of aqueous leaching of coal and mine OB with the natural weathering condition at mine area.

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