HEAVY METALS ASSESSMENT AND CHEMICAL REMEDIATION IN GROUND WATER IN LAKKI MARWAT, KHYBER PAKHTUNKHAWA

BY

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(2015)

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1. Heavy metals - Environmental aspects

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بسم الله الرحمن الرحيم

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Dedicated

To My Grand Father

HAJI ABDUR RAHMAN (LATE)

Who embraced Islam in his Childhood & by the way all of my family entered to the great religion of ISLAM

To my parents who taught me "to learn Science for the benefits of mankind and love humanity

DECLARATION

I hereby declare that the work presented in this thesis report is my personal effort, except where otherwise acknowledged, and that the thesis is my own composition The Similarity Index has also been calculated using Turnitin software and is within the limits prescribed by HEC and IIU Regulation It is further declared that worked and completed the report entirely on the basis of personal efforts made under the sincere guidance of my supervisor No part of the thesis has been previously presented for any other degree

Mumtaz Khan

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MUMTAZ KHAN

LIST OF ABBRIVIATIONS

AAS	Atomic Absorption Spectrometer
APHA	American Public Health Associations
CNT	Carbon Nano Tube
DO	Dissolved Oxygen
DTC	Dithiocarbamate
EC	Electrical Conductivity
FT-IR	Fourier Transform Infrared Spectroscopy
GW	Ground Water
HM	Heavy Metals
HMTEs	Heavy Metals and Trace Elements
BD	Below Detection
Pak EPA	Pakistan Environmental Protection Agency
ST	Sample Site
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis
TDS	Total Dissolved Salts
USEPA	United State Environmental Protection Agency
WHO	World Health Organization

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ABSTRACT

Presently, there is increased attention and focus on heavy metals pollution, which are becoming one of the most serious environmental problems due to their adverse health effects. These toxic heavy metals are not easily degraded and require removal from polluted water to protect people and the environment. The present study was carried out to assess the physicochemical characteristics of drinking water in District Lakki Marwat and treat water chemically for heavy metals removal by two Dithiocarbamate (DTC) ligands. Total of 75 water samples were collected from 25 sites from tube wells which are used for drinking water supply in 25 representative town and villages of Lakki Marwat. Standard sampling techniques were used for all sources recommended by APHA (1998). The results indicated that these parameters were in the range of pH 7.1-7.8, total dissolved solids (TDS) 412.6-879.6 mg/L, turbidity 0.17-2.78 NTU, electrical conductivity (EC) 286.6-1313.3 µS/cm, dissolved oxygen (DO) 68.6-86.7%, zinc (Zn) 0.003-1.538 ppm, iron (Fe) 0.001-1.799 ppm, copper (Cu) 0.004-051 ppm, chromium (Cr) 0.0003-0.072 ppm, nickel (Ni) 0.011-0.378 ppm, lead (Pb) 0.131-0.519 ppm, cobalt (Co) 0.011-0.08 ppm, manganese (Mn) 0.002-0.046 ppm and cadmium (Cd) 0.0003-0.041 ppm. Most of the physical parameters were found within the permissible limits except EC which was higher in 16 % samples than the limits set by WHO (2008). Mean Concentrations of Zn, Cu and Mn in all water samples sites were found within the permissible limits while concentrations of Fe in 4%, Ni in 40%, Pb in 100%, Co in 40 %, Cd in 28 % and Cr in 10% samples were in excess of the WHO (2008) permissible limits. The higher concentration of heavy metals were found in the samples which were collected from the west of the study area where huge exploration of radioactive metals were carried out for the last 20 years and the south mountainous part, where the seepage Cement factory effluents and geology of the mountains were responsible for higher concentration of heavy metals. Water samples were divided into two groups comprises the mountainous region at the south and west of the study area and plain desert area. Results of both the groups were compared by using ANOVA single factor which showed non-significant difference (*p* > 0.05) for pH, EC, TDS, Turbidity, DO, Fe, and Pb while significant difference (*p* < 0.05) was revealed for Zn, Cu, Cr, Ni, Co, Mn, and Cd. Two types of dithiocarbamate ligands were synthesised, characterized by FTIR and use them as chelators to remove the heavy metals from aqueous solution. Dithiocarbamates were selected because they have good binding ability and can precipitate metal ions as complexes due to heavy sulphur groups. The metal removal efficiency was compared between both ligands. The study indicated that 100% remediation was achieved by dibutyldithiocarbamate (DBC) at pH 5 for Co while 5% removal efficiency was observed by DBC at pH 7 for Mn. The decreasing order of remediation of heavy metals by DBC was Co>Ni>Cd>Zn>Cu>Pb>Fe,Cr>Mn. By treating with DBC more than 95% heavy metals were removed except for Mn. The study indicated that 99% remediation was achieved by Cyclohexyidithiocarbamate (CHC) at pH 5 for Mn, while lowest removal efficiency of 20% was observed by CDC for Ni at pH 7. The decreasing order of remediation of heavy metals by CHC were Mn>Pb>Fe>Cr>Co>Cu>Zn>Cd>Ni. CHC removed 99.10% of Ni, 82.12% Pb, 73.05% Fe, 72% Cr and Co, 50.3% Cu from aqueous solution. For Zn, Cd and Ni the removal efficiency was less than 50%. So CHC is effectively used for removal of Mn and Pb from water. It was observed that the adsorption capacity of dithiocarbamate (DTC) is pH dependent, and all these products showed weak adsorption capacity at pH 9. The adsorption capacity decreases with increasing pH values and the maximum capacity was achieved around pH 5. The remediation by both the DTC at pH 5, 7 and 9 were compared by using two tail t-test. The p ≤ 0.05 showed significant difference between the mean % remediation by both dithiocarbamate which confirmed by greater t critical than t stat.

CHAPTER 1

INTRODUCTION

Water is one of the most valuable supplies of the universe, which is natural granted drink It has numerous uses most of which are vital for life and humanity, without which no living thing could survive and is used for maintaining personal hygiene (Isengard, 2001) It is difficult to eliminate all the water supplies of the world, as water is constantly recycled through the natural hydrological cycle, maintaining the total quantity of water on this planet is about 1 4 trillion cubic meters (Farid et al , 2012)

Quality of water depends on its physical, biological and chemical parameters that arise as results of natural and anthropogenic activities These parameters of groundwater decide its applicability for the desired purpose (Kazi *et al* , 2009) The quality of water varies with time, place and base from which it originates, as it is a spontaneous process, comprising biotic, abiotic, soluble, suspended, organic and inorganic substances (Adeyeye and Abulude, 2004) It is possible to degrade the quality of water to the point where it is compressed, unsafe or sometimes even toxic (Radojevic and Bashkin, 1999)

Among the various sources, the ground and surface water are the vital freshwater reservoirs which are used for drinking, household and in some area for irrigation purposes (An *et al* , 2002) In addition huge quantity of water is required for rapid increase in population (Ho *et al* , 2003) Good health requires safe drinking water, which is the primary human right In the most part of the earth fresh water is a definite resource at present (Jackson *et al* , 2001)

Due to bond polarity and hydrogen bonding in water molecule, water has unique chemical and physical properties of suspension, dissolution, and adsorption for different substances Thus water is pure naturally, which is contaminated by its environment comprising human, animal and other natural activities (Mendie, 2005, Chitmanat and Traichaiyaporn, 2010)

Due to decline in surface water and varied nature of the monsoon in the arid and semi-arid regions of the world, the reliance on groundwater is increasing day by day (Sundary *et al*., 2005) In fact it is right for Pakistan, which is considered an arid country of the world and regarded that in the near future, it has been water anxious and water scared (Hamazah *et al*., 1997) At the end of this century due to climate change, urbanization and enlarged population, the quantity of water become more worsted (Jackson *et al* 2001) Water quantities in rivers, lakes and ground water are shrinking due to the collective effect of lower rainfall, snowfall and higher vaporization (Hamazah *et al*, 1997)

Variations in ground water are perceived by developing nations, which organize alternate sources of water Due to the purification and lack of distribution, ground water preferred over surface water The borehole water is superior then surface water, which is easily available from lakes, rivers, streams and springs (Adeyeye and Abulude, 2004)

In most part of the world the quality of water degraded continuously The drinking water in many countries does not match World Health Organization (WHO) standards which have been shown in numerous research studies (Aydin, 2007, Gupta *et al*, 2009, Gyamfil *et al*, 2012)

Overall deterioration of water quality and specifically groundwater is of most concern (Qadir *et al*, 2008) It is assessed that due to poor quality of water, 30% of all diseases and 40% of all deaths are produced in Pakistan (Global Water Partnership, 2000) According to the ranking of water quality, Pakistan takes the 80th position in the world (UNESCO, 2002, Azizullah *et al*, 2011) Open water sources or underground water is broadly utilized for drinking water supplies in Pakistan Almost one third of the entire drinking water deliveries are obtained from underground aquifers In several parts of Pakistan the quality of water does not fulfill the requirement of WHO/Pakistan guidelines for drinking water It is declining generally due to the discharging of the untreated metropolitan and industrial effluents and also because of the runoff of briny drainage from farming areas (Tahir *et al* , 1998, Chilton *et al* , 2001)

Though, the problem of drinking water quality has a significant problem in the developing countries, but the issues are negligibly discussed in developing countries Accessibility of water in Pakistan is about 1,200 m^3 per capita, which is reduced rapidly and for the reason Pakistan has categorized a water stress country Furthermore, in Pakistan only 3% of the total domestic and industrial wastewater of the total 4 million acre feet (MAF) per year are carried in proper treatment This small amount of treated and huge amount of untreated water are discharged directly into water bodies Almost one third of the total population in Pakistan depends on ground water for their everyday uses (Malik *et al* , 2010)

1.1. WATER POLLUTION

Pollution is a global problem and it has the unlimited effect of influencing the health of human population (Khan and Ghouri, 2011) Water pollution has been an issue of dynamic search for an extended time The water would become unfit for particular uses and the balanced system may be disturbed by any change in the natural water quality The accessibility of water has become threatening through surface and groundwater sources with the passage of time Drinking water must be of international standard, that is, free of contaminants in terms of physicochemical parameters and organism load (Ojutiku and Kolo, 2011)

The effect of pollution in the neighborhood of over crowded cities, from industrial effluents and automobiles has reached to an alarming point and is increasing public awareness (Begum *et al* , 2009) The main causes of water pollution and eventually of waterborne diseases are direct household release and runoff of industrial effluents, leakage from damaged septic water tanks and poor administration of agricultural wastes (Jain *et al*, 2005)

Furthermore, ground water in Pakistan decline qualitatively and quantitatively due to overload of human population, discarding of solid as well as liquid effluents, urban sprawl, unmaintainable and poor implemented policies and poor implementation of the law, nonexistence of tough management (WWF, 2007)

It is predicted that one fourth of all deaths are the results due infectious illnesses produced by pathogenic bacteria All over the world, the ratio of the annual death of the people from drinking inferior quality of water is greater than from all kinds of disaster including war (WHO, 2002, UNEP, 2008)

Extreme levels of pollution are causing a huge loss to human and animal health, plants including tropical rain forests as well as the general environment (Khan and Ghouri, 2011) Diseases spread due to Pollution which affect the old, the young, the energetic, all animals and plants (Kanmony, 2009)

Naturally, all metals and other chemicals have a potential for harmful effects on the population, Even if anthropogenic contamination is completely eliminated This problem may be reduced if groundwater is taken out for drinking after detailed chemical investigation Physical and chemical properties including trace element contents of the natural water are very important for public health studies Heavy metals are significant poisonous contaminants that firmly bound the usefulness of water for household and manufacturing use (Ojutikue *et al*, 2014)

1.2 HEAVY METALS POLLUTION

In the world heavy metals are considered one of the common pollutants in the environment (Papatilippaki *et al*, 2008) The existence of heavy metals in minute concentration and vital elements in higher concentration causes toxic effects if exposed to the human population (Fong *et al*, 2008) Overall the heavy metals greatly affect the freshwater ecosystem Heavy metals are the specific significance in the contaminants of ground water due to high toxicity even in minute quantity, whether the heavy metals exist naturally in the water which includes weathering of natural resources, discharge particles of different metals and substances that comes out due volcanic eruption or due to human activity i e solid waste dumping, industrial or home effluents, harbor channel dredging (Marcovecchio *et al*, 2007)

For regular body function vital elements like calcium, magnesium, potassium and sodium must be present for supporting the life Also, zinc (Zn), Cu, Fe, Mn, Co and molybdenum work as an activator for the enzyme processes are required at low levels Heavy metals occur in water in colloidal, suspended and soluble phases (Adepoju - Bello *et al*, 2009) Heavy metal pollution is a worldwide problem, though the severity and levels of pollution differ by location Once ground water contaminated by heavy metals and trace elements, these may badly affect the human health because the drinking of contaminated water is one of the main paths through which HMTEs ingested into the body (Kavcar *et al*, 2009. Wanga *et al*, 2010)

Out of total elements only 20 elements are considered as a toxic heavy metals 50% of them released into the environment in hazardous levels to human health Cu, Cd, Pb, Cr, Ni, Hg, Zn and As are most investigated water pollutants The discharge of these untreated metals poses a major risk to community health because of their persistence, bio-amplification and collecting in the recycling of food in the environment

The hazard due to heavy metal polluted water has negative impact in two ways Primarily, in natural ecosystem heavy metals persist for an extended time period Next, heavy metals have the capability to accumulate in successive stages of the biotic system, thus producing acute and chronic diseases Kidney failure heart and brain disease are due to acute gastrointestinal and respiratory problem caused by Cd and Zn (Nomanbhay and Palanisamy, 2005, Lon *et al*, 2008) In the most part of the world the agricultural land may be irrigated by effluents having high concentrations of heavy metals The addition of these toxic metals in the plant tissue have negative effects on plants and ultimately cause human health risk and also to other animals (Athar and Ahmad, 2002)

In severe cases nervous system damage, reduction in the growth rate, organ damage, development of cancer and in extreme cases may cause death The development of autoimmunity is caused due to the contact of Mercury and Lead, in which antibodies in a person outbreaks the individual cells, which may be converted in the joint diseases called rheumatoid arthritis, kidney disease, circulatory system and nervous system diseases (Rajendran *et al*, 2003, Johnson and Hallberg, 2005, Oelofse *et al*, 2007)

High concentration of Cu and Mn in drinking water causes Alzheimer's and Manganism which are mental diseases (Dieter *et al*, 2005, Wanga *et al*, 2010) Diseases of the brain, kidneys, nervous system and blood cells are related to Pb (Gump *et al*, 2008, Jusko *et al*, 2008, Kim *et al*, 2011) Pb has multiple effects and a probable human carcinogen (Bakare - Odunola, 2005) However, thyroid artery, polycythemia and increasing the formation of red blood cells (RBCs) are the abnormalities and causes due to ingestion of food and water which is highly polluted by Co Skeletal disease, kidney diseases and it-itai (ouch-ouch) diseases are linked to high intake of Cd (Nordberg *et al*, 2002, Robert and Mari, 2003)

1.3. TECHNIQUES USED FOR HEAVY METAL REMOVAL

Generally different physicochemical methods used for remediation of heavy metals from water are, chemical precipitation through ligands (Azetsu-Scott et al , 2007), ion exchange (Oehmen et al , 2006), membrane filtration (Bloche et al . 2003), adsorption (Mata et al , 2009), electro-chemical technology (Basha et al , 2008), electro dialysis, ultra-filtration, reverse osmosis (Fu and Wang, 2011)

Remediation by conventional chemical precipitation have numerous shortcomings and due to strict environmental principles, it is difficult to remove heavy metals from water by common precipitation methods For the remediation of heavy metals from aqueous solution by precipitation, the chelating ligands are used by many firms (Matlock *et al* , 2002)

One of the most strategic fields of the modern scientific research is to find new methods to eliminate heavy metals from water In the process of chemical precipitation, DTC ligands are one of the most fruitful research materials in this field DTC ligands are a type of dithiolate ligands, which contain a number of mono- and di-negatively charge groups

1.4. DITHIOCARBAMATE (DTC)

DTC are formed by the reaction of carbondisulphide with primary or secondary amine in the presence of base as catalyst Mono or dialkyldithiocarbamates are formed depending on the type of amine that is used in the synthesis of these compounds (Ramos, *et al* , 2013)

DTC are the coordination compounds that have been widely studied due to their proficiency of having different binding nature with different metals (Exarchos, 2001) DTC have the ability to stabilize the transition metals in a variable oxidation state and form useful complexes of the corresponding metals (Hogarth, 2009) There is an extra n-electron movement of nitrogen to sulfur through a planar delocalized π- orbital system which gives distinct characteristics to these ligands This effect results in strong electron donation and hence a high electron density on the metals leading to its next higher oxidation state (Pandeya et al , 1997)

Large number of DTC complexes have been synthesized since the last century, which comprises common lower alkyl groups like methyl and ethyl This increasing awareness in the field of DTC chemistry is the characterization of the support so that new applications and relations can be established This research field is in premature phases, although previously interesting possible characterization has been studied, comprising the characterization of gold nanoparticles, the stepwise build-up of multi-metallic collections, the production of DTC-containing supramolecular systems which can be used for anion linkage, the synthesis of technetium radiopharmaceuticals (Hogarth, 2009)

DTCs are a group of metal coordinating, antioxidant complexes having large number of uses in the medical fields for the curing of fungal and bacterial infections, and potential treatment of AIDS (Milacic *et al* , 2008)

A ligands form a bond with heavy metal ions to form stable and insoluble complexes, so the heavy metals are effectively removed from the aqueous solution in the form of insoluble precipitates Presently DTC and its derivatives are systematically studied for remediation of heavy metals from wastewaters (Jiang *et al*, 2004, Li *et al*, 2004) The dithiocarbamate, due to its strong binding ability to heavy metals while do not form complex with alkali and alkaline earth metals, have been widely used in the in the removal and pre-concentration of heavy metals from waste water and environment treatment (Mahmoud *et al* ,2004, Venkatesan *et al* ,2002, Dimos *et al* ,2009)

DTCs are widely used on a various crops, mostly due to their effectiveness in the treatment of fungal diseases in the plants and comparatively little acute toxicity in the milk feeding animals (Caldas, 2001) Due to their extensive efficacy as a powerful anticancer agent, they got much attention in pharmaceutical field (Ronconi, 2006) They are used as vulcanization accelerators in rubber production (NieuWenhuizen *et al*, 1999), in controlled radical polymerization techniques (Wood *et al*, 2006), and currently in the production of ionic liquids and in solid-phase organic synthesis it acts as binders (McClain and Hsieh 2004, Morf*et al*, 2006), and in the synthesis of peptide in protein, the amine group is protected by DTC ligands (Greene and Wuts, 1999)

For remediation of heavy metals from water, the present study use the DTC that are made from cheap, common, simple substances, easily achieved, safe and that are chiefly planned to adsorb various heavy metal ions from aqueous solutions or wastewaters

1.5. PROBLEM STATEMENT

Lakki Marwat is located in the south of the Khyber Pakhtunkhwa, people of district Lakki Marwat dep end on water from bore holes and tube wells for drinking and irrigation uses

Considering the deep water table and the depth of hand-dug wells (approximately 60-300 meters) and water scarcity in this semiarid area, the suitability of groundwater for drinking in the area has raised some concerns which increase possibility of contamination of the underlying ground water by heavy metals Due to the local government authority inability to extend potable water supply to the entire area, lack of maintenance of public water supply and increased population, groundwater consumption has become a common practice with many homes having resorted to the use of hand-dug and hand-pump wells for domestic purposes

The absence of permanent rivers in Lakki Marwat have an accumulative effect on the heavy metals as rivers help carry some of the metals downstream hence reducing their concentration Moreover the huge exploration of radioactive metals in the western mountainous part of the study area increased the ground water contamination by heavy metals

Lakki Marwat is tumbledown with poverty and therefore this community cannot afford to live with the effects of these pollutants as this was costly for them to look for treatment Regardless of this, no work has been reported on the level of heavy metals on water in the study area This study, therefore, recommends determining the levels of Cd, Cr, Pb, Zn and Mn in underground water of Lakki Marwat and chemical remediation for the removal of these metals from water

1.6 SIGNIFICANCE OF THE STUDY

The assessment of heavy metals in water of Lakki Marwat will be used to sensitize the general population of the area on the importance of environmental conservation The study will also be helpful for the authorities in environment administration in district Lakki Marwat to establish a baseline for the future studies The present study will help take possible remedial action, including treatment of the water to remove the heavy metals where the levels were too high

1.7. AIM OF THE STUDY

- The aim of this study was to contribute knowledge on protection of public health

1.8. SPECIFIC OBJECTIVES

- Assessment of heavy metals in ground water of the study area
- Improvement of water quality by chemical remediation of the identified heavy metals

CHAPTER 2

LITERATURE REVIEW

The international organizations such as WHO USEPA, EPA, and EUC set the guidelines for the protection of human health from the of heavy metals pollution in water WHO set the standard of numerical value with a tolerable margin of safety to ensure no adverse effect on human health, which is the enforceable standard for the presence of heavy metals having a maximum contaminant level [MCL] (Marcovechio *et a* , 2007)

Khan *et al* , (2015) studied the drinking water quality and human potential health risk in Peshawar, which is the most populous district of Khyber Pakhtunkhwa Province, Pakistan Atomic absorption spectrometer was used to analyze the samples for heavy metal (As, Cd, Co, Cu, Cr, Hg, Ni, Pb, and Zn) The contaminations of Cd and Pb were significantly higher ($p <$ 05) than their maximum allowable limits set by the World Health Organization Drinking water treatments and contamination controlling policies were suggested to avoid the hazardous effects of toxic heavy metals

Saeed *et al* , (2014) inspected the quality of underground water used irrigation in Lakki Marwat, Khyber Pakhtunkhwa The EC and the pH values indicate that the groundwater in the region is slightly saline and alkaline The overall study shows that none of the water samples have a negative effect on the yield of barley, sorghum and wheat while 7% and 17% of this water respectively reduce the yield of corn and onion by 50% Also, 7% of this water reduces the production of alfalfa by 25% The deep ploughing, provision of adequate drainage and crop rotation like management practices can improve the utilization of such water was concluded in the cogitation

Arain *et al*, (2014) reported the study of heavy metals in drinking water of district Bannu, Khyber Pakhtunkhwa, Pakistan All physicochemical parameters and concentration of heavy metals was within the WHO permissible range except TDS and EC

A research study was conducted to evaluate the heavy metals concentration in drinking water of district Karak The heavy metals including Zn, Mn, Fe and Cd were at the permissible limit of WHO (1993), while Cu, Ni, Cr and Pb concentrations exceeds the WHO standards of drinking water which can cause serious health problems (Hassan *et al* 2014)

Jabeen *et al*, (2014) studied the surface and ground water quality of Haripur basin (including industrial state), Pakistan The average metal concentrations in surface and ground water were found in the decreasing order Fe> Mn> Zn > Ni > Pb > Co > Cr > Cu > Cd > As > Hg and Zn > Fe > Pb > Mn > Cr > Cu > Ni > Cd > Co > As respectively The drinking water show no health risk as specified from chronic daily intake (CDI) and hazard quotient (HQ) of these elements

Hussain *et al*, (2014) conducted the study to assess the drinking water quality of Islampura area, Swat These samples were investigated for physical and chemical parameters including heavy metals (Pb, Zn, Ni and Cr) The results indicate that most of the physico-chemical parameters such as total suspended solids (TSS), pH, salinity, TDS, chloride, sodium, potassium and Zn were within the permissible limits when compared with international standard Whereas EC, alkalinity, hardness, Pb, Cr, nickel, calcium and magnesium were above their permissible limit In this respect the drinking water quality of the area is unsafe for drinking purposes

Bilal *et al*, (2013) described the concentration of heavy metals (Cr, Cd, Cu, Fe, Mn, Ni and Zn) and light metals (Na, K, Ca and Mg) in the drinking water of Hasan Abdal Town, Punjab, Pakistan The result determines that all the physical-chemical properties were present under the permissible limits recommended by different national & international organizations No toxic pollutants were present in urine and is non-toxic for drinking purposes

Mahar, (2013) studied the heavy metals (Cd Co, Cr Cu, Mn, Ni, Pb, Zn and As) concentration in groundwater samples in the area of distillery spent wash evaporation ponds and reference groundwater samples collected 2 to3 kilometres far away from the source The study investigates the possible effect of drinking heavy metal contaminated water The results were compared to permissible limits of Pakistan Environmental Protection Agency (PEPA) and WHO, set for industrial effluents and drinking water The health risk assessment such as Chronic Daily Intake (CDI) and Hazard Quotient (HQ) were calculated on the sources of HM concentration The CDI of heavy metals in ground water was in following decreasing order Fe> Zn > Mn > Ni > Co > Cu> C r > Cd > Pb > As The HQ indexes of HM in the GW samples near the distillery spent wash evaporation ponds was in the order As > Cd> Ni >Cu > Mn > Zn > Pb > Cr The results revealed that the distillery spent wash was the cause for the deviation in HM contents of the study area

Khan *et al*, (2013) reported the concentrations of heavy metals in drinking water sources (surface and groundwater) of Swat valley Khyber Pakhtunkhwa, Pakistan The concentrations of Cd, Cr, Ni and Pb were higher than their respective permissible limits, while Cu, Mn and Zn concentrations were observed within their respective limits Multivariate and univariate statistical analyses showed that geologic and anthropogenic activities were the possible sources of water contamination with heavy metals in the study area

Ahmed *et al*, (2012) conducted a study to assess the quality of drinking water, including heavy metals of District Kohat For the assessment of water quality samples from

Billitang, KDA, Nasrat Khel and Chongee were collected The results showed variation from the WHO/Pakistan standard for drinking water The results indicated that most of the samples were contaminated due to geological bands Among the sources, storage and Wells were found highly polluted while tube wells were found to be the most suitable source for drinking water

Khan *et al*, (2012) in Kohat (KPK) indicates most of the samples taken from wells, tube wells, hand pumps, streams and tanks were contaminated particularly in Shakardrara, Lachi and Ara Khail Evaluating the various sources of water storage tanks and wells were highly polluted whereas tube well water found safe for human use

The study investigated the concentration of various pollutants and health risk in Charsadda district, Khyber Pakhtunkhwa, Pakistan Pb, Cd Ni, and Fe concentration were higher than their respective permissible limit set by different organizations Additionally, in some sampling point the coliform bacterial contamination (2-5 MPN / 100ml) was found also in water, showing that drinking water was bacterial contaminated (Khan *et al*, 2012)

Shah *et al*, (2012) investigated drinking water (surface water and sub-surface water) quality of Mohmand agency, northern Pakistan Heavy metal (HM) concentrations were analyzed using graphite furnace atomic absorption spectrometer Statistical analyses like one-way ANOVA, were used for contamination sources The heavy metals concentration were found in the order of Cr > Fe > Ni > Cu > Mn > Zn > Co > Pb > Cd and Ni > Cd > Cu > Mn > Pb > Zn > Cr respectively Water contamination was the main source of diseases like diarrhea, viral hepatitis headache, hypertension, abdominal pain liver and kidney problems and fatal cardiac arrest as complained by most of the respondents during field visit and reported in basic health unit (BHU)

Muhammad, (2010) conducted a study in Kohistan region, north Pakistan, where the exposure of mafic and ultramafic rocks (Kohistan island arc and Indus suture zone) and meta sedimentary rocks (Indian plate) were apparent In some samples, the Fe and arsenic concentrations higher than their permissible limits For a health risk assessment of arsenic, the values of HQ were found >1 in the samples collected from Jabba, Dubair, while HQ values were <1 in the rest of the samples This level of contamination should have low chronic risk and medium cancer risk when compared with US EPA standard Water quality has been changing rapidly for the last few decades in developing countries This large scale variation in the water quality could be either due to geogenic or anthropogenic sources

Furthermore, a study conducted by Pakistan Council of Research in Water Resources (PCRWR) in all four provinces of Pakistan reported that a large number of the samples of water found insecure for drinking purposes In the chief industrial cities of Punjab high arsenic concentration was reported due to industrial and chemical waste discharge, In Khyber Pakhtunkhwa (KPK) high Fe concentration was investigated while in Sindh high turbidity level was observed (Soomro *et al* , 2011)

Gul *et al* , (2010) conducted a study on water in the district Mardan Among the major cations and heavy and trace metals, concentrations of Ca, Na, Fe, Cu and Pb were relatively high in some water samples However, concentrations of K, Mg, Cd, Cr, As, Ni and Zn in all the water samples were found within the allowable limits of WHO and USEPA

The groundwater quality of Sialkot, an industrial city of Pakistan, was assessed The results disclosed that the groundwater of the study area cannot be considered of good quality as it is highly turbid (57% of total sites) with high level of Zn, Fe and Pb, which were above WHO and PSQCA permissible limits The distribution maps served as important information to understand the ecological status of the groundwater systems and for the identification of groundwater quality parameters with concentrations above the allowable limits of WHO and to find out potential areas where water treatment plants and technologies can be targeted in Sialkot (*Ullah et al* , 2009)

A study was conducted in Islamabad to evaluate the microbiological quality of water and food items The samples were collected from different schools and colleges Results show that out of 30 water and 10 food samples, 20 water samples and 7 food samples were highly toxic and not safe for human use (Saddozai *et al* 2009)

Chromium and Lead levels were reported high in almost all ground water sources, however extremely high concentrations were found in industrial areas of Karachi Presence of any one of the heavy metal contamination necessitate the need for the estimation of other heavy metals as significant positive correlation was found between chromium and lead concentration, indicating the possibility of similar contamination sources in Karachi (Arain *et al* , 2009)

Tariq *et al* , (2006) evaluates the possible impacts of effluents of Hayatabad Industrial state on the quality of underground water Variable results were obtained for various parameters in underground water samples The pH, TSS, TDS, Fe and Zn were within the permissible limits in all but Cd, Cr, Cu, Mn, Ni and Pb exceeded the allowable limits in one or more water samples compared with the WHO and US-EPA standards established for drinking water These results suggested that effluents discharged from various industries showed variable characteristics and are a potential risk to underground water contamination It is therefore recommended that wastewater treatment plants must be built with each industry

Similarly, Nickson *et al* , (2005) reported that drinking water sampled in Muzaffargarh, Pakistan, reached up to 906 $\mu g\ L^{-1}$ As and that in 58% of samples > 10 $\mu g\ L^{-1}$ As were found

Lodhi *et al*, (2003) investigated the assessment of heavy metals in drinking water of Skardu, Pakistan, followed the order Zn > Fe > Ni > Pb > Co > Cu > Cr but no survey regarding the portability of water has been conducted in the past

It has been reported that the water quality of main cities such as Sialkot, Gujarat, Faisal Abad, Karachi, Qasur, Peshawar, Lahore, Rawalpindi and Shekhupura is deteriorating because of the unchecked disposal of untreated municipal and industrial wastewater and excessive use of fertilizers and insecticides (Bhutan *et al*, 2002)

Baig *et al*, (2009) studied the heavy metals in surface and groundwater resources of Jamshoro Sindh, Pakistan Hydride generator atomic absorption spectrophotometry (HG-AAS) is employed for the determination of arsenic in water samples In most of the water samples Arsenic levels exceeded the WHO provisional guideline was due to widespread water logging from Indus river irrigation system which causes high saturation of salts in this semi-arid region and lead to enrichment of As in shallow ground water It may be concluded that originate from coal combustion at brick factories and power generation plants

2.1. CHEMICAL REMEDIATION OF WATER

Abu-El-Halawa, (2015) compared the chelating ability of aliphatic and aromatic carbamate, diethyldithiocarbamate and diphenyledithiocarbamate respectively and use as a chelators to remove Pb, Cd, Cu and Zn from polluted water Dithiocarbamates were selected because of a good binding ability and precipitate metal ions as complexes The metal removal efficiency is compared between both ligands and also compared with the efficiency of activated carbon in an adsorption process to remove the same metals The results show that the diphenyledithiocarbamate ligand was more efficient in removing the studied metals due to active binding sites of the phenyl group than the diethyldithiocarbamate analogues

Additionally, the metal removal efficiency of the diphenyledithiocarbamate ligand was more effective than using the activated carbon method

Li, Q *et al.*, (2015) reported DTC based a new carbon nanotube (CNT) composite, functionalized multi-walled CNT (DTCMWCNT), and was prepared by reaction of oxidized MWCNT with ethylene diamine and carbon disulphide The physical structure and chemical properties were characterized using FT-IR, TGA and SEM The adsorption conditions such as pH, adsorption time and initial concentration were systematically investigated The results indicated that the adsorption process matched well with the pseudo-second-order kinetic model The result indicates that the adsorption process was spontaneous and endothermic in nature DTC-MWCNT possesses adsorption capacities for Cd (II), Cu (II) and Zn (II) of 167 2,98 1,11 2mg/g, respectively, which is maximum for Cd (II) and minimum for Zn (II)

Liua *et al*, (2015) chemically modified chitosan Sr (II)-coordinated polymer with DTC groups was prepared. The adsorbent was characterized by FT-IR, XPS, SEM and nitrogen adsorption–desorption Sr (II) -IIP has regular spherical geometry and possesses a larger surface area, pore volume and average pore diameter as compared to those of chitosan. Batch adsorption experiments were performed to evaluate the adsorption conditions and selectivity The results showed that the maximum static adsorption capacity of Sr (II)-IIP for Sr (II) was 86 66 mg g1 at 45^{0}C which was larger than many other adsorbents The experimental data were in good agreement with pseudo-second-order and Langmuir isotherm model A continuous fixed-bed column study on Sr (II)-IIP showed that the adsorption capacity increased with increasing influent concentration, but decreased with increasing bed depth, flow rate and temperature Sr (II) -IIP was regenerated and found to be suitable for reuse in successive adsorption–desorption cycles seven times without significant loss of adsorption capacity, which showed that this novel adsorbent could be employed as an effective material for the selective removal of Sr (II) from aqueous solution

Xiang *et al*, (2015) work on three types of DTCs modified starch derivatives comprising DTC starch (DTCS), DTC enzymolysis starch (DTCES) and DTC mesoporous starch (DTCMS) were prepared, which showed the significant heavy metal adsorption potential The descending order of these three DTC modified starch derivatives on the basis of absorption was DTCMS > DTCES > DTCS An individual heavy metal removal from aqueous solution were the following decreasing order Cu (II) > Ni (II) > Cr (VI) > Zn (II) > Pb (II) The chelating between DTC ligands and heavy metal ions the through the pH effect measurements proved kinetics and mechanism of heavy metals The adsorption kinetics of Cu (II) on starch derivatives were found to follow the pseudo-second-order model Additionally, the adsorption potential of these three DTC modified starch derivatives were identical result in the presence and absence of EDTA

Giridhar *et al*, (2014) synthesized two new ligands, ammonium 2, 6- dimethyl morpholine dithiocarbamate (ADMM-DTC) and ammonium 3-methyl piperdine dithiocarbamate (AMP-DTC) The chelation of Co (II) and ADMM-DTC/AMP-DTC take in the presence of NaOH at pH 7 2 and 8 2 to produce catalytic hydrogen currents at -1 28 V and -1 38 V vs SCE respectively and prior detected by D C polarography Optimum polarographic conditions were documented by changing pH, holdup electrolyte (NH_4Cl), chelating agent & metal ion concentrations and influence of opposing ions on peak height to increase the sensitivity, selectivity and detection limits of the present method This technique is effectively used for the detection of Co (II) in different media with recoveries ranging from 93- 98 % and gives identical results with the differential pulse polarography (DPP)

Tavares, (2014) studied DTC functionalized groups based on silica and silica coated magnetite for the absorption of mercury The sorption condition including degree of functionalization, sorption time, sorbent dose, and initial Hg (II) concentration evaluated removal capacity of the synthesized materials were evaluated systematically checked by changing various factors Removal proficiencies up to 99 6-99 9% were attained, irrespective of dose, substrate and amount of functionalization in 8–24 h The original concentration of Hg was reduced by all the sorbent, taking the benefit of magnetic separation in the case silica coated magnetite applied by external field The strong binding between metals and DTC was indorsed by the removal of Hg from water

Shaaban *et al*, (2013) reported chelating resin (DTMAN) containing DTC group was synthesized by copolymerization of acrylonitrile with N,N^0-methylenebisacrylamide, and the obtained resin was subsequently treated with ethylene diamine and carbon disulphide, respectively The prepared chelating resin was characterized using FT-IR, SEM, (TGA) The kinetic and thermodynamic parameters showed that the adsorption process is spontaneous and followed the pseudo-second-order kinetics Additionally, using fixed bed column the absorption of metals by chelating resins was studied The study indicated that resins can use again and again up to five times with small reduction in removal In batch type technique different condition like pH, concentration of metal ions, temperature, and adsorption time were investigated High affinity toward Hg (II), Cd (II) and Pb (II) ions towards indicating by chelating resins The maximum sorption capacities for Hg (II), Cd (II) and Pb (II) were found to be 2 3, 1 94 and 1 14 mmol g^1 resin, respectively

Venkatesan *et al*, (2013) studied the extraction of Co (II) ion from aqueous solution using silica gel grafted with DTC ligand (Si–dtc) The ligands was prepared by reacting silica gel with amino propyltriethoxysilane followed by alkaline carbon disulfide NMR, IR spectra were taken to establish the attaching of DTC ligand on silica gel This modified surface contains 0 37 mmol g^{-1} of the ligand sites available for the extraction of Co The sorbent extracts Co only when the pH of the aqueous phase is above 7 and the extraction process does not follow ideal ion-exchange mechanism The electronic absorption spectra of Co present in the sorbent phase suggested the oxidation of Co (II) to Co (III) Kinetic data were fitted to surface complexation model and the rate constant (ks) for such model was found to vary from $1\ 5\times10^{-3}$ to $5\ 82\times10-3$ 1 mg^{-1} min^{-1} depending on the initial concentration of Co

Ullmann, (2013) reported an Advanced biodegradable and non-toxic organic chelators, which are soluble in organic media, were synthesized on the basis of the S,S-ethylene diamine-disuccinate (S,S-EDDS) ligand The new ligands were used for the simultaneous removal of both heavy metals and organic pollutants from contaminated soils, sediments or sludge The new chelators were designed to bind various target metal ions, to promote the extraction of these ions into organic solvents The results for one of them, N, -bis-dodecyl-S,S-EDDS (C24-EDDS), showed that the metal-ligand complexes were concentrated in the organic-rich phase in the Phase Transition Extraction process (more than 80%) The extraction of five toxic metals, namely, Cd, Cu Ni, Pb and Zn was examined In general, the extraction performance of the new ligand was not less than that of S, S-EDDS when a sufficient ligand-to-extracted ion ratio about 4 1 was applied

According to **Ahmad** *et al*, (2012) studied the adsorption of heavy metal ions in a continuous flow column having calcium carbonate as adsorbent was carried at laboratory scale The aqueous solutions of heavy metal passed through a column having a bed of precipitated CaCO3 The concentration of each metal was determined by atomic absorption spectrometer before and after treatment The major decrease in the concentration of all metal ions was observed after treatment The initial concentration of metals such as Zn^{2+} Cr^{3+}, Pb^{2+},

Cd^{2+}, Cu^{2-} and Fe^{3+} were 195, 156, 621, 342, 190 and 168 mg/L which were reduced up to the level of 0 0089, 0 1390, 0 3510, 0 0390, 0 0242 and 0 3397 mg/L, respectively in treated samples This significant removal of heavy metal ions indicates a remarkable efficiency of calcium carbonate as an adsorbent The adsorption capacity of calcium carbonate was calculated, which were found 400-1500 mg/g, while the effect of initial metal ion concentrations on the adsorption process was not pronounced It is concluded that this treatment method may hold good in order to reduce metal ion concentration in industrial effluents

Bajia, (2013) studied 2-aminnopyradinedithiocarbamates ligands for the fast, ordinary and consistent spectroscopic technique for the determination of metal cations by HPLC The method is based on the formation of stable colored DTC complexes by reaction metal salt and DTC ligands, which is then extracted methanol and separated by acetonitrile water mobile phase The different analytical parameters affecting the method such as pH for extraction, solvent for extraction, mobile phase and type of the column After the column elution the sample was allowed to pass into UV detector and then into ICP-MS The separate data have been observed from UV detector and ICP- MS for each sample and then from the help of both results the identification and determination of these complexes have been done The developed method was compared with other spectroscopic methods, no significant difference was observed

Liu Bingjie, (2013) synthesized bio-based Zr (IV) filled DTC modified chitosan beads (Zr-DMCB) for the removal of fluoride ions from aqueous solutions Batch adsorption experiments were performed to evaluate the adsorption conditions, selectivity and reusability The results showed that the saturation adsorption capacity was 4 58 mg/g at pH 7 0, 30°C for 40 min The adsorption kinetic data were fitted with pseudo-second-order model The maximum adsorption capacity calculated from was 7 78 mg/g The adsorption capacity of Zr-DMCB for F was significantly affected by co-anions The adsorption mechanism of Zr-DMCB for F was characterized by FTIR, SEM and EDX analysis The results above indicated that Zr-DMCB is a very promising bio sorbent for the removal of F from aqueous solutions

Jing , (2009) reported the N,Ndi(carboxymethyl)dithiocarbamate chelating resin (PSDC) was synthesized by attaching the chelating agent of N,N-di (carboxymethyl) dithiocarbamate to the chloromethylated PS-DVB (Cl-PS-DVB) matrix, as a new adsorbent for removing divalent heavy metal ions from waste-stream The physicochemical structures were characterized using FT-IR, elemental analysis (EA), and were further morphologically characterized using BET and BJH methods The adsorption performances of PSDC towards heavy metals such as Cu (II), Pb (II) and Ni (II) were systematically investigated In the above target, the classic batch adsorption experiments were conducted to explore the kinetics and isotherms of the removal processes with pH-value initial concentration, temperature, and contact time as the controlling parameters The strong affinity of PSDC toward these target soft acids could be well demonstrated with the electrostatic attraction and chelating interaction caused by IDA moiety and sulphur which were namely soft bases on the concept of hard and soft acids and bases (HASB) Thermodynamic parameters, involving H°, S° and G° were also calculated from graphical interpretation of the experimental data The standard heats of adsorption (H°) were found to be endothermic and the entropy change values (S°) were calculated to be positive for the adsorption of Cu (II), Pb (II) and Ni (II) ions into the tested adsorbents Negative values of G° indicated that adsorption processes for all tested metal ions onto PSDC were spontaneous

Fu *et al* , (2007) employed DTC-type supramolecular heavy metal precipitants, N,N^{0}-bis-(dithiocarboxy) piperazine (BDP) and 1, 3, 5- hexa hydrotriazinedithiocarbamate

(HTDC) in treating complex heavy metal wastewater Results indicated that both BDP and HTDC could effectively reduce heavy metal ions in wastewater to much lower than 0 5 mg/L

An efficient and water-soluble (102 g/kg at 293 K) heavy metals capturing agent was developed for removal of Cu in ethylene diamine tetra acetic acid–Cu (EDTA–Cu) wastewater The carbon disulphide react hydrazine hydrate to from the heavy metals extracting agents, which is named as Tetrathiobicarbamic Acid ($C_2H_4N_2S_4$) comprises DTC groups and was named DTC–TBA for short The structure was verified by IR, UV, NMR and elemental analysis From the batch jar experiment for treatment of simulated EDTA–Cu wastewater with DTC–TBA, dosage, pH, reaction time, and temperature on Cu^{2+} removal efficiency was investigated The optimized condition was pH of 3–5, molar ratio of DTC–TBA/Cu of 1 2 1, reaction time of 3 min, and PAM dosage of 2–6 mg/L With initial concentration of 100–1000 the removal efficiency of Cu^{2+} was greater than 99% mg/L, and the maximum adsorption capability with DTC–TBA towards Cu^{2+} was 287 05 mg/g Treatment of actual EDTA–Cu wastewater showed that DTC–TBA was an efficient and average concentration of residential Cu^{2+} was 0 372 mg/L These results indicated that DTC–TBA was stable in acidic condition and promising for application even when the pH was below 3 Cu^{2+} was replaced by DTC–TBA at a stoichiometric ratio from EDTA–Cu Thermodynamic parameters, were also calculated to prove the adsorption process being exothermic and spontaneous (Zhen *et al* , 2012)

Odeh *et al* , (2012) reported three polymers with N-ethanolamino-, N-benzylamino-, and N-t-butylamino-dithiocarbamate groups were synthesized from polyvinylbenzylchloride Each of the three polymers was integrated in a hydrogel membrane (PVA) cross-linked with glutaraldehyde to form a sensing element The latter was then, evaluated for its optical sensing behavior by subjecting it to varying concentrations (1 0x10-5 up to 0 1 M) of metal ions (Zn2+, Cd2+, Pb2+, Hg2+, Ca2+, Mg2+, K+, Na+, Cr3+, Ni2+, Cu2+) Significant response was observed for the Hg^{2+} ions while the others showed negligible or no response The turbidity absorbance increased consecutively from the DTC polymer derived from N-t-butylamine towards that from ethanolamine as the concentration of the Hg2+ solution increased The response time measured for the three polymer microspheres ranged between 2 and 30 minutes The aminodithiocarbamate polymers were stable at normal temperatures (25o - 40 o C) and at pH was changed between 2 and 7 In addition, the polymers demonstrated excellent stability with time and a capacity of 3 967, 3 787, 3 355 mmol Hg2+ ions per gram of polymer for the N-ethanolamino- N-benzylamino-, and N-t-butylamino-dithiocarbamate respectively SEM and Eds analyses showed an increase in size of about 25% in the case of complexation with N-ethanolamino-, no size change with N-benzylamino-, and a 16 6% decrease in size with N-t- butylamino-dithiocarbamate

Khan *et al*, (2011) studied the modified DTC biopolymer and used for the removal of heavy metals like Pb, Cu and Cd The batch type experiments indicated that the removal capacities were 2 24, 1 14 and 0 84 mmol/g for the divalent for the Pb, Cu and Cd respectively Maximum removal capacities were observed for Pb

Say *et al*, (2005) reported the DTC-anchored polymer/organosmectite composites were prepared for the remediation of heavy metal ions like Pb, Cd and Cr from aqueous media containing different amounts of these ions (50–750 ppm) and at different pH values (2 0–8 0) Then, modified smectite nanocomposites were reacted with carbondisulfide, in order to incorporate DTC functional groups into the nanolayer of organoclay Initially, the modification of the natural smectite minerals was performed by treatment with quartamin styrene and chloromethylstyrene The DTC-anchored nano-composites have been characterized by FTIR and used in the adsorption–desorption process The maximum adsorptions of heavy metal ions onto the DTC-anchored polymer/organosmectite composites from their solution was 170 7 mg g^{-1} for Pb(II), 82 2 mg g^{-1} for Cd(II) and 71 1 mg g for Cr(III) Competition between heavy metal ions (in the case of adsorption from the mixture) yielded adsorption capacities of 70 4 mg g^{-1} for Pb (II), 31 8 mg g^{-1} for Cd (II) and 20 3 mg g^{-1} for Cr (III) Desorption of the heavy metal ions from composite was studied in 0 5 M NaCl and very high desorption rates, greater than 93%, were achieved in all cases Adsorption–desorption cycles showed the feasibility of repeated uses of this nanocomposite

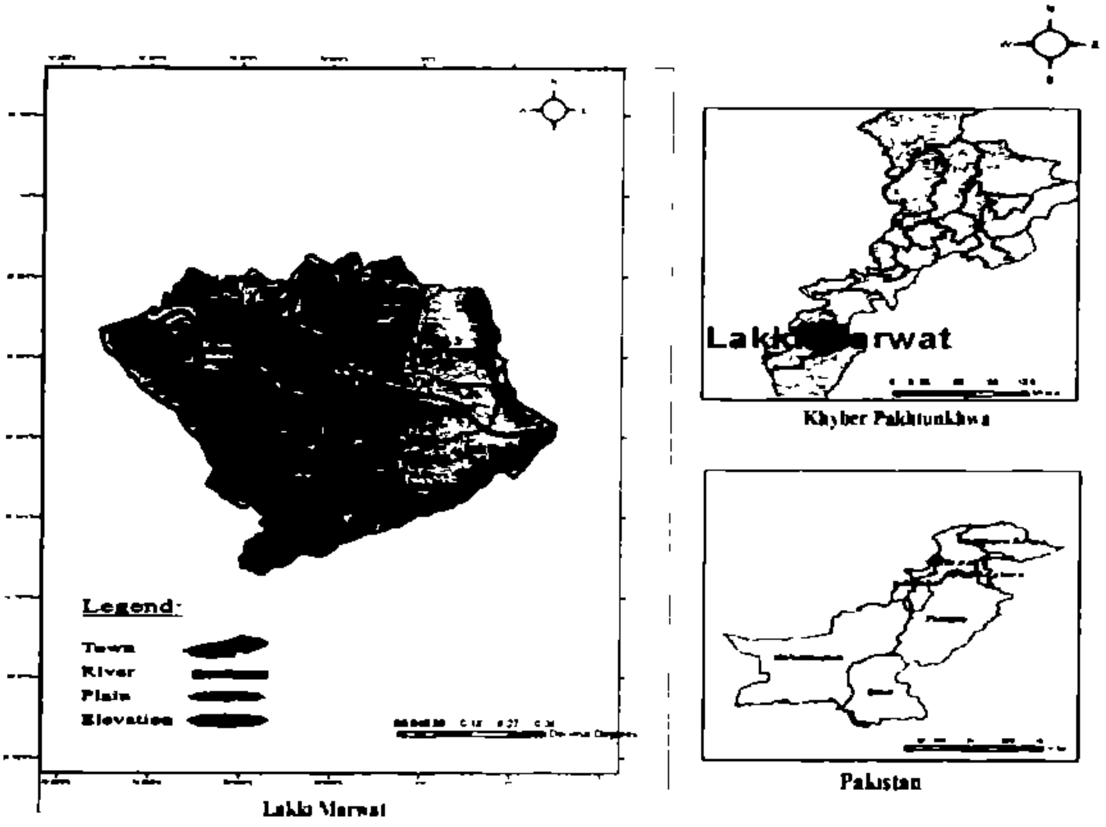
Todorovic *et al*, (2002) used 4-morpholine dithiocarbamate for the determination of trace metals in natural waters and model samples with standard metals concentrations The formed complexes were removed with chloroform The designed scheme was efficiently used for the determination of trace metals concentration in the water of, Barje, lake, Leskovac, Yugoslavia

3.1. STUDY AREA

Lakki Marwat is located in the southern part of the Khyber Pakhtunkhwa province of Pakistan It is located 32161N and 70191E at an elevation of 200–1000 m above sea level It covers a semi-arid region with an area of 3164 km^2 in which approximately 116,900 ha is cultivated The whole area is like a basin, the central area is comprised of a sandy plain surrounded by hills The central river is the Kurram River that runs from North Waziristan agency to the southeast in the Lakki Marwat and discharge to the Indus River in the south of Isa Khel in the province of Punjab The main tributary of the Kurram River is the Gambila River The gram, wheat, maize, sugarcane and vegetable are the main crops Fruits include melons, watermelons and dates (Khan *et al* , 2013)

The geology of the area covered a dense blanket of alluvial plain, containing unconsolidated, quaternary deposits, silt, gravels and sand This plain is bounded by an accumulation of the sandstone, clay and carbonates The main contents of foothills are loose sarsens of the sandstone of different shapes and sizes These are separated from the higher ranges by the daily change of temperature and eroded to the plain by the streams The talus is of variable size and shape and is dominantly sand and arenaceous in composition (Ullah *et al* , 2014)

The climate of the study area is semi-arid and 24 2 °C is the average annual temperature In the month of May and June sand storms temper in the whole area with regular intervals The annual average humidity in 2013 was 29% Nearly 326 mm is the annual rainfall in which most precipitation falls in August, with an average of 74 mm The November is the driest month, with 3 mm of rainfall Effective rain is the only hope for the farmers Tube wells and lift irrigation systems also irrigate a small portion of the land In the entire area very rare natural surface water resources are found while partial pinches with partial potentials of fresh groundwater is available The suitability of water for irrigation is determined not only by the total amount of salt present but also by the kinds of salt (Khan *et al* , 2013,Ullah et al 2014)



Lakki Marwat

Khyber Pakhtunkhwa

Pakistan

Figure 1 Map of Lakki Marwat (Ullah *et al.*, 2014)

3 2 SAMPLE COLLECTION AND PRE-TREATMENT

The ground water sample of tube wells were collected from 25 main town and villages of district Lakki Marwat The samples from local government water supply were also collected For a sampling of underground water standard sampling technique were used for the collection of water samples Specific safety procedures were used during water sampling, which are recommended by APHA (1998) Water sources were purged over for 10 minutes before taking the sample in the sample bottle Well stoppered clean polyethylene bottles were used for the collection of water samples All the sampling bottles were soaked in 10% nitric acid for 24 hour and rinsed with ultrapure water before the sampling (Arain *et al*, 2008, Korai *et al*, 2010) For heavy metals assessment, the samples were filtered from 0 45 µm Whattman filter paper and added 2ml/liter 10% HNO_3 as a preservative for heavy metals to bring the pH < 2 All the sample bottles were labeled properly and insulated cooler having ice packs were used for storing the water samples and delivered on the same day to laboratory All samples were stored in the laboratory at 4 °C until processing and analysis

3.3 PHYSICOCHEMIC AL ANALYSIS

3.3.1. Chemicals and Reagents

All the chemicals and reagents of analytical grade with percent purity more than 99% were used Carbon disulfide (99 5%) was supplied by Riedel-deHaen Dibutylamine (99%), cyclohexylamine, Perchloric acid and sodium hydroxide were obtained from Fluka Double distilled water was used throughout analytical work The standard solutions of all heavy metals were prepared by dilution of 1000 ml certified standard solution of corresponding metal ions During experimental work, all the glassware were washed with detergent, de-ionized water, soaked in HNO_3 (30%) and rinsed with double distilled water three times and electric drying cabin was used for drying

3.3.2. Analytical procedure

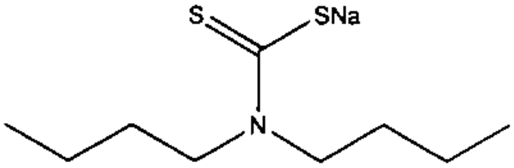
Physicochemical parameters like DO, total dissolved salts (TDS), pH, electrical conductance and turbidity were measured at the sampling sites by using Real Time data Logger multi-meter 9(YK-2005WA) The turbidity was measured by TN-100 turbidity meter (Eutech instruments) DO was measured by YK22 DO meter All instruments were calibrated by using a standard solution and procedure before taking the reading

Determination of Cu, Fe, Cd, Cr, Ni, Mn, Zn, Co, Pb, was carried out by using Perkin-Elmer 400 model flame Atomic Absorption Spectrometer All the stock solutions were prepared with de- ionized water

3.4. SYNTHESIS OF LIGANDS

3.4.1. Synthesis of Dibutylcarbamate.

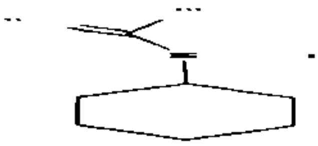
Sodium dibutyldithiocarbamate salt was prepared according to the reported methods with modification that methanol was used as solvent 0 05 M NaOH solution was prepared by dissolving 2 g of NaOH in 1000 ml of distilled water and mixed with 5 19 mL of dibutylamine $(C_4H_9)_2NH_2$ in a round-bottom flask The mixture was stirred for several minutes using a magnetic stirrer, and 3 5 mL of a carbon disulfide (CS_2) solution was added to the mixture drop wise until a pale yellow color appeared The mixture was then stirred for 2 hour and heated to evaporate the as much water as possible The mixture was left to cool at room temperature for 24 hour, and yellowish-white crystals precipitated The precipitate was washed with a 3 1 mixture of diethyl ether and ethanol and then air dried (Venugopal *et al* 2015)



sodium dibutylcarbamodithioate

3.4.2. Synthesis of Cyclohexyldithiocarbamate

In a clean beaker 0.1 moles of Cyclohexanamine dissolved in 20ml of absolute methanol and placed in an ice bath. 10 ml of sodium hydroxide (0.05 M) was added and 6.04 ml of carbondisulphide was added in a drop wise using separating funnel. All the reagent was stirred for 2 hour. After that precipitates of salt of sodium dithiocarbamate was separated, the mixture was left to cool at room temperature for 24 hour, and white crystals precipitated. The precipitate was washed with a 3:1 mixture of diethyl ether and ethanol and then air dried which was dried in open air and then desiccator. (Venugopal *et al* 2015)



Cyclohexy dithiocabamate

3.5. CHEMICAL REMEDIATION

3.5.1 Removal of Heavy Metals from Aqueous Solution by the treatment of Dithiocarbamate

The metal solutions of appropriate concentrations were prepared by diluting the reference solution of 1000 ppm. The pH of the metal solution was determined using a pH meter and was adjusted using drops of 1 M Perchloric acid ($HClO_4$) or 1 M NaOH. A total of 50 ml of metal solution at the required concentration was placed in a flask, and the 0.1g of dibutyldithiocarbamate (DBC) ligand was added to each flask, and the same process was repeated for the cyclohexyldithiocarbamate After precipitation, the precipitates were filtered and the filtrate was analyzed using an Atomic Absorption Spectrophotometer

A blank sample was prepared for each metal solution in the absence of ligand and at the same pH to confirm the initial concentration Afterwards, the average removals of the selected metals from their solutions were studied by observing the decrease in concentration using an atomic absorption flame spectrophotometer The samples were shaken properly before the measurement process to ensure the uniformity of the contents

Complex formation occurred depended on the factor of time (in which efficiency is directly proportional to time) For this reason, we maintained equal time periods of 6 hours for both ligand, which the maximum time for complex formation Then compared the quantity of the percent metal removal in this case with the quantity removed when using Cyclohexyldithiocarbamate ligand

3.6. INFRARED (FTIR) SPECTRUM ANALYSIS

Potassium bromide and DTC were mixed by mass ratio of 1 99, and pressed into the specific die to form thin pellets, which were scanned from 4000–400 cm^1 with Perkin Infrared spectrometer For the determination of functional group the data were analysed with Omnic analysis software

3.7. STATISTICAL ANALYSIS

To assess the analytical relationship between heavy metal concentrations and sampling site, the study area was divided into two groups One group comprises the plain area while the other was the mountainous region, two-way ANOVA test was used for the comparison between the mean of the two groups while t test was used for the comparison between the % remediation by two dithiocarbamates

CHAPTER 4

RESULTS AND DISSCUSSION

Numerous physicochemical properties were analysed to investigate the quality of the collected water sample according to the WHO (2008) guideline for drinking water Mean value and standard deviation of concerned parameters of all water samples from different sites located in Lakki Marwat are given in Table 1

Table I Results of physical parameters and heavy metals

Parameters Analysed WHO		**pH 6.5-8.5**		**EC 1000 µ s/cm**		**TDS 1000 mg/L**		**Turbidity 5 00 NTU**		**DO 110 %**	
Site Code	Sample location	**mean**	**std**	**Mean**	**Std**	**mean**	**std**	**Mean**	**Std**	**Mean**	**Std**
ST01	Darra e pezu	7 23	0 05	496 6	47 35	497	38 97	0 716	0 517	85 36	2 386
ST02	Chunda	7 5	0 2	560 3	78 35	565 3	75 83	0 843	0 075	85 5	1 4
ST03	Titer khel	7 4	0 1	560 3	55 5	753 3	25 23	0 24	0 115	84 56	1 950
ST04	Shahbaz khel	7 13	0 15	1120	70	753 3	55 53	0 33	0 137	85 46	0 901
ST05	Ghazni khel	7 2	0 2	303	30 5	576 3	95 02	0 656	0 090	83 7	0 264
ST06	Tajazi	7 23	0 25	286 6	5 7	473 6	14 84	0 293	0 161	73 13	3 265
ST07	Sarai gambella	7 6	0 2	856 6	15 2	700 3	30 00	0 173	0 015	72 5	0 793
ST08	Gandi khan khel	7 33	0 25	1233 3	20 8	643 6	15 17	0 633	0 066	82 2	0 360
ST09	Sarai Naurang	7 8	0 2	1277	395 1	516	14 79	0 473	0 359	86 33	2 159
ST10	Landiwa	7 23	0 115	1313 3	35 1	491	84 66	1 443	0 723	76 6	5 741
ST11	Manjewalla	7 4	0 2	560	30	604 3	91 90	1 583	0 751	73 13	5 559
ST12	Pahar khel	7 3	0 2	756 6	20 81	771 6	14 79	1 343	0 582	69 9	1 777
ST13	Lakki city	7 26	0 208	626 3	75 3	412 6	62 56	0 356	0 325	86 73	1 379
ST14	Dallo khel	7 16	0 208	803 6	82 7	601 3	65 04	0 95	0 03	84 73	3 789
ST15	Aba khel	7 2	0 2	710 3	105 3	494 6	8 50	2 785	0 473	85 9	2 523
ST16	Bagu khel	7 33	0 251	590	26 4	452	64 86	1 41	0 614	80 33	1 357
ST17	Isak khel	7 53	0 404	643 3	49 3	600 6	10 06	0 536	0 261	83 46	1 159
ST18	Langer khel	7 3	0 3	780 3	30	532 6	11 23	0 86	0 209	72 96	1 527
ST19	Wanda Ameer	7 2	0 2	667 3	90 8	879 6	16 50	0 383	0 178	70 2	4 430
ST20	Machan khel	7 1	0 1	587	55 1	539	17 52	1 636	1 037	68 96	1 401
ST21	Tajori	7 2	0 1	717	124 5	419 6	27 79	1 18	0 289	75 13	2 800
ST22	Chuki jand	7 2	0 2	738 3	186 4	775	30 51	0 416	0 241	80 56	0 850
ST23	Kachi kamer	7 2	0 2	827	15 3	566	77 65	1 24	0 385	76 23	0 450
ST24	Darra tang	7 4	0 1	582 3	39 2	561 6	8 621	1 686	0 380	76 96	1 721
ST25	Qabul khel	7 43	0 20	861 6	24 6	539	168 6	1 303	1 055	78 13	1 814
Maximum		**7 8**		**1313.3**		**879 6**		**2 78**		**86.7**	
Minimum		**7.1**		**286 6**		**412 6**		**0 17**		**68 9**	
P value (ANOVA)		**0.9**		**0.7**		**0.6**		**0 4**		**0.6**	

4.1. PHYSICOCHEMICAL ANALYSIS

4.1.1. pH values in water samples

The mean pH values ranged from7 1 to7 8 The pH values greater than 7, makes the drinking water slightly alkaline The result shows slightly alkaline water in the study area Although the maximum permissible level of pH of 6 5 to 8 5 recommended by the WHO (2008) for drinking water standard (Jain *et al* , 2005) According to ANOVA, the results are not significant as the p > 0 05

pH is one of the major parameters in the evaluating of drinking water quality Even, pH has no straight relation with adverse effect on human health, but indirectly changing the water quality It indicates the pathogen in the drinking water and dissolution of metal ion High pH values were responsible for the somewhat bitter taste of drinking water and can change the aesthetic parameters of water

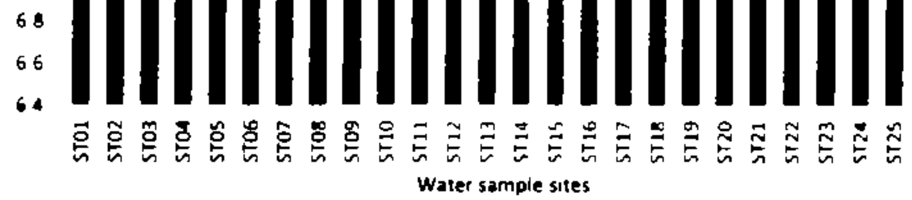


Figure 2 pH of drinking water samples collected from district Lakki Marwat

4.1.2. Conductivity in water samples

The mean value of EC measured in the water samples varied from 286 6 µs/cm to 1170 µs/cm According to WHO (2008) the recommended value of EC is 1000 µs/cm (Qadir *et al*, 2009) The mean levels of EC in four water samples sites ST04, ST08, ST09, and ST10 exceed than WHO levels For the EC the value of p =0 7 which is greater than 0 05 showing that there is no significant difference between the mean of the two groups

EC is in fact the degree of the concentration of the ions in the water, its value directly indicates the concentration of mineral salts dissolved in the water Kumar *et al* (2010) proposed that EC can be used for the assessment of water quality of the study area and it may use in water quality management of the other study areas

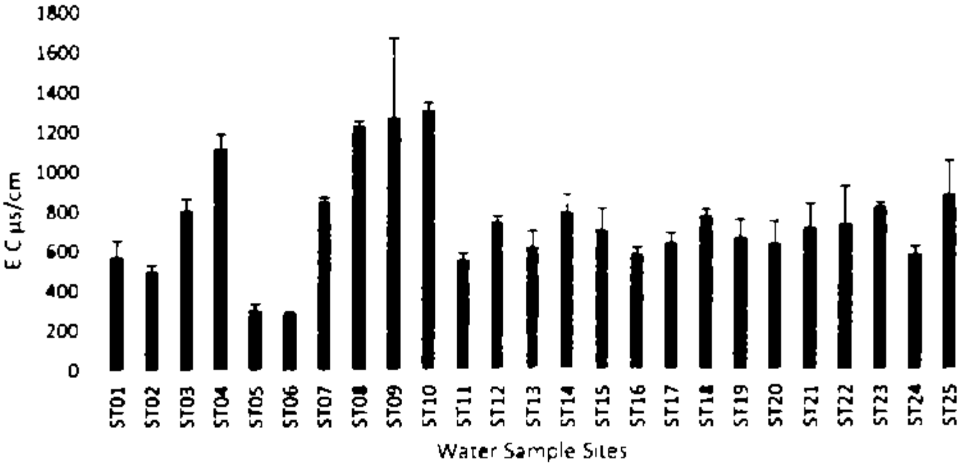


Figure 3 EC of drinking water samples collected from district Lakki Marwat

4.1.3. Total dissolved solids (TDS) in water samples

The maximum mean TDS value of 879 6 mg L^{-1} was recorded in the ST21, while the mean minimum value of 412 6 mgL^{-1} was recorded in the ST13 As the maximum value was below than permissible limits (1000 mg/L) set by WHO (2008), which means that TDS in all water sample sites were in safe limits. ANOVA showed no significant difference between the means of the two groups.

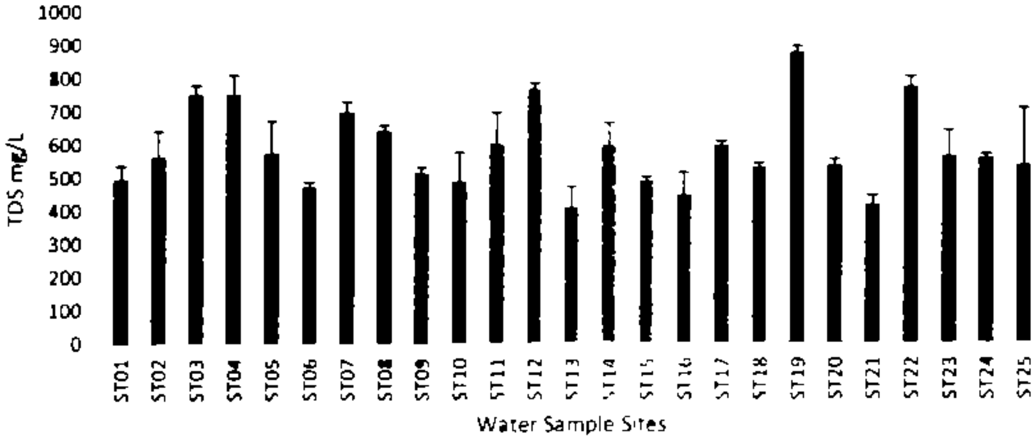


Figure 4 TDS of drinking water samples collected from district Lakki Marwat

4.1.4. Turbidity in water samples

The mean turbidity in water samples varied from 0.017 NTU to 2.78 NTU. The maximum turbidity was calculated at abba khel in sample site ST16. In all water samples the mean turbidity level was lower than the WHO (2008) ermissible level. The p value for turbidity were greater than 0.05, which is non-significant.

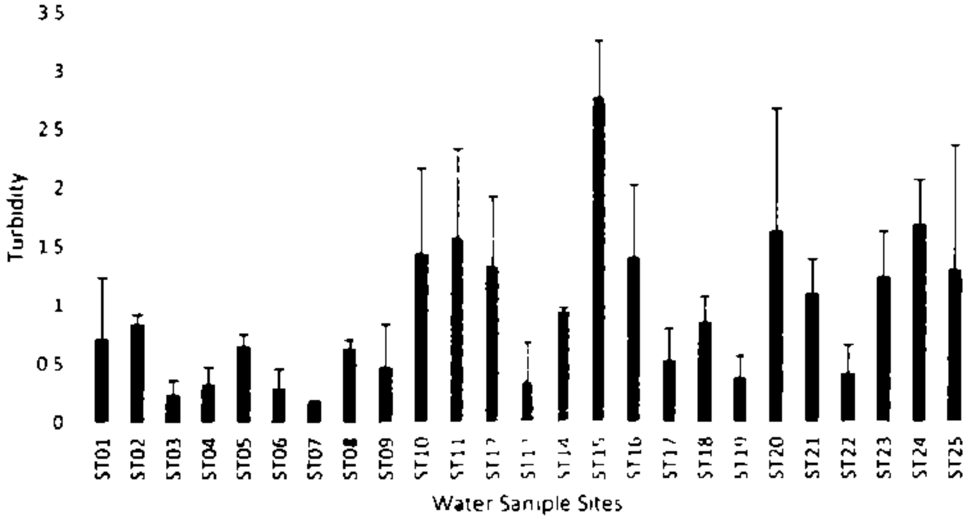


Figure 5 Turbidity of drinking water samples collected from district Lakki Marwat

4.1.5 Dissolved Oxygen in water samples

DO in water samples ranged with mean value from 68 9% to 86 7 % while the maximum permissible level is 110% The results indicated that neither of the sample has higher levels of DO than permissible limits The two way ANOVA showed the p value for DO was 0 6 which is greater than 0 05 and non-significant

In the drinking water quality assessment, the DO plays a vital role Its relationship with water body gives important information, e g photosynthesis, bacteriological activity, Stratification, availability of nutrients, etc (Vikal, 2009)

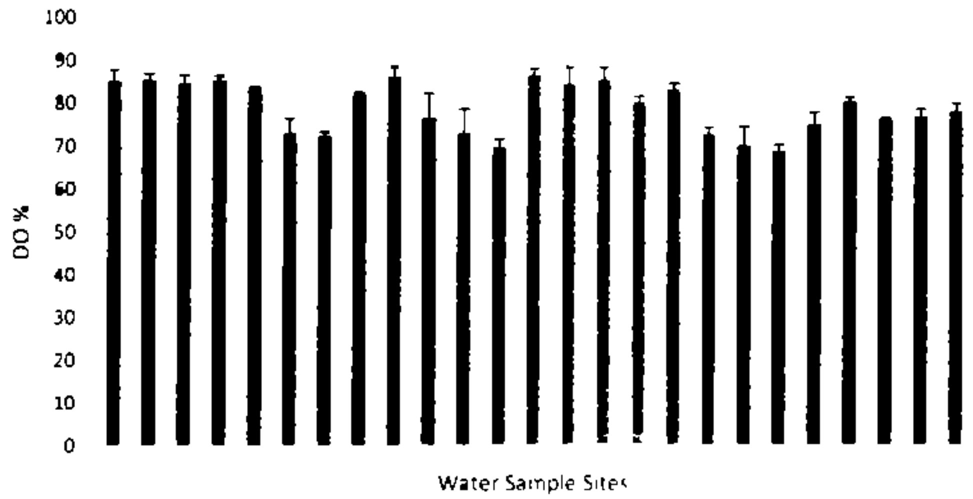


Figure 6 DO in drinking water samples collected from district Lakki Marwat

4.2. HEAVY METALS ANALYSIS

The concentration of nine heavy metals i e Zn, Fe, Cu, Cr, Ni, Pb, Co, Mn, Cd detected in all drinking water sample sites are shown in Table 2 and table 3

Table 2 Concentrations (ppm) of Heavy metals in water samples

Parameters Analysed WHO Limits		Zn(ppm) 3.0		Fe (ppm) 0.3		Cu (ppm) 2.0		Cr (pppm) 0.05	
Site Code	Site name	mean	Std	mean	std	Mean	Std	Mean	Std
ST01	Darra e pezu	0.415	0.048	0.084	0.029	0.0517	0.0096	0.025	0.0133
ST02	Chunda	0.454	0.023	0.077	0.017	0.035	0.0065	0.034	0.0075
ST03	Titer khel	0.386	0.034	0.211	0.011	0.051	0.021	0.043	0.0075
ST04	Shahbaz khel	0.173	0.050	0.122	0.022	0.028	0.0036	0.054	0.0061
ST05	Ghazni khel	BD	-	0.028	0.010	BD	-	BD	-
ST06	Tajazi	0.066	0.020	0.035	0.009	BD	-	BD	-
ST07	Sarai gambella	0.077	0.021	0.113	0.014	0.004	0.0037	0.012	0.0035
ST08	Gandi khan khel	0.012	0.005	0.073	0.017	0.016	0.009	0.022	0.0055
ST09	Sarai Naurang	0.097	0.064	0.087	0.057	0.017	0.0111	0.024	0.007
ST10	Landiwa	0.009	0.007	0.107	0.089	0.024	0.0211	0.031	0.0075
ST11	Manjewalla	0.005	0.002	0.136	0.039	0.014	0.0085	0.0003	0.0005
ST12	Pahar khel	0.037	0.004	0.165	0.031	0.005	0.001528	BD	-
ST13	Lakki city	0.068	0.050	0.161	0.071	0.010	0.0106	0.0223	0.0195
ST14	Dallo khel	0.019	0.023	BD	-	0.021	0.0025	0.0333	0.002
ST15	Aba khel	BD	-	BD	-	0.022	0.005	0.02333	0.0075
ST16	Bagu khel	0.0036	0.006	0.001	0.002	0.015	0.003	0.01433	0.007
ST17	Isak khel		0.003	1.799	1.027	0.034	0.0095	BD	-
ST18	Langer khel	0.0853	0.010	0.057	0.008	0.021	0.006	0.014	0.00854
ST19	Wanda AmeerS	BD	-	0.050	0.002	0.019	0.008	0.00033	0.00057
ST20	Machan Khel	0.0616	0.018	BD	-	0.004	0.0036	0.0016	0.00057
ST21	Tajori	1.538	0.103	0.002	0.003	0.028	0.0085	0.0216	0.0095
ST22	Chuki jand	0.007	0.006	BD	-	BD	-	BD	-
ST23	Kachi kamer	0.107	0.008	0.363	0.072	0.017	0.0045	0.072	0.0095
ST24	Darra tang	0.251	0.008	0.425	0.075	0.036	0.006	0.0526	0.0125
ST25	Qabul khel	0.244	0.104	0.487	0.203	0.033	0.010	0.0443	0.0061
Maximum		**1.538**		**1.799**		**0.051**		**0.072**	
Minimum		**0.003**		**0.001**		**0.004**		**0.0003**	
P value (ANOVA)		**1×10^{-6}**		**0.7**		**0.008**		**0.0001**	

- **ST sample site code**

Table 3 Concentrations (ppm) of Heavy metals in water samples

Parameter analysed **WHO Limits**		**Ni** **(ppm)** **0.02**		**Pb** **(ppm)** **0.01**		**Co** **(ppm)** **0.04**		**Mn** **(ppm)** **0.003**		**Cd** **(ppm)** **0.003**	
Site Code	Site location	Mean	Std	mean	std	mean	Std	Mean	Std	Mean	Std
	Darra e pezu	0.076	0.005	0.366	0.057	0.079	0.012	0.046	0.0075	0.041	0.002
ST01	Chunda	0.137	0.124	0.3646	0.011	0.026	0.005	0.043	0.0058	0.0266	0.0107
ST02	Titer khel	0.135	0.088	0.306	0.013	0.046	0.0025	0.033	0.0228	0.01933	0.004
ST03	Shahbaz khel	0.013	0.004	0.4636	0.011	0.074	0.01	0.031	0.0105	0.02366	0.003
ST04	Ghazni khel	0.036	0.006	0.375	0.011	BD	-	0.003	0.001	0.003	0.001
ST05	Tajazi	0.026	0.008	0.1733	0.039	0.013	0.003	0.003	0.0035	0.006	0.002
ST06	Sarai gambella	0.028	0.007	0.1336	0.005	0.021	0.002	BD	-	BD	-
ST07	Gandi khan khel	0.018	0.005	0.4276	0.012	0.043	0.0005	BD	-	BD	-
ST08	Sarai Naurang	0.014	0.004	0.4546	0.073	0.032	0.0076	0.015	0.0037	0.00133	0.0011
ST09	Landiwa	0.026	0.017	0.2753	0.108	0.014	0.012	0.011	0.0081	0.00133	0.0011
ST10	Manjewalla	0.017	0.007	0.1313	0.002	0.043	0.0035	BD	-	0.0023	0.0025
ST11	Pahar khel	0.011	0.001	0.3383	0.013	0.044	0.003	BD	-	0.0003	0.0005
ST12	Lakki city	0.090	0.051	0.421	0.079	0.036	0.0062	0.021	0.0091	0.0033	0.0025
ST13	Dallo khel	0.034	0.021	0.3743	0.065	0.027	0.024	0.019	0.0090	0.0003	0.0005
ST14	Aba khel	0.154	0.009	0.3536	0.046	0.034	0.03	0.004	0.0054	BD	-
ST15	Bagu khel	0.136	0.009	0.143	0.029	0.025	0.004	0.012	0.0041	BD	-
ST16	Isak khel	0.085	0.008	0.3613	0.025	0.011	0.002	0.027	0.0091	0.002	0.001
ST17	Langer khel	0.07	0.007	0.4843	0.021	0.065	0.001	BD	-	0.003	0.002
ST18	Wanda Ameer	0.205	0.014	0.464	0.044	0.028	0.0011	0.000	0.0011	0.0015	0.0007
ST19	Machan khel	0.043	0.007	0.5193	0.024	0.044	0.002	0.002	0.0034	BD	-
ST20	Tajori	0.032	0.002	0.3335	0.084	0.023	0.0202	0.011	0.0079	0.002	0.001
ST21	Chuki jand	0.093	0.008	0.511	0.038	0.038	0.006	BD	-	BD	-
ST22	Kachi kamer	0.056	0.007	0.2773	0.015	0.041	0.003	0.022	0.0173	0.0133	0.0023
ST23	Darra tang	0.220	0.052	0.2716	0.042	0.064	0.029	0.036	0.0045	0.038	0.0014
ST24	Qabul khel	0.387	0.069	0.468	0.240	0.0803	0.013	0.017	0.0051	0.0443	0.0106
ST25		**0.387**		**0.519**		**0.08**		**0.046**		**0.044**	
Manimum		**0.011**		**0.131**		**0.01**		**0.002**		**0.0003**	
P value (ANOVA)		**0.0004**		**0.4**		**0.0004**		**0.0001**		**1.4×10^{9}**	

4.2.1. Zinc (Zn) in water samples

The mean value of Zn in all water samples ranged from 0 003 ppm to 1 538 ppm with the highest concentration shown in the sample ST21 The maximum permissible limits for Zn set by WHO (2008) is 3ppm The value of Zn in all the water samples found within the permissible limits set by WHO for drinking water ANOVA single factor gives p value of 1×10^{-6} which is less than 0 05 that showed significant results for Zn between the two groups

Zn is a vital heavy metals for the development of human but high consumption cause toxic effect on the health (Singh *et al* , 2006)

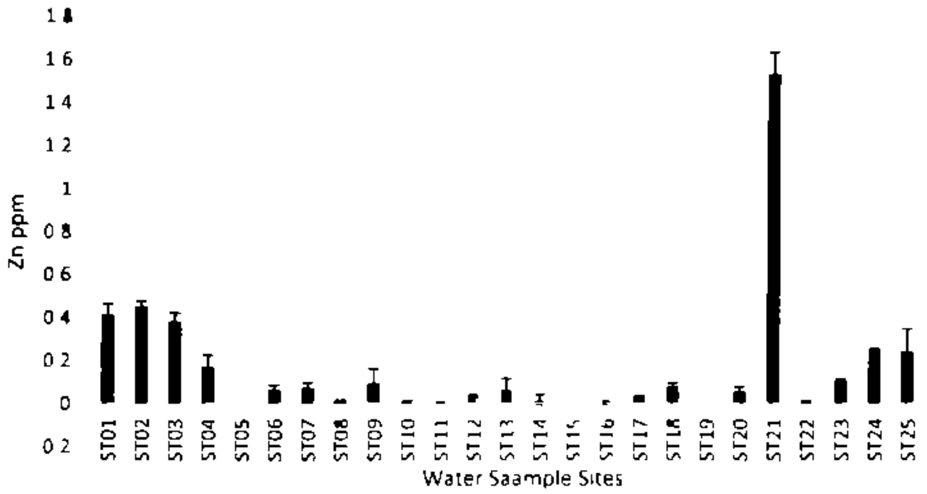


Figure 7 Zn drinking water samples collected from district Lakki Marwat

4.2.2. Iron (Fe) in water samples

The mean concentration of iron in water samples ranged from 0 001 ppm to 1 799 ppm The maximum value found in ST30 The maximum permissible level for Fe set by WHO (2008) is 0 3 ppm In the sample site ST17, the mean level of Fe exceed than permissible limits The ANOVA single factor gives the p value of 0 77 which is greater than 0 05 and gives non-significant result for the comparison the concentration of Fe in the samples of mountainous and plain area

Unexpected concentrations of Fe commonly originate inky taste, bitter and biting taste (Hassan, 2012)

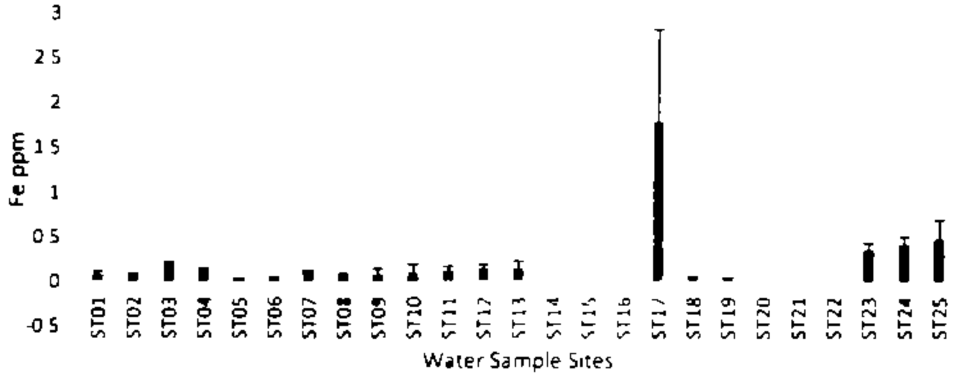


Figure 8 Fe in drinking water samples collected from district Lakki Marwat

4.2.3. Copper (Cu) in water samples

The mean level of Cu in water samples varies from 0 004 ppm to 0 0517 ppm The highest value of Cu found in the sample site ST01 The lower mean value than WHO(2008) permissible limits means that neither of the water samples was polluted by Cu ANOVA single factor gives significant results for Cu with p value of 0 008 ($p< 0\ 05$)

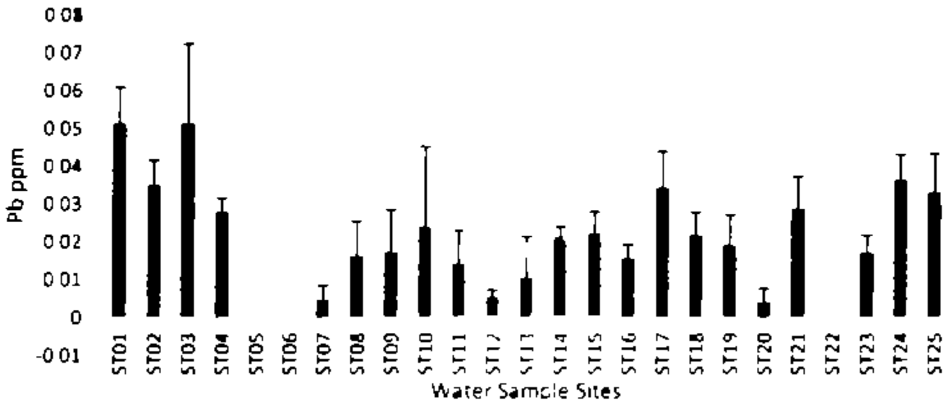


Figure 9 Cu drinking water samples collected from district Lakki Marwat

4.2.4. Chromium (Cr) in water samples

The mean concentration of Cr in water samples ranged from 0.0003 ppm and 0.072 ppm. The maximum mean concentration of 0.072 ppm was noticed in the sample ST23. The maximum permissible limit for Cr in drinking water is 0.05 ppm. In the sample sites ST4, ST23 and ST24, the Cr mean levels exceed than WHO (2008) allowable limits. Based on ANOVA single factor the p =0.0001 which is less than 0.05 and showed very significant results for Cr when compared the mean of the mountainous and plain area water samples.

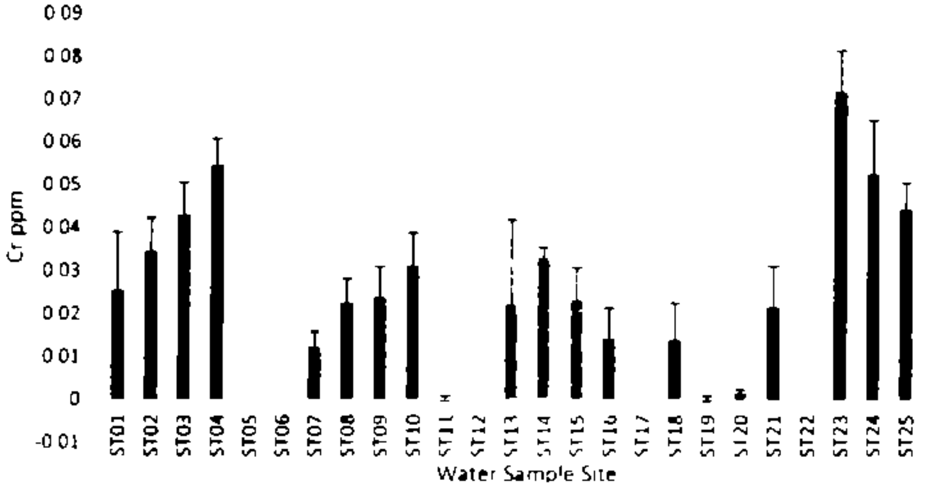


Figure 10 Cr in drinking water samples collected from district Lakki Marwat

4.2.5. Nickle (Ni) in water samples

The mean concentration of Ni in water samples varied from 0.011 ppm to 0.387 ppm. The maximum permissible concentration of nickel in drinking water allowed by WHO(2008) is 0.02ppm. The result indicated that 40 % of the sample sites have the nickel concentration beyond the WHO guidelines. The p value of 0.0004 is less than 0.05 and showed significant result that revealed that there is large difference between the means of the two groups of the water samples

The drinking water that contain nickel compound was the sources of different diseases like, kidney problem, heart problems, lung fibrosis, allergy of skin and cause cancer in the respiratory tract (Filon *et al*, 2009)

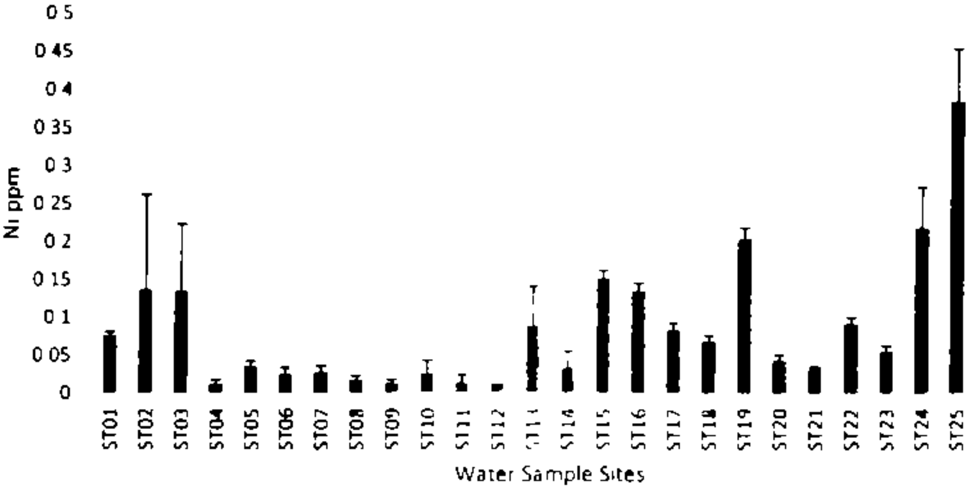


Figure 11 Ni in drinking water samples collected from district Lakki Marwat

4.2.6. Lead (Pb) in water samples

According to WHO (2008) the maximum permissible limit is 0 01 ppm for Pb concentration in drinking water, as it is a common toxicant that collects in the skeleton and there long term exposure results negative neurological effects The mean concentration of Pb in water samples was ranged from 0 131 ppm to 0 519 ppm The results indicated that Pb level in all samples exceeds the WHO maximum permissible The maximum Pb concentration of 0 519 ppm was present in the west of the study area where exploration of some radioactive element is also carried out The ANOVA single factor showed non-significant difference for Pb between the mountainous and plain area

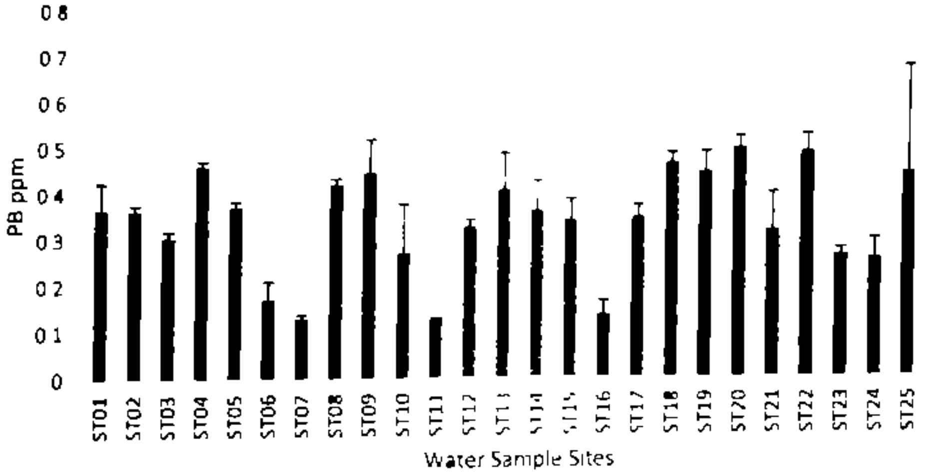


Figure 12 Pb in drinking water samples collected from district Lakki Marwat

4 2.7. Cobalt (Co) in water samples

The mean concentration of cobalt in water samples varied from 0 011ppm to 0 08 ppm The highest mean was calculated in ST25 and lowest concentration was at ST5 The maximum permissible level set by WHO (2008) for Co is 0 04 ppm The mean concentration of Co was higher in the sample sites of ST01,ST03,ST05,ST08,ST11,ST12,ST23,ST24 and ST25 which is mostltly located in the south and the west mountainous region of the study area The ANOVA single factor gives the p value of 0 004 which is less than 0 05 and showed very significant results

4.2.9. Cadmium (Cd) in water samples

The mean concentration in water samples ranged from 0.0003 ppm and 0.044 ppm. The maximum level of Cd was 0.044 ppm was noticed. The safe concentration of Cd in drinking water set by WHO(2008) is 0.003ppm. The result revealed that 28 % samples have the Cd level greater than the WHO permissible limits. The difference between the mean of the two groups of the samples is very large as indicated by small $p = 1.4 \times 10^{-9}$, which is less than 0.05 and show significant

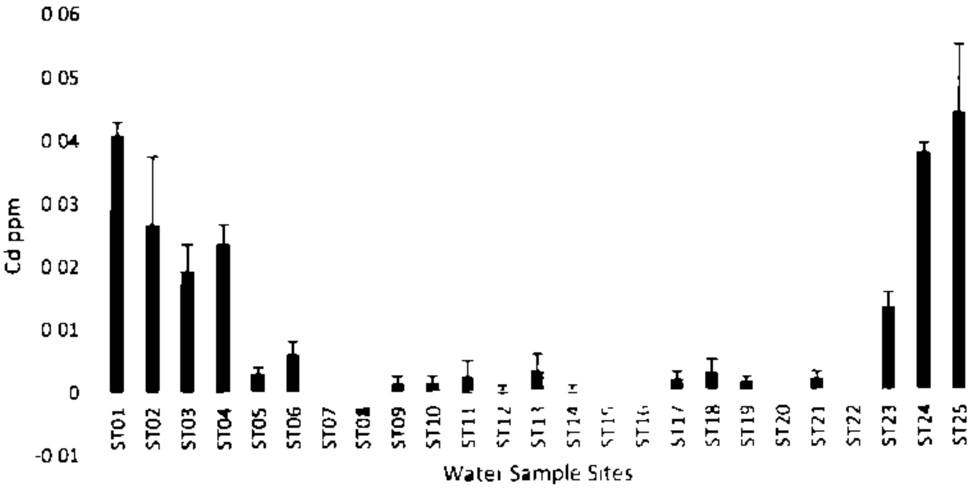


Figure 15 Cd in drinking water samples collected from district Lakki Marwat

4.3. CHARACTERIZATION OF LIGANDS

FTIR study of both ligands was carried out in order to confirm the functional group PerkinElmer FTIR Spectrometer (4000-400cm^{-1}) was used to take Infrared spectra using KBr pellets. By applying FTIR spectroscopy, the existence of important functional groups in the compound can be identified. The 1404-1550 cm^{-1} region, which was mainly related with υ (N-CSS) stretching vibrations. The 950-1000 cm^{-1} region, which is linked with υ (C-S) stretching vibrations.

The characteristic band at 1410 and 1474cm^{-1}, was assigned to υ (N-CSS), this band defines a carbon Nitrogen bond order between a single bond (υ =1250-1350cm-1) and a double bond (υ = 1640–1690cm-1).

A single sharp band at 1040.48 cm^{-1} was assigned to the stretching vibrations of the C-S bond. The band at 3346 and 3463 cm^{-1} associated with the υ (N-H) stretching vibrations.

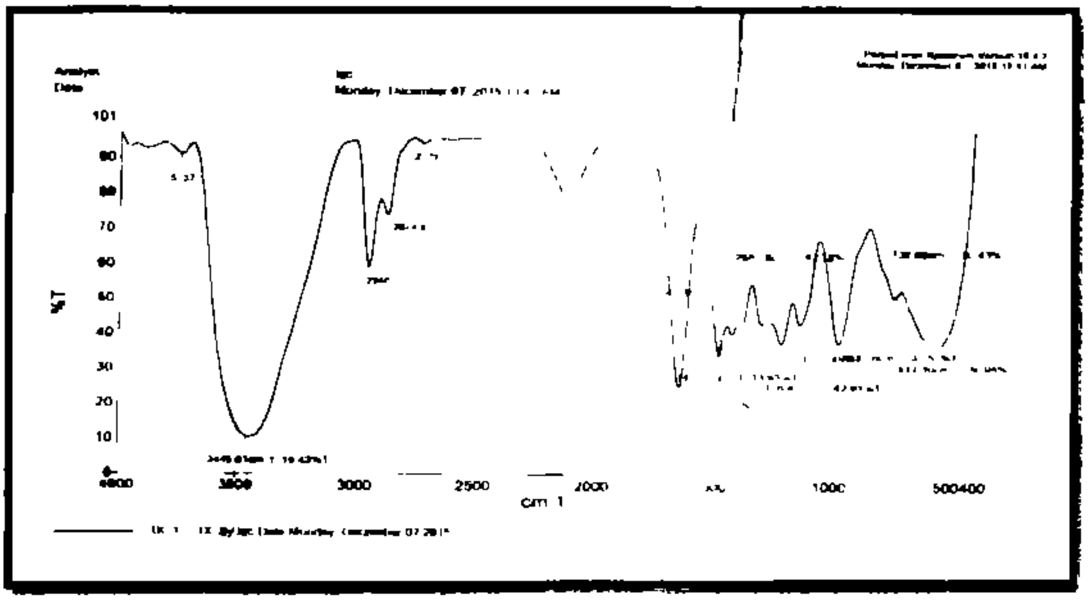


Figure 16 Showing the FTIR spectra of dibutyl dithiocarbamate

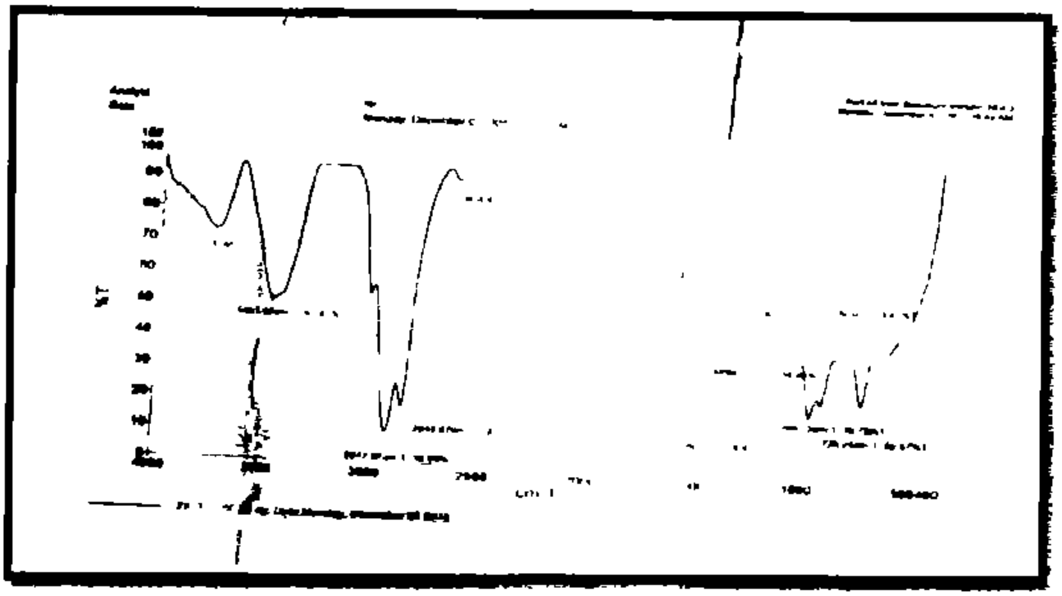


Figure 17 Showing the FTIR spectra of cyclohexyl dithiocarbamate

4.4. REMEDIATION OF HEAVY METALS

The remediation of removing heavy metals from its 10ppm solution by two DTC at pH 5, 7 and 9 was shown in the table 5 and 6 The pH plays a vital role in the remediation of heavy metals The two ligands showed different percentage removal of the heavy metal.

According to Baia (2011) DTC are unstable at pH less than 4 The comparison between remediation of heavy metals by the two DTC was shown in table 4 and it was indicated that dibutyl dithiocarbamate has a higher removal efficiency compared to the Cyclohexyl dithiocarbamate with exception of Mn result that revealed that there is large difference between the means of the two groups of the water samples

The drinking water that contain nickel compound was the sources of different diseases like, kidney problem, heart problems, lung fibrosis, allergy of skin and cause cancer in the respiratory tract (Filon *et al* , 2009)

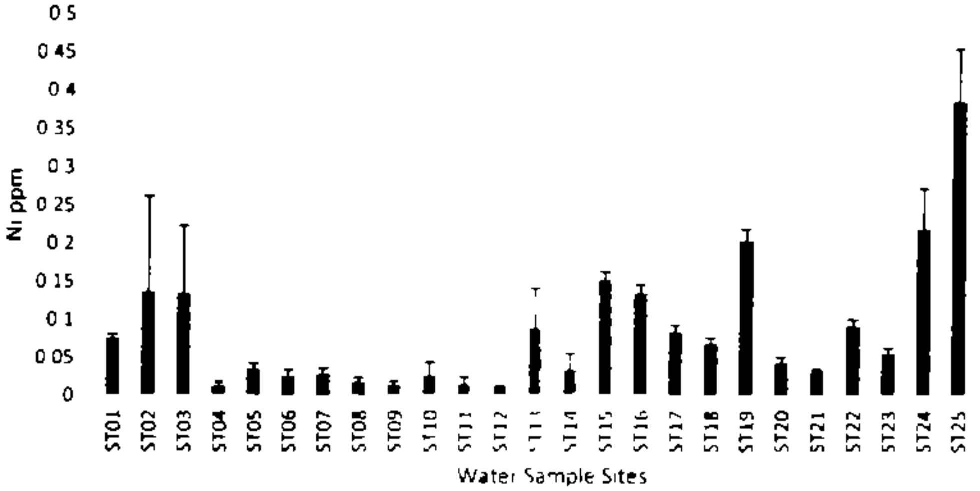


Figure 11 Ni in drinking water samples collected from district Lakki Marwat

4 2.6. Lead (Pb) in water samples

According to WHO (2008) the maximum permissible limit is 0 01 ppm for Pb concentration in drinking water, as it is a common toxicant that collects in the skeleton and there long term exposure results negative neurological effects The mean concentration of Pb in water samples was ranged from 0 131 ppm to 0 519 ppm The results indicated that Pb level in all samples exceeds the WHO maximum permissible The maximum Pb concentration of 0 519 ppm was present in the west of the study area where exploration of some radioactive element is also carried out The ANOVA single factor showed non-significant difference for Pb between the mountainous and plain area

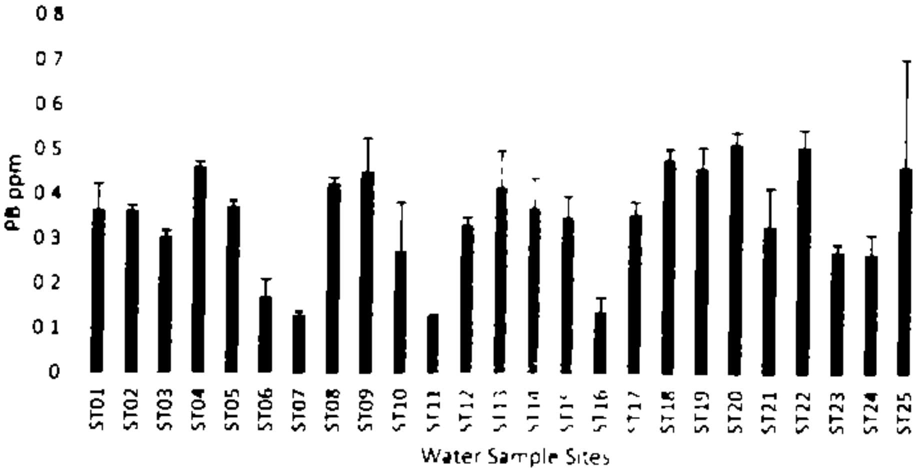


Figure 12 Pb in drinking water samples collected from district Lakki Marwat

4 2.7. Cobalt (Co) in water samples

The mean concentration of cobalt in water samples varied from 0 011ppm to 0 08 ppm The highest mean was calculated in ST25 and lowest concentration was at ST5 The maximum permissible level set by WHO (2008) for Co is 0 04 ppm The mean concentration of Co was higher in the sample sites of ST01,ST03 ST05,ST08,ST11,ST12,ST23,ST24 and ST25 which is mostltly located in the south and the west mountainous region of the study area The ANOVA single factor gives the p value of 0 004 which is less than 0 05 and showed very significant results

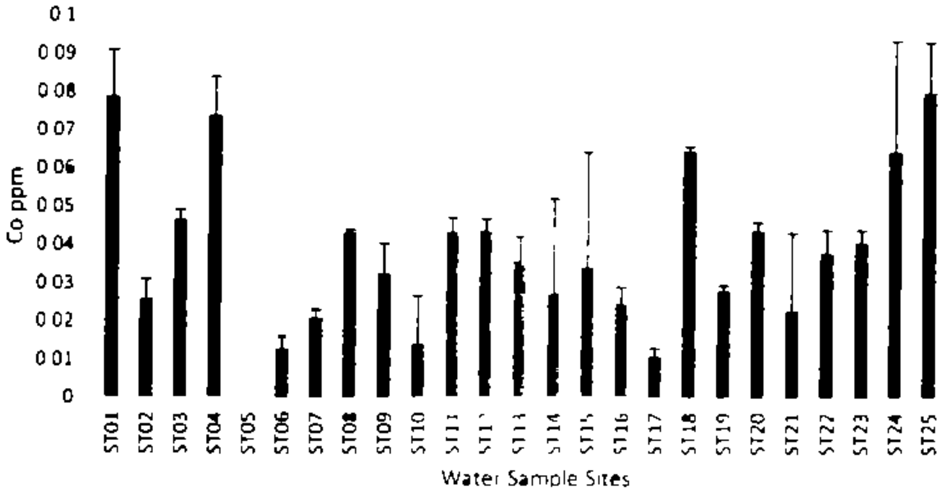


Figure 13 Co in drinking water samples collected from district Lakki Marwat

4.2.8. Manganese (Mn) in water samples

The 0 05 ppm maximum acceptable The mean maximum concentration of Mn found was 0 046 ppm, which indicates are in the safe limits set by WHO (2008) By comparing the means of the two groups of the samples the two way ANOVA gives very significant results for Mn indicated by the very small p value of 0 0001, which is less than 0 05

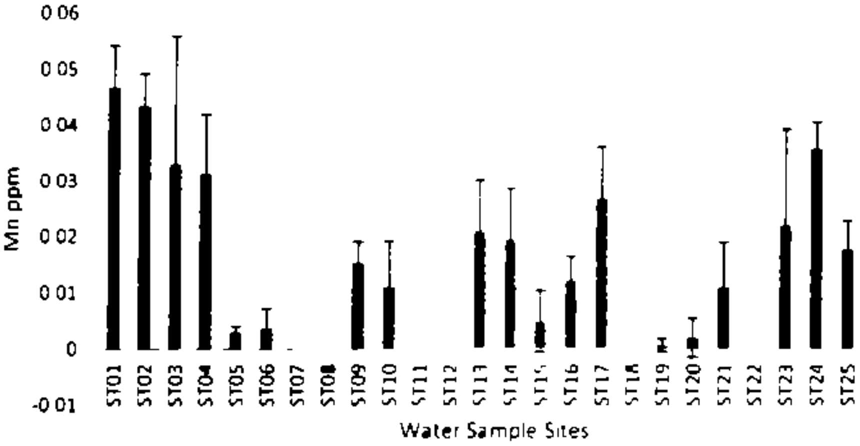


Figure 14 Mn in drinking water samples collected from district Lakki Marwat

4.2.9. Cadmium (Cd) in water samples

The mean concentration in water samples ranged from 0.0003 ppm and 0.044 ppm. The maximum level of Cd was 0.044 ppm was noticed. The safe concentration of Cd in drinking water set by WHO(2008) is 0.003ppm. The result revealed that 28 % samples have the Cd level greater than the WHO permissible limits. The difference between the mean of the two groups of the samples is very large as indicated by small $p = 1.4 \times 10^{-9}$, which is less than 0.05 and show significant.

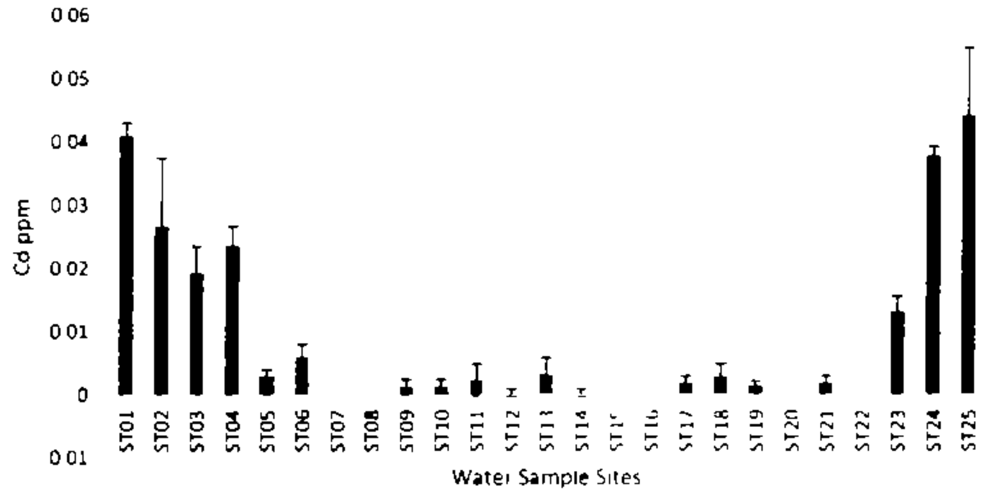


Figure 15 Cd in drinking water samples collected from district Lakki Marwat

4.3. CHARACTERIZATION OF LIGANDS

FTIR study of both ligands was carried out in order to confirm the functional group. PerkinElmer FTIR Spectrometer (4000-400cm^{-1}) was used to take Infrared spectra using KBr pellets. By applying FTIR spectroscopy, the existence of important functional groups in the compound can be identified The 1404-1550 cm^{-1} region, which was mainly related with υ (N-CSS) stretching vibrations The 950-1000 cm^{-1} region, which is linked with υ (C-S) stretching vibrations

The characteristic band at 1410 and 1474cm^{-1} was assigned to υ (N-CSS), this band defines a carbon Nitrogen bond order between a single bond (υ =1250-1350cm-1) and a double bond (υ = 1640–1690cm-1)

A single sharp band at 1040 48 cm^{-1} was assigned to the stretching vibrations of the C-S bond The band at 3346 and 3463 cm^{-1} associated with the υ (N-H) stretching vibrations

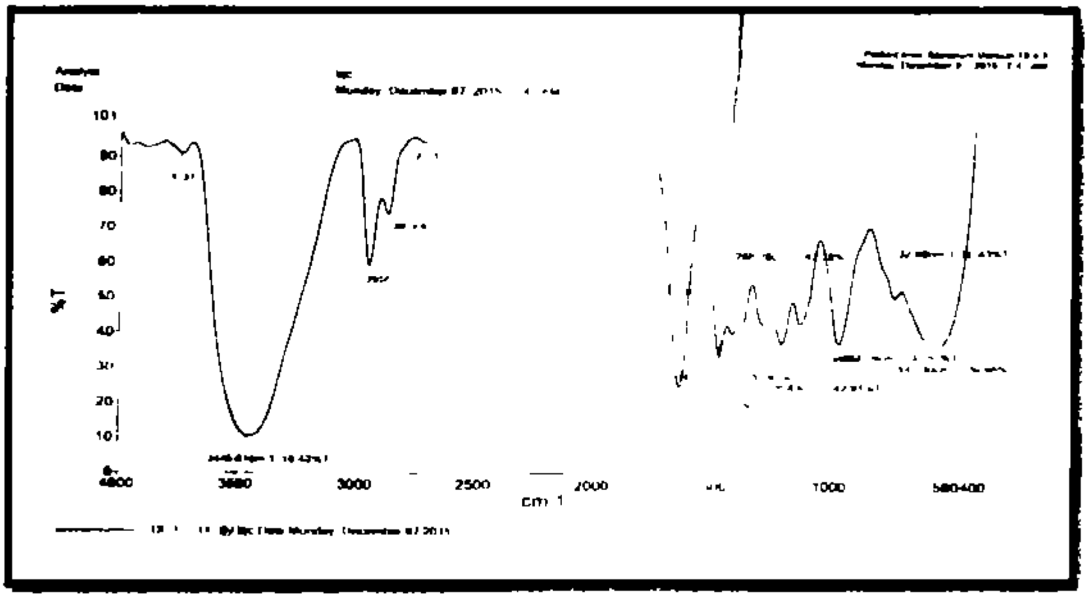


Figure 16 Showing the FTIR spectra of dibutyl dithiocarbamate

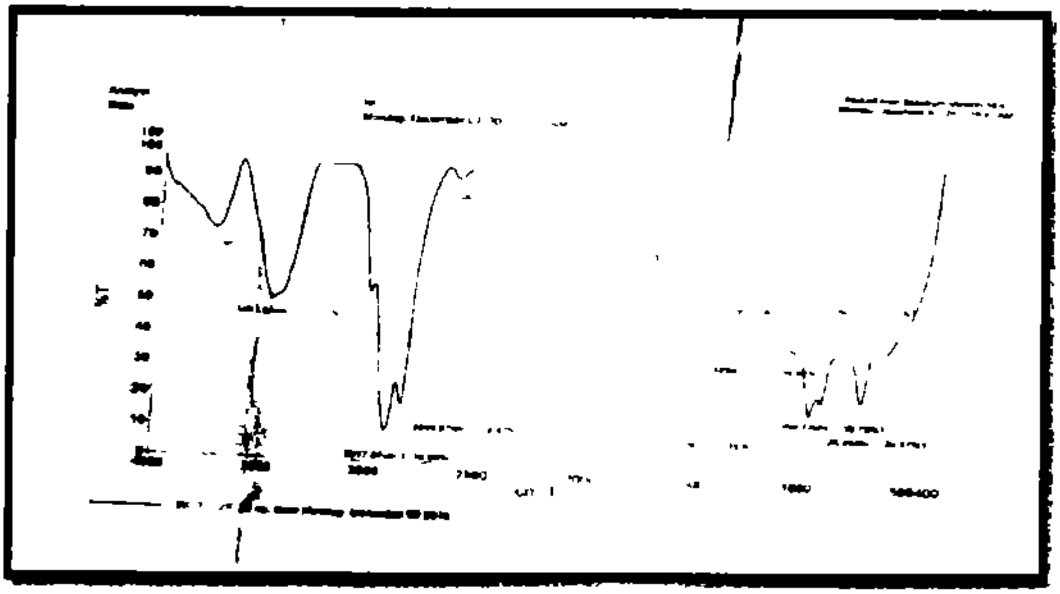


Figure 17 Showing the FTIR spectra of cyclohexyl dithiocarbamate

4.4. REMEDIATION OF HEAVY METALS

The remediation of removing heavy metals from its 10ppm solution by two DTC at pH 5, 7 and 9 was shown in the table 5 and 6 The pH plays a vital role in the remediation of heavy metals The two ligands showed different percentage removal of the heavy metal.

According to Baia (2011) DTC are unstable at pH less than 4 The comparison between remediation of heavy metals by the two DTC was shown in table 4 and it was indicated that dibutyl dithiocarbamate has a higher removal efficiency compared to the Cyclohexyl dithiocarbamate with exception of Mn

Table 4 Metal Removal Efficiency of Dibutythyldithiocarbamate

Metal	Initial Concentration (ppm)	Concentration After DTC treatment (ppm)	pH	Removal efficiency (%)
Zn	10	0 19	5	98 1
	10	2 87	7	71 3
	10	3 85	9	61 5
Fe	10	0 47	5	95 3
	10	1 67	7	83 3
	10	4 11	9	58 9
Cu	10	0 21	5	97 9
	10	1 42	7	85 8
	10	3 60	9	64 0
Cr	10	0 96	5	90 4
	10	2 08	7	79 2
	10	0 47	9	95 3
Ni	10	0 104	5	98 96
	10	2 042	7	79 58
	10	2 410	9	75 9
Pb	10	0 291	5	97 09
	10	0 371	5	96 29
	10	1 90	7	81 00
Co	10	0 00	5	100
	10	0 804	7	91 9
	10	4 090	9	59 1
Mn	10	9 14	5	8 6
	10	9 43	7	5 7
	10	7 99	9	20 7
Cd	10	0 156	5	98 4
	10	2 104	7	78 9
	10	2 832	9	71 6

Table 5 Metal Removal Efficiency of Cyclohexyldithiocarbamate

Metal	Initial Concentration (ppm)	Concentration After DTC treatment(ppm)	pH	Removal efficiency (%)
Zn	10	7 90	5	21 00
	10	7 06	7	29 40
	10	8 87	9	11 30
Fe	10	2 65	5	73 05
	10	3 67	7	63 30
	10	7 21	9	27 90
Cu	10	5 20	5	48 00
	10	6 05	7	39 50
	10	4 97	9	50 30
Cr	10	4 099	5	59 01
	10	5 80	7	42 00
	10	2 76	9	72 40
Ni	10	8 99	5	10 10
	10	8 10	7	19 00
	10	9 5	9	5 00
Pb	10	1 788	5	82 12
	10	2 99	7	70 10
	10	5 66	9	43 40
Co	10	2 789	5	72 11
	10	3 54	7	64 60
	10	6 64	9	33 6
Mn	10	0 09	5	99 10
	10	1 27	7	87 30
	10	1 76	9	82 40
Cd	10	7 78	5	22 11
	10	7 09	7	29 10
	10	8 21	9	17 9

Table 6 Comparison of Remediation of Heavy metals by dibutyl dithiocarbamate and cyclohexyl dithiocarbamate

Metal	pH	%Remediation of Dibutyle – dithiocarbamate	% Remediation of cyclohexyl dithiocarbamate
Zn	5	78 1	21 00
	7	61 3	29 40
	9	51 5	11 30
Fe	5	95 3	73 05
	7	63 3	63 30
	9	48 9	27 90
Cu	5	97 9	48 00
	7	85 8	39 50
	9	64 0	50 30
Cr	5	90 4	59 01
	7	79 2	42 00
	9	95 3	72 40
Ni	5	98 96	10 10
	7	79 58	19 00
	9	75 9	5 00
Pb	5	97 09	82 12
	7	81	70 10
	9	679 7	43 40
Co	5	100	72 11
	7	91 9	64 60
	9	59 1	33 6
Mn	5	8 6	99 10
	7	5 7	87 30
	9	20 7	62 40
Cd	5	98 4	22 11
	9	78 9	29 10
	9	71 6	17 9

4.4.1. Remediation of heavy metals by Sodium dibutyl dithiocarbamate

The study indicated that highest remediation was achieved by dibutyl dithiocarbamate at pH 5 for Cobalt in which concentration of Co was reduced from 10 ppm to 0 00 ppm means that 100% remediation of heavy metals was achieved, while lowest removal efficiency was observed by dibutyldithiocarbamate at pH 7, which reduced the concentration of Mn from 10ppm to 9 43 ppm The decreasing order of remediation of heavy metals by dibutyl dithiocarbamate was Co > Ni> Cd> Zn> Cu> Pb> Fe, Cr>Mn By treating with dibutyl dithiocarbamate more than 95% remediation was achieved except Mn

The result indicates that maximum remediation was attained at pH 5 except for Cr in which shows removal efficiency, higher at pH 9 So dibutyl dithiocarbamate was effectively used for remediation of heavy metals in the acidic medium except Mn from aqueous water or effluents, while for Cr contaminated water dibutytldithiocarbamate was used in alkaline medium

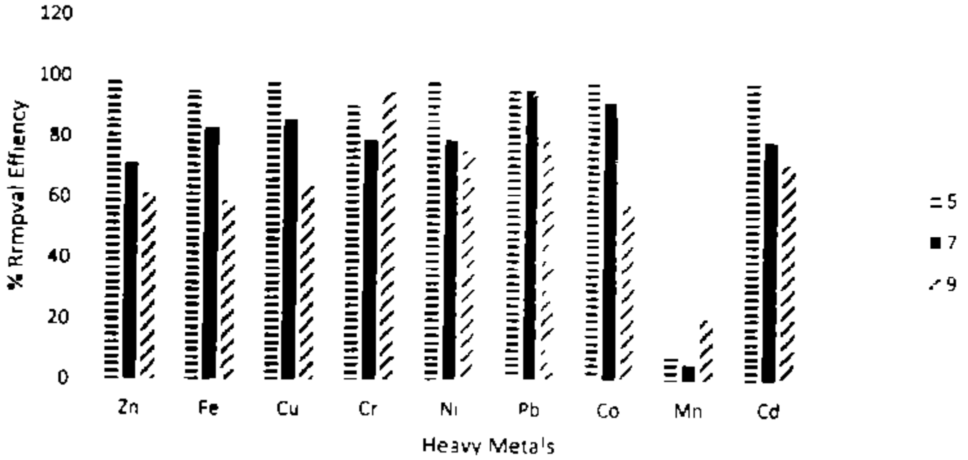


Figure 18 Removal efficiency of Sodium dibutyl dithiocarbamate at pH 5, 7 and 9

4.4.2. Remediation of heavy metals by Sodium Cyclohexyl dithiocarbamate

The study indicated that highest remediation was achieved by cyclohexyl dithiocarbamate at pH 5 for Mn, in which concentration of Mn was reduced from 10 ppm to 0 09 ppm while lowest removal efficiency was observed by cyclohexyl dithiocarbamate for Ni at pH 7, which reduced the concentration of nickel from 10ppm to 8 10ppm The decreasing order of remediation of heavy metals by cyclohexyldithiocarbamate was Mn > Pb> Fe> Cr> Co> Cu> Zn>Cd> Ni Cyclohexyldithiocarbamate remove 99 10% of Ni, 82 12% Pb, 73 05%

Fe, 72% Cr and Co, 50 3% Cu from aqueous solution For Zn, Cd and Ni the removal efficiency was less than 50%

So cyclohexyldithiocarbamate was effectively used for remediation of Mn and Pb from aqueous water or effluents

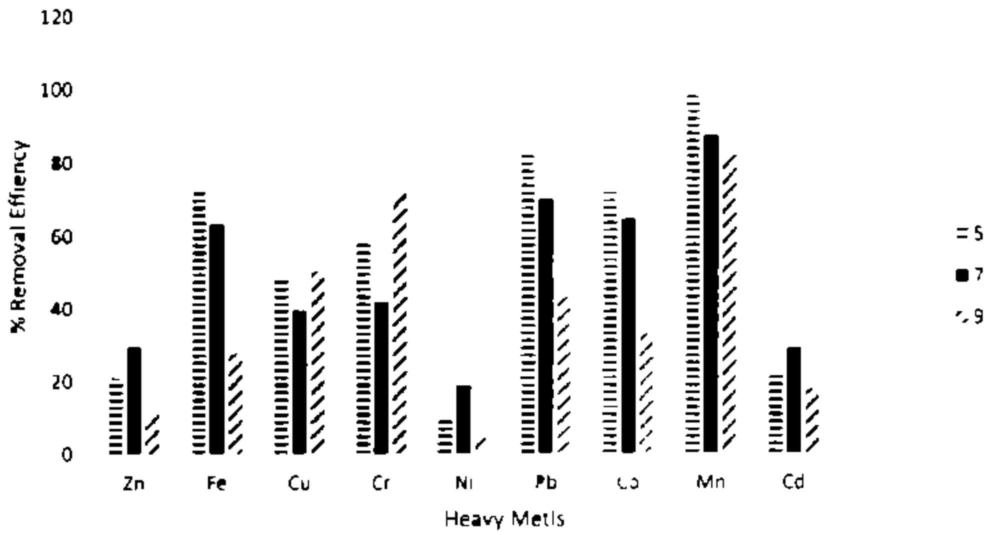


Figure 19 Removal efficiency of Cyclohexyl dithiocarbamate at pH 5, 7 and 9

4.4 3 Effect of PH on removal capacity of dithiodiCarbamate

In the heavy metal adsorption process, the pH of the aqueous solution is a significant regulatory factor (Gu *et al*, 2013) Two types of DTC were put into the metals solutions over a pH range of 5, 7 and 9 at room temperature to investigate the influence of pH on heavy metals adsorption property It is observed that the adsorption capacity of DTC is pH dependent, and all these products show a weak adsorption capacity at high pH values The adsorption capacity decreases with increasing pH values, and the maximum capacity was achieved at pH 5 The remediation of heavy metals by two dithiocarbamate were compared by using two tailed t test at pH 5, 7 and 9 At pH 5, 7 and 9, the remediation result was significant as revealed by the p value ≤ to 0 05 and t critical was greater than t stat The p ≥ 0 05 indicates that there are large difference between the mean remediation by the two types of DTC, which is confirmed by critical value

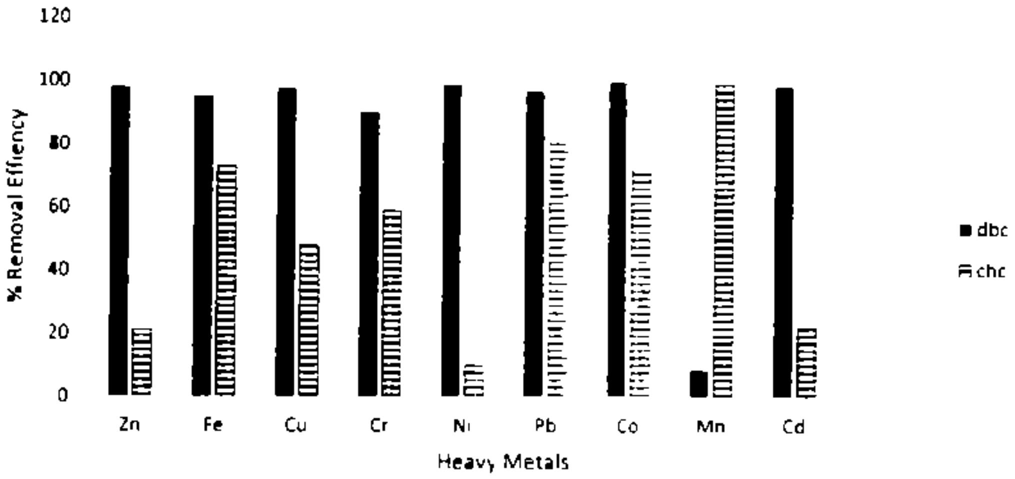


Figure 20 Removal efficiency of Dibutyl dithiocarbamate and cyclohexyl dithiocarbamate at pH 5

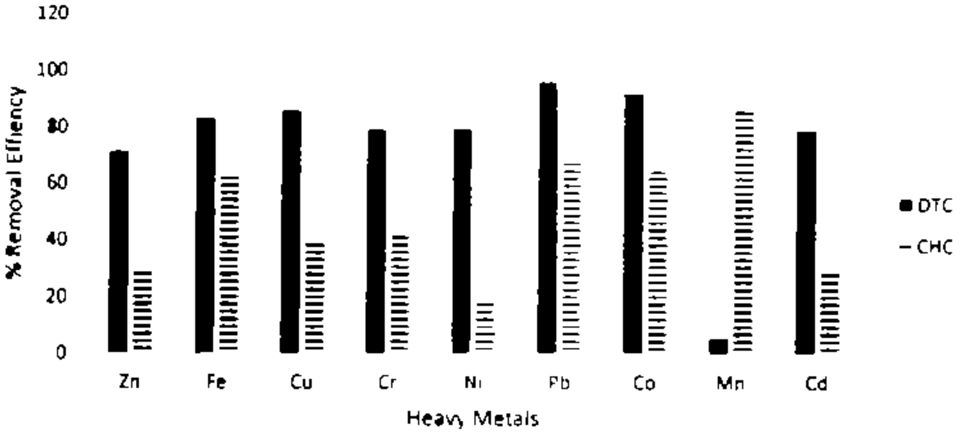


Figure 20 Removal efficiency of Dibutyl dithiocarbamate and cyclohexyl dithiocarbamate at pH 7

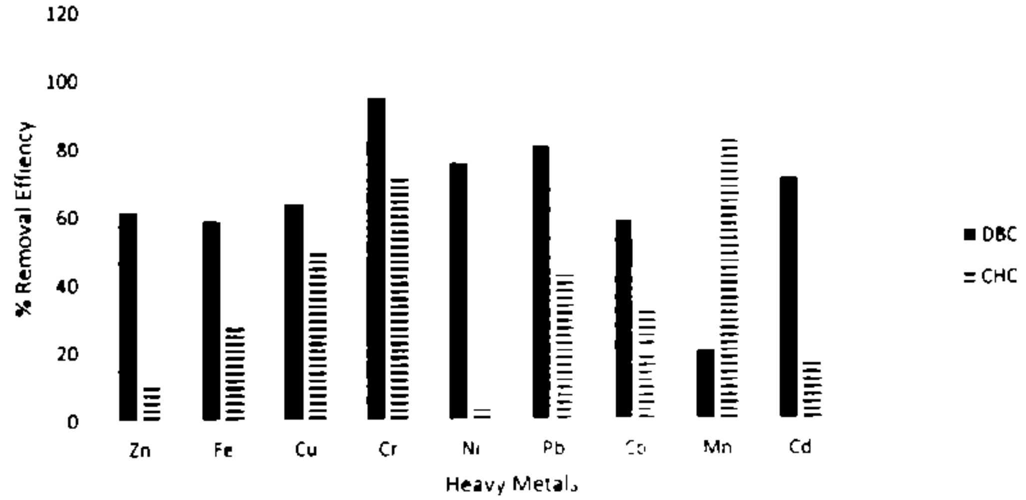


Figure 21 Removal efficiency of dibutyl dithiocarbamate and cyclohexyl dithiocarbamate at pH 9

The residents of Lakki Marwat depend on underground water for drinking water and other uses The results of physicochemical analysis of water in the study area considered depreciated and concerning health problems to the user populace The study has revealed that there was significant quantity of heavy metals in underground water, however the average levels were below than Maximum permissible levels set by WHO (2008), EC (European Community), EPA (Environment Protection Agency) In some cases the levels of Fe, Cr, Pb, Ni, Co and Cd exceeded the WH (2008) maximum permissible limit It is evident from the study that maximum concentration of these metals was detected in the south and west mountainous part of the study area It was concluded that in the west part of the study area the heavy metals concentration higher probably due to huge amount of radioactive elements is present and their exploration was carried out from last 20 years In the south mountainous part of the Lakki Marwat, Pakistan largest Cement factory operated from last 22 year, the seepage of the effluents and geology of the mountains were responsible for higher concentration of heavy metals The results indicate that on the basis of EC the water of the study area are slightly saline and pH indicates that it is slightly alkaline

This study revealed that in the remediation of heavy metals from aqueous solution by dithiocarbamate ligand, at the same pH removal efficiency of dibutyldithiocarbamate was higher than cyclohexyldithiocarbamate This is because the dibutyldithiocarbamate ligand is more stable with a high bonding capacity for heavy metals This study showed that the heavy metal removal efficiency depends on the type of ligand used Therefore, dibutyldithiocarbamate was effective in removing the selected heavy metal ions from aqueous solutions, providing a potential approach for the treatment of polluted water containing multiple heavy metal ions

The study also indicated that the type of ligands play an important role in the remediation of heavy metals from aqueous solution or waste water The Dibutyldithiocarbamate was highly efficient for the adsorption of metal ions by batch methods In the light of the above result, it is concluded that this method is economical and extremely specific for the removal of heavy metals

Recommendations

The following may be recommended from this research and should be taken to the researchers in this area

I Concentration of Heavy metals in the underground water should be periodically examined to check on Heavy Metals pollution

II Due to unavailability of local bodies treatment plant in the entire area, the resident cannot afford to purchase expensive bottled mineral water Thus the alternate feasible source for drinking water should be arranged and drinking of heavy metal contaminated water should be stopped immediately

III In the south part of the study area, the sources of Heavy metals i e Effluents of Cement factory should be properly treated before discharge to the environment

IV Research on the concentration of radioactive metals in soil and underground water should be conducted in the west mountainous part of the study area

V Research should be conducted on the milk and meat of the animals drinking contaminated water in the west mountainous part of the area

VI For the topography characterization geological and hydrological research should be conducted in high hazardous Heavy metals affected areas

VII The remediation by dithiocarbamate should be optimized by considering the effect of ligands dose, temperature Moreover column experiments play important role in the removal process, in which flow rate, bed volume and temperature should be studied

VIII Furthermore ligands regeneration may be investigated so that reusing potential of the ligands and safe disposal of the dithiocarbamate should be studied

IX The public should be trained by using different remediation technologies

X Conferences and seminars should be arranged on a regular basis in cooperation with local and international organizations are recommended In addition, key people and experts from other heavy metals affected areas should be invited to attend such events

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Appendix I

Table 7 Results of t test of % Remediation of DBC and DHC at pH5

t-Test paired two sample for mean		
	Variable 1	*Variable 2*
Mean	87.19444	54.06667
Variance	876.5624	951.2326
Observations	9	9
Pearson Correlation	-0.56973	
Hypothesized Mean Difference	0	
Df	8	
t Stat	1.855679	
P(T<=t) one-tail	0.050298	
t Critical one-tail	1.859548	
P(T<=t) two-tail	0.100596	
t Critical two-tail	2.306004	

Table 8 Showing the results of t test of % Remediation of DBC and DHC at pH7

	Variable 1	*Variable 2*
Mean	74.66333	49.36667
Variance	724.1738	522.27
Observations	9	9
Pearson Correlation	-0.42603	
Hypothesized Mean Difference	0	
Df	8	
t Stat	1.803611	
P(T<=t) one-tail	0.054475	
t Critical one-tail	1.859548	
P(T<=t) two-tail	0.10895	
t Critical two-tail	2.306004	

Table 9 Showing the results of t test of % Remediation of DBC and DHC at pH 9

	Variable 1	*Variable 2*
Mean	65.33333	38.24444
Variance	422.9025	707.7378
Observations	9	9
Pearson Correlation	-0.26563	
Hypothesized Mean Difference	0	
Df	8	
t Stat	2.155619	
P(T<=t) one-tail	0.03161	
t Critical one-tail	1.859548	
P(T<=t) two-tail	0.063219	
t Critical two-tail	2.306004	

Appendix II

Table 10 Concentration of Heavy metals of the three samples from each site

HM WHO	Zn (3ppm)			Fe (0 3ppm)			Cu (2 0ppm)			Cr (0 05ppm)		
Site code	SI	S 2	S 3	S 1	S 2	S 3	S 1	S2	S3	SI	S2	S3
ST1	0 368	0 414	0 465	0 071	0 064	0 119	0 041	0 053	0 06	0 011	0 029	0 037
ST 2	0 458	0 43	0 476	0 077	0 095	0 061	0 036	0 028	0 041	0 035	0 027	0 042
ST 3	0 388	0 42	0 351	0 214	0 198	0 221	0 05	0 073	0 031	0 042	0 051	0 036
ST 4	0 18	0 12	0 22	0 125	0 098	0 143	0 029	0 031	0 024	0 056	0 048	0 06
ST 5	DB	DB	DB	0 021	0 024	0 041	DB	DB	DB	DB	DB	DB
ST 6	0 09	0 06	0 05	0 032	0 046	0 029	DB	DB	DB	DB	DB	DB
ST 7	0 098	0 079	0 056	0 112	0 118	0 109	0 002	0 009	0 003	0 012	0 009	0 016
ST 8	0 012	0 018	0 008	0 071	0 092	0 057	0 015	0 026	0 008	0 023	0 028	0 017
ST 9	0 023	0 143	0 126	0 118	0 122	0 021	0 009	0 013	0 03	0 032	0 021	0 019
ST 10	0 014	DB	0 013	0 015	0 194	0 112	0 04	DB	0 032	0 031	0 024	0 039
ST 11	0 004	0 008	0 003	0 133	0 099	0 178	0 014	0 023	0 006	DB	DB	0 001
ST 12	0 033	0 039	0 041	0 167	0 133	0 195	0 004	0 007	0 006	DB	DB	DB
ST 13	0 0104	0 096	0 098	0 154	0 237	0 094	0 004	0 023	0 005	0 042	0 003	0 022
ST 14	DB	0 012	0 045	DB	DB	DB	0 021	0 024	0 019	0 031	0 035	0 034
ST 15	DB	DB	DB	DB	DB	DB	0 022	0 028	0 017	0 023	0 016	0 031
ST 16	DB	0 011	DB	DB	0 004	DB	0 016	0 012	0 019	0 015	0 007	0 021
ST 17	0 032	0 036	0 029	2 943	1 502	0 953	0 034	0 025	0 044	DB	DB	DB
ST 18	0 083	0 097	0 076	0 058	0 049	0 065	0 021	0 028	0 016	0 013	0 006	0 023
ST 19	DB	DB	DB	0 05	0 049	0 053	0 019	0 011	0 027	0 001	DB	DB
ST 20	0 062	0 043	0 08	DB	DB	DB	DB	0 005	0 007	0 002	0 001	0 002
ST 21	1 511	1 451	1 652	DB	0 002	0 006	0 035	0 019	0 032	0 022	0 012	0 031
ST 22	0 012	0 009	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB
ST 23	0 108	0 099	0 116	0 364	0 435	0 291	0 016	0 013	0 022	0 071	0 082	0 063
ST 24	0 244	0 26	0 251	0 425	0 351	0 501	0 038	0 042	0 029	0 066	0 041	0 051
ST 25	0 351	0 142	0 241	0 342	0 399	0 72	0 035	0 042	0 022	0 051	0 043	0 039

Appendix III

Table 11 Concentration of Heavy metals of the three samples from each site

HM WHO	Ni 0.02ppm			Pb 0.01ppm			Co 0.04ppm			Mn 0.003ppm			Cd 0.003ppm		
Site Code	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
ST1	0.071	0.076	0.081	0.431	0.346	0.321	0.079	0.067	0.091	0.054	0.039	0.047	0.043	0.039	0.041
ST2	0.278	0.091	0.042	0.362	0.377	0.355	0.026	0.021	0.031	0.041	0.039	0.05	0.022	0.039	0.019
ST3	0.234	0.106	0.065	0.301	0.296	0.321	0.047	0.049	0.044	0.059	0.024	0.016	0.018	0.024	0.016
ST4	0.012	0.018	0.009	0.465	0.452	0.474	0.074	0.064	0.084	0.031	0.042	0.021	0.023	0.027	0.021
ST5	0.037	0.029	0.042	0.378	0.362	0.385	DB	DB	DB	0.003	0.002	0.004	0.003	0.002	0.004
ST6	0.024	0.019	0.035	0.174	0.134	0.212	0.013	0.01	0.016	DB	0.004	0.007	0.006	0.004	0.008
ST7	0.028	0.021	0.036	0.132	0.129	0.14	0.021	0.019	0.023	DB	DB	DB	DB	DB	DB
ST8	0.017	0.013	0.024	0.425	0.441	0.417	0.043	0.044	0.043	DB	DB	DB	DB	DB	DB
ST9	0.015	0.01	0.018	0.414	0.411	0.539	0.041	0.026	0.031	0.011	0.017	0.018	0.002	0.002	DB
ST10	0.047	0.016	0.017	0.153	0.359	0.314	0.022	0.021	DB	0.02	0.004	0.009	0.002	DB	0.002
ST11	0.015	0.011	0.025	0.132	0.129	0.133	0.044	0.04	0.047	DB	DB	DB	0.002	0.005	DB
ST12	0.012	0.009	0.012	0.345	0.323	0.347	0.044	0.041	0.047	DB	DB	DB	DB	0.001	DB
ST13	0.137	0.035	0.099	0.501	0.42	0.342	0.034	0.031	0.043	0.013	0.019	0.031	0.001	0.003	0.006
ST14	0.028	0.017	0.059	0.433	0.303	0.387	0.047	DB	0.036	0.011	0.029	0.019	DB	0.001	DB
ST15	0.158	0.143	0.161	0.347	0.311	0.403	DB	0.056	0.047	0.004	0.0108	DB	DB	DB	DB
ST16	0.137	0.127	0.146	0.152	0.11	0.167	0.025	0.029	0.021	0.011	0.009	0.017	DB	DB	DB
ST17	0.087	0.076	0.092	0.352	0.39	0.342	0.011	0.009	0.013	0.025	0.037	0.019	0.002	0.001	0.003
ST18	0.075	0.073	0.062	0.49	0.502	0.461	0.065	0.066	0.064	DB	DB	DB	0.003	0.001	0.005
ST19	0.202	0.193	0.221	0.457	0.512	0.423	0.029	0.029	0.027	DB	DB	0.002	0.001	DB	0.002
ST20	0.044	0.036	0.051	0.513	0.499	0.546	0.044	0.046	0.042	0.006	DB	DB	DB	DB	DB
ST21	0.035	0.031	0.032	0.274	0.393	0.317	DB	0.031	0.038	0.017	0.014	0.002	0.001	0.003	0.002
ST22	0.091	0.102	0.086	0.526	0.467	0.54	0.038	0.032	0.044	DB	DB	DB	DB	DB	DB
ST23	0.057	0.049	0.063	0.263	0.293	0.276	0.041	0.038	0.044	0.042	0.012	0.012	0.016	0.012	0.012
ST24	0.163	0.231	0.267	0.223	0.303	0.289	0.064	0.036	0.094	0.037	0.031	0.04	0.037	0.039	70.0395
ST25	0.342	0.353	0.467	0.318	0.341	0.745	0.093	0.067	0.081	0.022	0.019	0.012	0.042	0.035	0.056