ENVIRONMENTAL APPLICATION OF NANO-TECHNOLOGY FOR INDUSTRIAL WASTEWATER TREATMENT

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NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

RISALPUR CAMPUS

SESSION 2017-2021

ENVIRONMENTAL APPLICATION OF NANO-TECHNOLOGY FOR TREATMENT OF INDUSTRIAL WASTEWATER

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Submitted in partial fulfillment of the requirements for the degree of Bachelor in Engineering (BE) Civil Engineering at Military college of Engineering Risalpur NUST.

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This research is dedicated to our parents and teachers.
For their endless love, support and encouragement

APPROVAL SHEET

This is to certify that the contents and format of this research titled ‘‘ENVIRONMENTAL APPLICATION OF NANO-TECHNOLOGY FOR TREATMENT OF INDUSTRIAL WASTEWATER” submitted by FYP Group #06 in partial fulfillment of the requirements for the award of degree of BE have been approved.

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ABSTRACT

Liquid industrial waste which is disposed in water bodies is not only dangerous for aquatic life, but also for people consuming it and using that water for irrigation. Heavy metals like lead, mercury, cadmium, arsenic, tin, selenium etc. are classified among the major pollutants due to their harmful and toxic characteristics, which pertains to them being un-metabolizable by the human body. Heavy metals present a public health issue due to their alarming effects. There are many ways to eliminate the heavy and toxic metals from the water before it is released into the environment including iron extraction, chemical precipitation, membrane separation, surface complexation, adsorption and electrolysis. One of the most used techniques among these is adsorption in terms of being inexpensive, highly efficient, simple and still flexible. Adsorption technique (Carbon adsorbent) has been used in the present research. Samples of wastewater were collected from each of the three industries i:e Cement ,Steel and Leather Industry. The sample size from each is kept to roughly 4.5 liters, collected in three bottles of 1.5-liter capacity. Prototype adsorption unit is small portable setup developed for the treatment of wastewater. Prototype was primarily prepared by National Centre of Physics (NCP); For the present experiment, used Carbon adsorbent has been prepared by treating modified charcoal at nano level. Half of the quantity from each sample was collected and was deposited to PCRWR (Pakistan Council of Research in Water Resources) for atomic adsorption analysis, prior to adsorption and post adsorption, respectively. Highest removal percentage obtained was of Lead i:e 95.5% and lowest removal efficiency came out to be of Nickel i:e 52.17%. Almost half of the nickel content passed without being adsorbed. Overall heavy metals adsorption percentage for all 10 elements came out to be 76.562%. This percentage is fine enough to cause a valuable decrease in the detrimental effects caused through excessive heavy metals. Main purpose of this study was to inspect the efficacy of this lab-based prototype in removal of heavy metals from industrial waste up to a level that they remain un harmful to environment. Now once it has produced desired results, upscaling of this sample prototype into a wastewater treatment plant, to meet the requirements of high industrial discharge remains an immediate requirement. Production of adsorbent at mass scale as well as development of other supporting equipment/components would remain a demanding task.

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ENVIRONMENTAL APPLICATION OF NANO-TECHNOLOGY FOR INDUSTRIAL WASTEWATER TREATMENT

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Nomenclature:

BDL : Below detection Limit

Pb: Lead element

Ba: Barium element

Mn: Manganese element

Cr: Chromium element

Cu: Copper element

Al: Aluminum element

Co: Cobalt element

Cd :Cadmium element

Ni: Nickel element

Sr: Strontium element

µg : Microgram

Chapter 1 Introduction

1.1 Background

Industrialization has an essential part in the development and growth of any country. However, it is also one of the major reason for pollution. This is due to the industrial waste produced like concrete, dirt, scrap metal, chemicals, solvents, wood, oil etc. Liquid industrial waste which is disposed in water bodies is not only dangerous for aquatic life, but also for people consuming it and using that water for irrigation. (T. Ahmed et al., 2019) Waste dumped in oceans is a huge issue as it has damaging effects on marine life as well as their habitat. Some industries contribute to the release of many gases like nitrogen oxide NO, carbon dioxide CO_2 and sulfur dioxide SO_2 which are the main pollutants of air pollution. The air surrounding industrial areas is known to cause irritation to the eyes, throat, nose and skin, in addition to lung disease. Industrial wastewater also includes many chemicals like ammonia, nitrate, nitrogen and heavy metals which makes it toxic (Shayesteh et al., 2020).

Heavy metals are classified among the major pollutants due to their harmful and toxic characteristics, which pertains to them being un-metabolizable by the human body. Constant high exposure to heavy metals like arsenic, mercury, zinc and cadmium are likely to cause damage to the vital organs to the population living close by to the source. (Gupta, Nayak, Bhushan, & Agarwal, 2014) In any developing country, rivers are the most crucial of the resources, as they are a source of crop irrigation and drinking water. However, industrialization has led to various industrial effluents being released into these water bodies. (Shahid et al., 2019)

Many heavy metals that include elements like lead, mercury, cadmium, arsenic, tin and selenium have become a part of the environment due to their accumulation in lakes and rivers. Heavy metals present a public health issue due to their alarming effects(Abdel-Raouf & Abdul-Raheim, 2017). The aquatic flora and fauna are the most affected, and when they are consumed by people, they can lead to poisoning due to toxicity, and eventually result in cancer and severe brain damage(Abdel-Raouf & Abdul-Raheim, 2017).

Table 1 Sources, router of entry and hazardous effect of some heavy metals (Abdel-Raouf & Abdul-Raheim, 2017)

Heavy Metal	Possible Source	Route of Entry for humans	Toxicity Effect on humans	Permissible Level (mg/L)
Arsenic	From glass, dyes, metal adhesives, paper	From contaminated food or water Or inhaling through polluted air	Lung problems Abdominal problems Cognitive developments in children Skin irritation and cancer	0.020
Lead	Surgical equipment manufacturing Steel industry Dyes and pigments Automobiles Battery manufacture	From contaminated food or water Medicines Inhalation from industrial air pollution	Anemia, hypertension, Cognitive problems in children. Miscarriage of unborn children Blood disorders	0.15

			Kidney problems	
Cadmium	Batteries Cigarette smoke Smelters Burning of fuels	Inhalation from particulate matter and ingestion from water or food	Cancers of urinary, reproductive, nervous system and respiratory system	0.06
Nickel	Cement industry Tanning Carpet industry	Inhalation from polluted air Ingestion from contaminated food	Respiratory tract-lun Kidney issues Nasal cancer Gastro intestinal issues	0.1
Mercury	Burning coal Industrial boilers Mining	From air pollution From contaminated food and water	Kidney damage Skin and eye irritation	0.01 (vapor)

	Batteries Electronics		Gastrointestinal and kidney toxicity	
Chromium	Electronics Batteries Pigments Finishing of metals Wood preservation	Polluted air Oral exposure Skin absorption	Respiratory tract Dermatitis Skin ulcers Nasal and sinus cancer	0.05

Many environmental laws implemented internationally require the removal of harmful substances like heavy metals from wastewater including conventional methods, that may include physical, chemical or even biological techniques. The physical methods consist of screening, sedimentation, membrane separation, as well as filtration. Chemical methods are the techniques like coagulation, adsorption, solvent extraction, ion exchange, and precipitation (T. Ahmed et al., 2019).Whereas there are two types of biological methods including aerobic and anaerobic. Where the ion exchange method may cost a lot, it provides high treatment quality. Similarly, coagulation may be simple but the method itself produces sludge and transfers the toxic compounds in solid phase (Abdel-Raouf & Abdul-Raheim, 2017)

1.1.1 Water Usage

Water may be used for various direct and indirect purposes. (CDC, 2020) The direct purpose include drinking, cooking or other personal uses, whereas the indirect purposes include mostly industrial use in addition to agriculture, thermo-electricity, and recreation (CDC, 2020) In any country, the utilization of water is vital to be managed, so that every sector gets the requisite amount without causing water shortage. Pakistan has great natural sources, but the water resources are diminishing because the poor water management in the country (Zahra & Khan, 2019a).

1.1.1.1 Groundwater Irrigation

In South Asian countries like Pakistan irrigation practices based on the utilization of groundwater are essential in boosting agricultural production and improving the likelihood of the farmers. Pakistan annually extracts around 60 bm^3 of groundwater (Zahra & Khan, 2019a). In comparison to the rest of the world, South Asian countries including Pakistan, use twice the amount of groundwater for agricultural purposes which are around 85%. The reason behind the intensive use of groundwater is to meet the food requirements of these heavily populated regions.(Gerbens-Leenes, Hoekstra, & Bosman, 2018)

The decline in surface water supplies is due to the shortage of storage capacities and rising concerns regarding climate change have threatened the future scope of Pakistan's irrigated agricultural sector that has a major contribution of 90% in total grains produced. (Javed & Kabeer, 2018; Walker, Baumgartner, Gerba, & Fitzsimmons, 2019)

The climate condition of Pakistan also makes irrigation a mandatory process for sustainable production of crops as Pakistan faces a high rate of evapotranspiration and even rainfall rate is insufficient and unreliable. The contribution of rain is only capable of meeting the 15% requirement of crop water whereas the remaining 85% is fulfilled through irrigation. The inadequacy of surface water has left farmers with the only option of abstracting groundwater while compromising the quality along with the pumping cost required (Zahra & Khan, 2019a)

1.1.1.2 **Domestic water supply**

In Pakistan for domestic needs, around forty million people are dependent on the supply of irrigation water. Water sources of Pakistan depend solely on a single river system, namely the Indus Basin. It forms the Indus Basin Irrigation System (IBIS), which excludes the Canal Command Areas above the Jinnah Barrage (Simons, Bastiaanssen, Cheema, Ahmad, & Immerzeel, 2020). The whole surface water system supplies approximate 138 MAF (million-acre feet) water per year. From this, 65% is supplied solely by the vast Indus river system. (Zahra & Khan, 2019a)

Billions of people cannot drink clean water as they lack access, resources, and good water management, and this condition is prevalent in Africa and Asia. Due to the unavailability of clean drinking water and poor hygiene practices, communicable diseases are more predominant in these regions. Diarrhea is the leading disease as a result of poor domestic water supply. According to UNICEF (2001) report, there have been four billion cases of diarrhea and 2.2 million deaths (Ensink, Jeroene, & Aslam, 2002)

More than 80% of people in Pakistan do not have the resources or just lack the access to clean drinking water. The available water supply either does not meet the permissible levels of drinking water, or they simply do not have access to drinking water. The main source of contamination in the case of domestic water is excessive seepage from the sewerage pipelines and the main pathogen that causes disease from this sort of contamination is *Escherichia coli* (Daud et al., 2017).

The supply system of water in urban centres of Pakistan is either based on surface water or abstraction of groundwater by use of tube wells. Islamabad, Hyderabad and Karachi are dependent on surface waters for drinking purpose. Cities like Lahore, Faisalabad, Quetta, Abbottabad and Peshawar supply drinking water by groundwater. (R. Khan, Israili, Ahmad, & Mohan, 2005) Almost all cities that depend on surface suppliers face shortages whereas, the condition of Lahore and Peshawar is better because of high yielding aquifers. (Zahra & Khan, 2019a)

1.1.1.3 Sanitation and Sewerage

In Pakistan coverage of sanitation is only sixty per cent in urban region and 13.5% in rural region. Mostly the wastewater generated from the municipal areas of most cities is discharged into natural surface water reservoirs.

Table 2 The estimated flow of water and sewage in cities Source: (Zahra & Khan, 2019a)

CITY	Population 1998 (million)	Water Rate	Water Supply		Sewage Flow	
			Rate (gpcd)	Total (mgd)	Rate (gpcd)	Total (mgd)
Islamabad	0.525	80	4200	80	64	3360
Karachi	9.269	60	55615	80	48	44492
Lahore	5.063	80	40508	85	68	34432
Faisalabad	1.977	50	9886	80	40	7090

Multan	1.182	50	5912	80	40	4730
Hyderabad	1.151	50	5756	80	40	4605
Gujranwala	1.124	50	5624	80	40	4499
Peshawar	0.988	60	5928	80	48	4742
Quetta	0.560	40	2241	80	32	1793
Sargodha	0.455	40	1821	80	32	1457
Sialkot	0.417	45	1879	80	36	1503
Sukkur	0.329	50	1646	80	40	1317
Mardan	0.244	50	1223	80	40	978
Kasur	0.241	40	967	80	32	773

Sewerage is collected and disposed of through a managed system. RCC pipes and open drains are utilized for the collection of the sewage, and then is dumped in water bodies in the vicinity either naturally or through the proper installation of sewage pump stations (Javed & Kabeer, 2018) Where such facilities are not available, sewage is directly discharged into the groundwater without passing through any treatment process through soakage wells. It usually results in the formation of huge ponds (Zahra & Khan, 2019b)

Currently, there are very few plants for the treatment of effluents in the municipal sector. Ideally, sewage through pass through primary treatment in which large particles like a wooden blog, plastic pieces etc., are separated then comes the primary treatment in which chemicals are used for the processes of sedimentation or flocculation in which the contaminates and smaller particles are separated, then secondary processing is done in which microbes are used for biodegradation of the organic matter and the last step is tertiary processing in which water is purified by the use of chemical like ozone, the treated water is than safe to use for agricultural process and can even be utilized in industries for different purposes like washing etc.(A. Y. Khan, Fatima, & Ali, 2021)

1.1.1.4 **Industrial waste water**

The waste generated by the industries goes untreated into nearby water facilities. Industrial effluents have toxic chemicals like heavy metals and several industries especially food and pharmaceutical companies generate both biological and chemical waste. (Mikosch, Berger, Huber, & Finkbeiner, 2021)

Pakistan has many industrial zones and almost all of them are located near the main cities of Pakistan like Faisalabad, Sialkot, Lahore, Karachi, Peshawar, Kasur and Hyderabad. These domains discharge industrial effluents without any processing into the streams from where it further flows to the sea via rivers. Whereas in the case of isolated industries, the waste is disposed of in nearby fields or waterbodies and such ponds can be frequently observed near industries. (Zahra & Khan, 2019b)

It's now mandatory to have treatment facilities for multinational companies in order to do business across the globe. But still, developing countries are lagging far behind in adopting such practices, the main reasons could be the lack of awareness that how deadly the effluents can be or lack of will to spend money on such treatment plants. (Mikosch et al., 2021)

Currently, in Pakistan, industrial water effluents are discharged directly into water reservoirs and such water is mainly being used for the purpose of irrigation for four decades. It has been observed in Punjab that farmers used to irrigate the crops twice every year with contaminated water discharged from industry. This type of water is not only contaminated with toxic chemicals, pathogenic microbes but is also contaminated with heavy metals. (R. Khan et al., 2005) These toxic metals accumulate in the soil and gradually pass into the crops and the edible parts of crops and finally into the food chain, resulting in a great threat to humans and animals. Even the imbalance of trace elements because of the industrial effluents can also cause retardation in growth and metabolic processes. So, the toxicity of heavy metals in irrigation is an essential topic for industrialists and researchers (Noreen et al., 2019) The process of mining also increases toxicity levels in the water reservoirs (Javed & Kabeer, 2018)

1.1.2 Water quality

Water quality is a collective of all the characteristics of the water including chemical, biological and physical, especially in regards to whether it is suitable for any desired use like drinking or irrigation. (Daniels, Scott, Haggard, Sharpley, & Daniel, 2009) Water quality standards are ensured to protect any uses of a water resource. For the evaluation of whether a water body meets the standards set, quality assessments are performed by authorities determined by the set parameters. (Daniels et al., 2009)

All the activities and the reactions on the water, from the environment varies from location to location as well as its depth, which then collectively affect the quality of water. The water quality may be affected due to impurities that are physical, biological and chemical in characteristics. The most critical among these is the biological contamination, which may cause health issues or even lead to fatal conditions. (Deeba, Abbas, Butt, & Irfan, 2019) Due to the flowing nature, the biological contaminants may be transported from one location to another. Industrial and domestic waster disperses toxic chemicals to water bodies, or they may leach into the freshwater or groundwater. The rainy season takes the bacterial dispersion at its peak, which leads to various water-borne diseases. (Daud et al., 2017).

1.1.2.1 Quality Standards For Drinking Water In Pakistan

Table 3 Chemical Assessment Parameters according to Pakistan Standard. Source (Khwaja & Aslam, 2018)

Essential inorganic	**mg/L**
Aluminum (Al) mg/L	≤0.2
Antimony (Sb)	≤0.005 (P)
Arsenic (As)	≤0.05 (P)
Barium (Ba)	0.7
Boron (B)	0.3

Cadmium (Cd)	0.01
Chloride (Cl)	<250
Chromium (Cr)	≤0.05
Copper (Cu)	2
Toxic inorganic	**mg/L**
Cyanide (CN)	≤0.05
Fluoride (F)	≤1.5
Lead (Pb)	≤0.05
Manganese (Mn)	≤0.5
Mercury (Hg)	≤0.001
Nickel (Ni)	≤0.02
Nitrate (NO_3)	≤50

Nitrite (NO_2)	≤3 (P)
Selenium (Se)	0.01 (P)
Residual chlorine	0.2–0.5 at the consumer end, 0.5–1.5 at source
Zinc (Zn)	5.0
Phenolic compounds (phenols) mg/L	≤0.002
Polyaromatic hydrocarbons (PAH) g/L	0.01 (by GC/MS method)

Various raw municipal and industrial effluents, in addition to the agricultural runoff, have led to the decline in surface water quality. Mostly drinking, water comes from the underground or surface aquifers, which are found near the canals or rivers. When the river flow reaches its apex, it consists of excessive solid suspension (Khuhawar, Brohi, Jahangir, & Lanjwani, 2018). These water bodies are also contaminated with fecal waste, and toxic effluents, which require suitable processing and treatment before using for drinking. The drinking water supply lines are intermixed with sewer lines, which come from domestic as well industrial sources. (Daud et al., 2017) Many rural areas do not have pretreatment facilities, which mean water reaching these areas for drinking purposes is actually of very poor quality.

1.1.2.2 Quality Standards For Municipal And Liquid Industrial Effluents In Pakistan

The quality standards defined for industrial waste in Pakistan are articulated in Table 4.

Table 4 National Environmental Quality Standards for Municipal and Liquid Industrial Effluents mg/L unless otherwise defined, Source: NEQs, 2000

Parameter	Into Inland Waters	Into the Sewage Treatment	Into the Sea
Temperature	$\leq 3^oC$	$\leq 3^oC$	$\leq 3^oC$
pH	6-9	6-9	6-9
BOD at 20ºC	80	250	80
COD at 20ºC	150	400	400
TSS at 20ºC	200	400	200
TDS	3500	3500	3500
Oil and Grease	10	10	10

Phenolic compounds	0.1	0.3	0.3
Chloride	1000	1000	SC
Fluoride	10	10	10
Cyanide	1.0	1.0	1.0
Anionic detergents	20	20	20
Sulphate	600	1000	SC
Sulphide	1.0	1.0	1.0
Ammonia	40	40	40
Pesticides	0.15	0.15	0.15

Cadmium	0.1	0.1	0.1
Chromium	1.0	1.0	1.0
Copper	1.0	1.0	1.0
Lead	0.5	0.5	0.5
Mercury	0.01	0.01	0.01
Selenium	0.5	0.5	0.5
Nickel	1.0	1.0	1.0
Silver	1.0	1.0	1.0
Total toxic metals	2.0	2.0	2.0

Zinc	5.0	5.0	5.0
Arsenic	1.0	1.0	1.0
Barium	1.5	1.5	1.5
Iron	8.0	8.0	8.0
Manganese	1.5	1.5	1.5
Boron	6.0	6.0	6.0
Chlorine	1.0	1.0	1.0

1.1.2.3 **Water Quality Parameters**

These can be classified as: physical, biological and chemical. The physical parameters include color, taste, odor, TDS (total dissolved solids), total hardness as $CaCO_3$, turbidity and pH (Deeba et al., 2019)

1.1.2.3.1 Total Hardness

The total hardness is measured in terms of calcium and magnesium hardness. It is the total concentration of the calcium and magnesium ions expressed as an equivalent of $CaCO_{3.}$(Racho & Namseethan, 2017) It should be under 75 to 85 mg/l as $CaCO_3$. Magnesium hardness needs to be less than 40 mg/l as $CaCO_{3,}$ in order to reduce scaling at a higher temperature. (Racho & Namseethan, 2017) According to Pakistan Standards, the total hardness as $CaCO_3$ must be <500 mg/l. (Daud et al., 2017)

1.1.2.3.2 Turbidity

Turbidity is an evaluation of the clarity, which is affected due to fine particles, amount of suspended solids and dissolved colored substances. Highly turbid water would have more haziness (World Health Organisation, 2017). It is a highly beneficial indicator giving significant information in an inexpensive way. Sources of turbidity are varied like clay, silts, organic debris and chemical precipitates etc. It is usually measured through the turbidimetric method, others include formazin, or Jackson candle. (World Health Organisation, 2017)The turbidity needs to be <5 NTU according to Pakistan Standards. (Khwaja & Aslam, 2018)

1.1.2.3.3 TDS

TDS is a quantification of the total concentration of dissolved substances in the water sample. It includes inorganic salts in addition to a small number of organic substances These salts may be cations-positively charged-like calcium, magnesium, sodium and potassium, or anions-negatively charged- like chlorides, carbonates, bicarbonates, nitrates, and sulfates. (Corwin & Yemoto, 2020) High TDS in water does not mean it is a health hazard. The mineral water in packaged bottles contains raised levels of dissolved solids. However greater values of TDS, more than 1200 mg/l are unacceptable and produces hard water. (Corwin & Yemoto, 2020) The hard water is not only a health hazard and harmful to humans but also a hazard for the pipes and filters, as it causes a buildup of minerals. For Pakistan standard, TDS needs to be <1000 mg/l (Daud et al., 2017)

1.1.2.3.4 pH

The pH is a measure of how acid or basic the water is. The pH scale values are from 0 to 14, where 7 points to neutral. The pH values lower than 7 are acidic, and above 7 are basic. NSDWQ-Pak has set the pH of drinkable water to be around 6.5 to 8.5.

1.1.2.3.5 Chemical Assessment

The chemical assessment includes the quantities of inorganic substances like Arsenic, Fluoride, Chloride, Lead and copper etc. Since it also includes toxic inorganics, the levels of each are specified, to avoid toxicity in drinkable water.

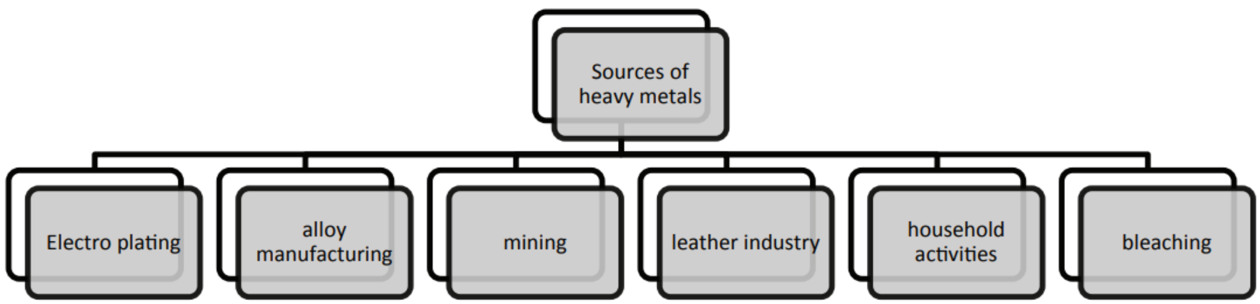


Figure 1 Main sources of heavy metals

1.1.2.3.6 Biochemical DO, BOD and COD

Oxygen is quantified in its dissolved state, as dissolved oxygen (DO). DO levels are dropped when more oxygen is utilized than is produced. In lower levels of DO, many animals cannot survive. (Haider, Al, & Haydar, 2016)

Microorganisms continuously decompose organic material in wastewater, using oxygen in the process. The quantity of oxygen utilized by these organisms for decomposing organic waste is called biochemical oxygen demand (BOD). (Haider et al., 2016)

Chemical Oxygen Demand is the quantification of every oxidizable chemical in the water. It is the amount of oxygen consumed in chemical oxidation occurring in the water. (Geerdink, van den Hurk, & Epema, 2017)

1.1.2.3.7 Microbiological assessment

It includes all the microorganisms, that pose a serious threat to human health, although all the microorganism found in water are not harmful. (SDWF, 2019)

Some protozoan parasites cause ill health effects like the Cryptosporidium causes gastrointestinal disease with the severity of disease leading to the weakened immune system. Giardia lamblia causes beaver fever. (SDWF, 2019)

Algae can impact the physical properties of water, in addition to some producing dangerous toxins eg. Blue-green algae releases hepatotoxins and neurotoxins. (SDWF, 2019)

Bacteria are the most common cause of water-borne diseases, e.g *Escherichia coli* causes gastroenteritis and kidney failure, *Salmonella* species cause anorexia, arthritis and meningitis, and *Campylobacter jejuni* also causes meningitis and in severe cases paralysis. *Shigella* species cause dysentery and kidney failure, *Vibrio cholere* is the leading cause of cholera and *Yersinis enterocolitica* causes joint pain and gastroenteritis (SDWF, 2019)

The Pakistan Standard sets out bacterial parameters which include "E.coli or thermotolerant coliform bacteria and total coliform bacteria must not be detectable in any 100 ml sample of…" (Khwaja & Aslam, 2018) water for drinking, any treated water entering the system, and treated water in the distribution system. For larger supplies, these species of bacteria must not be in 95% of the samples taken in one year consistently. (Khwaja & Aslam, 2018)

1.1.2.4 **Water Quality in Islamabad and Rawalpindi**

From a total of 130 samples tested in the twin cities, 56.1% were observed with microbial contamination. The presence of E.coli was 20%, total coliforms were 12.3% and fecal coliforms were 23.8% (Khwaja & Aslam, 2018) Other parameters show TDS, alkalinity and hardness were at safe levels. However, the amount of magnesium and calcium carbonate has led to a higher level of hardness in some of the areas of Islamabad. (Khwaja & Aslam, 2018)

1.1.2.5 Water Quality in Punjab

The physicochemical evaluation of drinking water from Faisalabad was conducted. The hardness, pH and turbidity were within safe and permissible limits. However, all the samples were found to have E. coli and total coliforms. The water temperature of samples from supply lines was very high, which is usually due to microbial activity. The alkalinity, sulphates, chlorides and TDs were observed to be higher than the safe limits. (Daud et al., 2017)

Samples from Lahore showed that they were within the safe pH limits. The turbidity, however, was less than the necessary limit of 0.5 NTU. In addition, the TDS was also within the critical levels. (Daud et al., 2017)

Other cities also show microbial contamination in 73%, 94%, and 100% of the drinking water samples Sheikhupura, Multan and Kasur respectively. TDS in most of the cities was found to be above the acceptable levels (Daud et al., 2017) Fecal coliform bacteria were not found in these areas, however, E. coli was present in most of the samples.

Water in River Ravi was a little alkaline with pH 8.5, and excessive concentrations of BOD, EC, Cr, Mn, Fe and Pb. This is due to sewage and industrial waste, making it unfit for human consumption and irrigation. (Shahid et al., 2019)

Characteristics of polluted river water collected from river Ravi, Lahore, Pakistan.

Parameter	Value	Water quality guidelines (WWF)		NEQs (Pakistan)
		Irrigation	Fish/aquatic life	Wastewater discharge
pH	8.5 (0.10)	6.5–8.4	6.5–8.5	6–9
EC (mS cm^{-1})	2.3 (0.04)	15	15	NG
TSS (mg l^{-1})	290 (38)	NG	NG	150
COD (mg l^{-1})	405 (6.24)	NG	NG	150
BOD_5 (mg l^{-1})	190.3 (5.51)	NG	8	80
TOC (mg l^{-1})	110.5 (2.00)	NG	NG	NG
TN (mg l^{-1})	37.5 (1.14)	NG	NG	NG
NO_3^{-1} (mg l^{-1})	33.3 (1.53)	NG	NG	50
TP (mg l^{-1})	2.63 (0.12)	NG	NG	NG
Fe (mg l^{-1})	1.53 (0.12)	5.0	0.3	8.0
Ni (mg l^{-1})	0.54 (0.01)	0.20	0.05	1.0
Mn (mg l^{-1})	0.85 (0.02)	0.20	0.1	1.5
Pb (mg l^{-1})	0.83 (0.06)	0.1	0.01	0.5
Cr (mg l^{-1})	0.36 (0.02)	0.01	0.05	1.0

[*]Water Quality Guidelines for Pakistan proposed by World Wide Fund (WWF) for Nature, Pakistan (2007). NEQs: National Environmental Quality Standards. NG: Not given in the list. Standard deviation are presented in parenthesis.

Figure 2 River Ravi water quality Source (Shahid et al., 2019)

1.1.2.6 **Water Quality in Khyber Pakhtunkhwa**

From the samples collected in Peshawar, 13% did not have microbiological contamination, and 47% had high contamination of E. coli. TDS, turbidity and carbonates were in permissible limits, however, the magnesium was above the safe limit. Samples from rural areas of Peshawar showed they had slightly higher concentrations of Cobalt, Mercury, Arsenic, Copper, zinc and Nickel. Lead and Cadmium were in significantly higher concentrations, which makes them unfit for drinking. TSS (Total suspended solids) were found to be 60% at storage points in the distribution channels. (Daud et al., 2017)

1.1.2.7 **Water Quality in Baluchistan**

The water quality assessment in Ziarat, Quetta, Khuzdar and Loralai was found to be critically contaminated with harmful microorganisms. The concentration of nitrates was higher than the permissible levels, in more than 50% of these samples. The electrical conductivity and Chemical Oxygen Demand (COD) was found to be higher than the recommended levels. Drinking water in Quetta also lacks other physical characteristics, with a foul odor, bad taste and with 39% pathogens.

1.1.2.8 **Water Quality in Sindh**

Drinking water in Khairpur was found to be unsuitable for drinking, as it had high levels of coliform bacteria and fecal coliform. The quality of water deteriorates as it goes further down the distribution system because of the leaks in the pipes at points where contaminated sewage water goes in the supply water. (Daud et al., 2017)

Samples from Karachi were tested and analyzed. They indicated that the water quality was acceptable, they were highly polluted with E. coli, total coliform and fecal coliform. pH, temperature, TDs, and turbidity were within safe limits.

Samples from Sukkur and Hyderabad showed significant microbial and chemical contamination, making it unfit for human consumption.

1.2 Water Pollution and it's Health Impacts

Water pollution is a relative expression which means that it depends on the intended water use. If water is to be used for drinking, a small quantity of contaminant would qualify the water sample as polluted, however, if the intended use is irrigation, the very same sample would not be considered as polluted. (Walker et al., 2019) From pathogens to chemicals, there are many sources of pollution.

Water pollution, along with overuse and climate change, has led to 80% of the global population being endangered of water shortage. (Nabi, Ali, Khan, & Kumar, 2019) Pakistan ranks 3rd, among all the countries that face water scarcity. According to the Pakistan Council of Research in Water Resources (PCRWR), there would be left with little or no unpolluted water by the year 2025, in Pakistan (Nabi et al., 2019). Water pollution not only leads to lower water quality but also affects human, plants and animal health. In Pakistan, waterborne microorganisms account for 40-50% of gastroenteritis, 47-59% diarrhea, 28- 35% dysentery, 35% hepatitis A, 15% hepatitis B and 5% of hepatitis C. (Daud et al., 2017). Water pollution has caused more than two million deaths per year worldwide due to waterborne diseases like typhoid, cholera, polio and other infections (Chen et al., 2019)

1.2.1 Surface Water

Surface Water pollution is the release or emission of various materials into the rivers, lakes, oceans, such that the materials effect and inhibit the efficacy of the water for personal and industrial use or even disturb the natural ecosystem. (Walker et al., 2019) There are many ways water gets polluted including biological, physical and chemical sources as discussed above. Viruses mostly occur due to contamination from human and animal fecal waste. Some waterborne viruses include Astovirus causing Gastroenteritis, Coxsackievirus A causes meningitis and Coxsackievirus cause heart diseases, diabetes myelitis and eye infections. Echoviruses lead to rash fever and gastroenteritis, Hepatitis A and E cause Hepatitis, which may further lead to liver failure in severe cases. Poliovirus causes paralysis. (SDWF, 2019)

Many people in Pakistan rely on water polluted by sewerage, fertilizers and industrial contaminants. This polluted water is accountable for 80% of all illnesses or infections and 30% of the fatalities (Nabi et al., 2019).Approximately 4000 cases of Hepatitis were recorded only in Islamabad, which were attributed to unsuitable and contaminated water.

1.2.2 Sub Surface Water

Sub surface water pollution is the release or emission of various materials into the ground. In a case study various areas in Punjab showed higher values of iron, manganese, lead, chloride ions, nitrates and sulphates in groundwater, which made them unfit for drinking. In villages, an analysis showed municipal wastewater contamination which was causing gastroenteritis. (Daud et al., 2017) e.g. Tanneries in Kasur have contaminated the groundwater, leading to skin diseases and gastroenteritis, in addition to dental fluorosis. (Daud et al., 2017

The ground water of different rural areas in the province of Sindh also indicated that all the samples were unfit, not only for human consumption, but also for irrigation purpose, due to microbiological contamination. (J. Ahmed, Wong, Chua, & Channa, 2020) In addition, the organic and fecal contamination, turbidity and most of the chemical parameter were higher than the critical limits. Only phosphates, sulfates and pH were within the limit (J. Ahmed et al., 2020)

Similar results were concluded in other two provinces. There are more than 60 million Pakistanis who are at a risk of being impacted by very high levels of heavy metal due to drinking contaminated water specially arsenic (Guglielmi, 2017) Arsenic poisoning leads to pulmonary diseases, cancer, cardiovascular issues, diabetes, neurological issues in addition to kidney and liver problems. (Chen et al., 2019).

1.2.3 Major Source of Pollution

Water pollution due to contaminants from municipalities, resource extraction-production, construction, industry and agriculture are among the key sources in Pakistan. Most of the contaminants are from anthropogenic processes and materials. (Chen et al., 2019). To avoid contamination of drinking water, the water distribution should be properly maintained with chlorination done according to the regulations. Proper functioning, quality assurance, and analysis are required to keep drinking water up to par with the set standards. (J. Ahmed et al., 2020)

We will limit our research to Heavy Metals only as it lies within the scope of study.

1.2.4 Permissible limits of Heavy metals

Heavy metals are necessary to sustain life, but in high concentrations, most of them pose a serious threat. The accumulation of heavy metals in water from industrial effluents can lead to three things: water pollution, soil pollution and bio-accumulation. The water pollution will make the drinking water and irrigation water contaminated. Drinking water with toxic metals will lead to various diseases(Waseem et al., 2014). The water for irrigation will reach the crops and increase heavy metal content in them. From the water, many heavy metals have the characteristic of seeping into the soil. Heavy metals in soil are a huge risk because soil retains it longer than anything else. From the soil, they will reach the crops. Humans will end up taking more heavy metals than necessary, and they will start affecting normal body functions, a phenomenon known as bio-accumulation (W. Rehman, Zeb, Noor, & Nawaz, 2008)

A survey in 2014 indicated that the levels of various heavy metals in Pakistan were quite high in the major waterbodies utilized in daily use and agricultural uses, as seen in figure 3 and 4 (Waseem et al., 2014). Heavy metals have detrimental effects on human health in addition to the flora and fauna utilizing the polluted water. In order to prevent that, international organizations set limits for the levels of heavy metals discharged in the wastewater from any industrial unit. Every industry needs to follow the regulations of the local government.

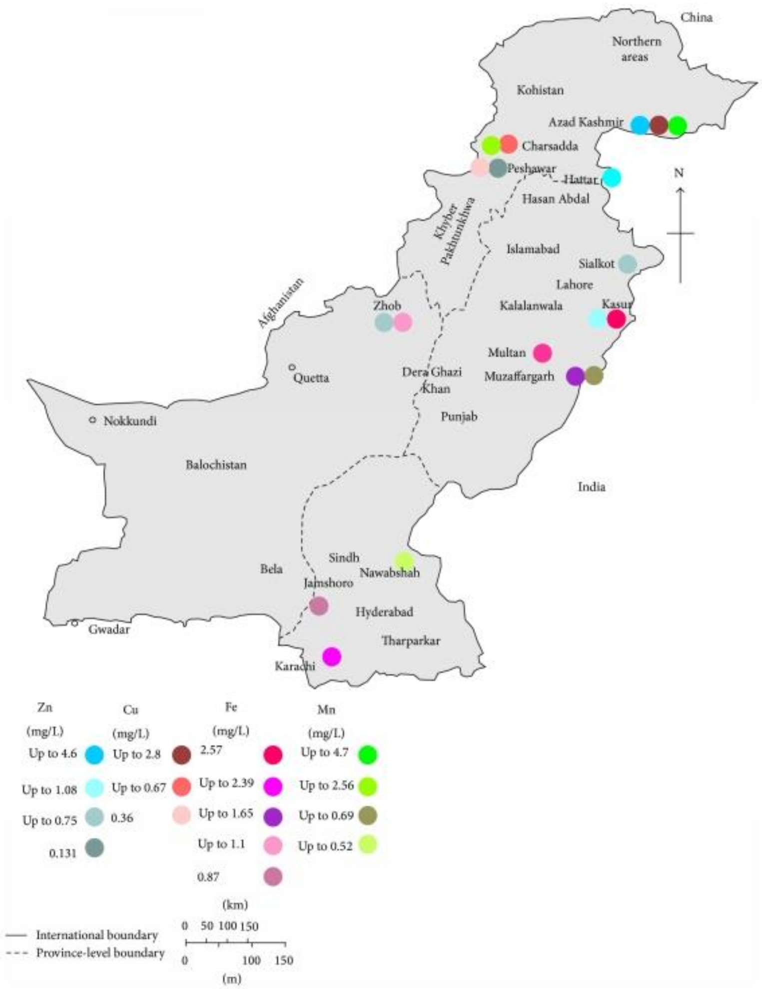


Figure 3 Map of Pakistan that shows zinc, copper, iron and manganese in ground water Source: (Waseem et al., 2014)

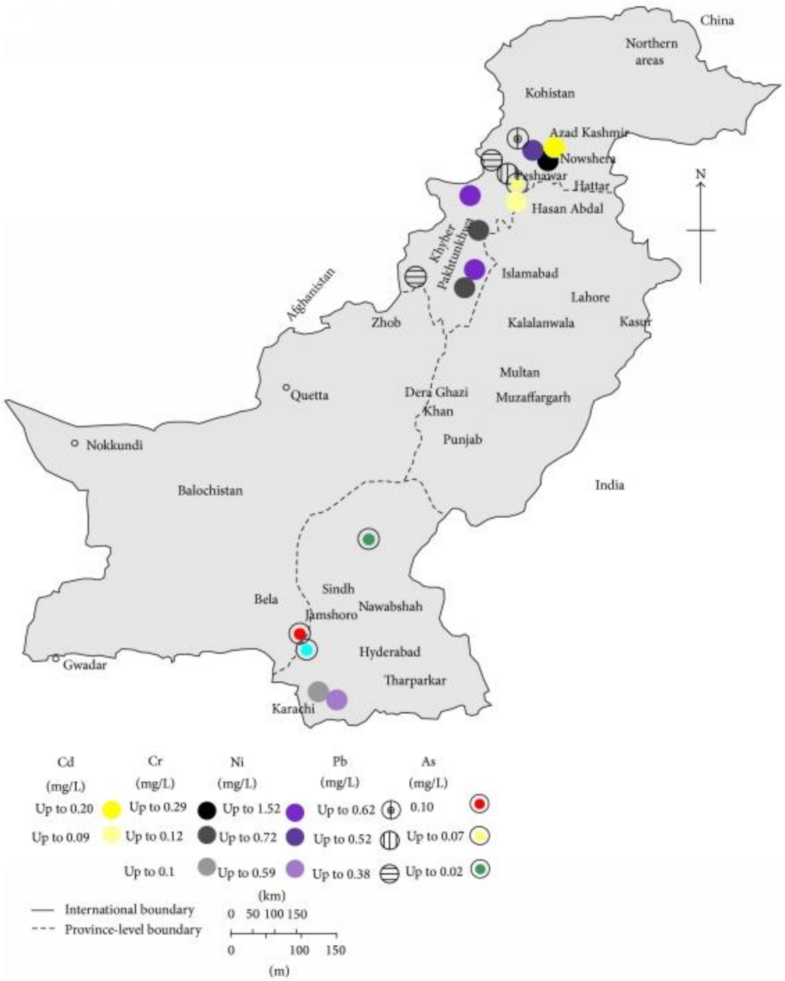


Figure 4 Map of Pakistan that shows the concentration of cadmium, chromium, nickel, lead and arsenic in surface water Source: (Waseem et al., 2014)

The Environmental Protection Agency allows the release of heavy metals into the environment to be less than 2.0 mg/L. Pakistan industrial sector follows the National Environmental Quality

Standards for Municipal and Liquid Industrial Effluents, see Table 5 (NEQS, 2000) This standard was revised in 1999, with updated values for all the parameters.

1.2.4.1 Arsenic

It is one of the most toxic metals. It may be organic or inorganic. The inorganic carcinogen is carcinogenic. The mono- or dimethylarsinic acids are organic arsenic compounds that also possibly cause various types of cancer. The International Agency for Research on Cancer (IARC) categorizes Arsenic in its organic form as Group 1 and the organic arsenic compounds as Group 2B (IARC, 2021). Elevated exposure to arsenic causes various cancers including kidney, liver, lung, colon, and bladder in addition to skin cancer. High concentrations of arsenic were found in Punjab and Sindh. The level of contamination in Punjab was 3%, and in Sindh, it was 16%, with a contamination level of more than 50µg/L. 10 µg/L of As was found to be present in 20%of water resources in Punjab and 36% in Sindh. A national survey presented that from 8712 samples, 9% (Waseem et al., 2014) were found with high concentrations of As, above 10µg/L, which is the permissible level set by WHO and NEQs, see Table 5 (NEQS, 2000). 0.70% of these samples had As the concentration of above 50µg/L. (Waseem et al., 2014). As was also found accumulated n mint, spinach and coriander, in Sindh, at around 0.9 to 1.2 mg/L.

1.2.4.2 Cadmium

Cadmium exists naturally in the environment and seawater. It is highly toxic and is categorized as Group 1 (IARC, 2021) Elevated levels of cadmium lead to cancers on the lung, prostate and kidney. In addition, the intoxication of cadmium leads to itai-itai disease, lung diseases, bone damage, and kidney issues. The levels of Cadmium set as the permissible limit is 0.1 mg/L (NEQS, 2000), as compared to the WHO recommended level which is 0.003 mg/l. (Khwaja & Aslam, 2018) . Metal plating, mining, steel, and marbles industrial units create effluents with high cadmium concentration. In Pakistan, the observed levels have gone as above as 0.21 to 0.29 mg/l in KPK province (I. Rehman et al., 2020), and 5.35 mg/l in the Korangi industrial area of Sindh (Waseem et al., 2014) The soil sampling indicated high concentrations of 24.34 mg/kg in Girzi Creek and

21.34 mg/kg in Lyari, Karachi. (Waseem et al., 2014). Airborne Cadmium was also found in Pakistan at the concentration of 5 ng/m^3 (Waseem et al., 2014)

1.2.4.3 Lead

Lead in its inorganic form is categorized as Group 2A, i.e. probably carcinogenic and its organic compounds are classified as Group, which means not classifiable as carcinogenic (IARC, 2021). Constant exposure can lead to cardiovascular disease, hypertension and weakened kidneys, in addition to prostate diseases. Children getting higher exposure to lead will have lead poisoning, which may lead to behavioural issues, learning disabilities and other brain dysfunctions. Pregnant women with lead poisoning may give birth to underweight, premature babies with possible slower brain functions and developmental growth (Miracle, 2017)

Lead occurs naturally in as a compound called galena, however, the reason for present higher concentrations in the environment are due to anthropogenic activities. When it is mined to its processing, from any point, it can be released into the environment. The acceptable level for lead is 0.01 mg/l for water meant for drinking and for wastewater it is 0.5 mg/l (NEQS, 2000). A study on the Hattar industrial estate exhibited levels that were well above the permissible level, 0.26mg/l. Another industrial city analyzed, and 100% of the samples had values above the permissible level. (Waseem et al., 2014)

The highest levels of the metal lead were found in the coastal area 121 mg/kg was found in the sediments (Waseem et al., 2014) Elevated level of lead has also been found in the airborne particulate matter, soil, and the vegetation. Through all these sources, higher exposure may cause lead poisoning. This is concerning because it will affect the health of children and adults in the worse way possible. (Miracle, 2017)

1.2.4.4 **Nickel**

Nickel is naturally found in the environment and the organisms. It is classified as Group 1, meaning they are carcinogenic (IARC, 2021). High exposure to nickel can cause toxic effects that may lead to nasal and lung cancer, lung fibrosis, epigenetic effects, skin issues, and gastrointestinal problems. Many compounds of nickel are the reason for sinus, nasal and lung cancers. (Genchi, Carocci, Lauria, Sinicropi, & Catalano, 2020).

Nickel is discharged into the environment due to the processes of mining, smelting and refining. It is also released due to solid waste incineration of the waste containing high levels of nickel alloys and compounds. The maximum level set as permissible is 0.07 by WHO, however, the NSDWQ-Pak has set the limit to a 0.02 mg/L for drinking water (Dil, Qazi, Baig, Khan, & Tahir, 2008). For wastewater, the amount of nickel permissible is 0.1 mg/l. Wastewater collected from various locations of Pakistan was found to be in of 0.91 to 5.94 mg/l, which are way above the permissible limits. In coastal sediments in Karachi, 74 mg/kg of Nickle was found in the area of Lyari (Waseem et al., 2014)

1.2.4.5 **Copper**

Copper plays a vital role as a reductant in the various enzymes that help reduce molecular oxygen. 0.90 mg/day of copper is the RDA (Recommended Daily Allowance) for adults. However, extremely elevated levels of copper through various sources like water and food can lead to damaging the liver, heart, kidney and brain. (M. Rehman et al., 2019) It is released from the plumbing systems and during the manufacture of various alloys. (Shrivastava, 2009)

The permissible level of copper is 1.0 for wastewater (NEQS, 2000) and 2.0 mg/l for drinking water (Khwaja & Aslam, 2018). The surface and groundwater samples from Pakistan indicated that copper levels were within permissible levels. One study found it to be around 2.8 mg/l in one sample of municipal water in Azaz Jammu and Kashmir. The sediment from River Ravi, however, showed alarming amounts of copper at 159.79 mg/kg. (Waseem et al., 2014)

1.2.4.6 **Chromium**

There are two forms of chromium, +3 (Cr III) and +6 (Cr Vi). Cr III has food utilization for human beings, and the adequate amount for copper is considered to be 25-35 µg/day. Cr VI is the toxic form of copper, classified as Group 1 i.e. carcinogenic (IARC, 2021). Cr VI may cause lung and nasal cancer if exposed to constant high exposure. Chromium is notable for its use in pigments, wood preservation process, and finishing of metals. The dying and leather tanning leads to the accumulation of copper in the water streams.

The permissible levels of copper according to national standards is 1.0 mg/l in wastewater (NEQS, 2000) and in drinking water its 2.0 mg/l (Dil et al., 2008). The highest level of copper was found in samples taken from wells in Kasur, with contamination levels ranging from <0.001 to 9.8 mg/l (Waseem et al., 2014). Surface water contamination in the samples from Bara River, Nowshera, was from 0.16 to 0.29 mg/l (Waseem et al., 2014)

1.2.4.7 **Iron**

Iron is one of the most important elements. It acts as a functional unit of many proteins and enzymes, like haemoglobin. The RDA for iron is 8 mg/day. Excessive intake of iron leads to gastrointestinal problems. (Schreinemachers & Ghio, 2016)

The permissible limit of iron in wastewater is 8.0 mg/l (NEQS, 2000), whereas no guideline is provided by NSDWQ-Pak (Dil et al., 2008). Iron concentrations were found to be highest in groundwater samples from Kasur 11.8 mg/l and Jamshoro 4.28 mg/l (Waseem et al., 2014). Wastewater from most other areas in Pakistan was at an acceptable level. The soil in Kohistan contaminated with around 25080 to 26960 mg/kg, which is extremely high and toxic to the environment. (Waseem et al., 2014)

1.2.4.8 Zinc

Zinc is one of the essential nutrients and helps with many body processes like enzyme activity, gene expression regulation and the formation of protein structure. Although it is necessary for organisms, its high concentration leads to gastrointestinal issues and a weakened immune system. The daily recommended amount of zinc is 8 to 11 mg per day (Hajianfar et al., 2021)

The permissible limit for zinc is 5 mg/L (NEQS, 2000) for drinking water. For sewage sludge, it is around 150 to 300 mg per kg. In a case study of water and soil assessment of Chitral, Zn exceeded the limits by 94% in soil. (I. Rehman et al., 2020)

1.3 Role of various Industries (specifically cement, steel and leather)

The biggest role in terms of water use and water pollution is played by the production processes of various industries that include, but are not limited to, steel, cement, leather, marble and glass. (Gerbens-Leenes et al., 2018) These industrial giants have operations that have led to the irreversible damages to water pollution, soil degradation and serious toxic waste production.

The industrial sector of Pakistan includes various small medium and large plants, that have all kinds of technological units. Most of these plants are located in Faisalabad, Karachi, Sialkot, Multan, Kasur and Lahore. The industrial sector has many subunits including textile, cement, dyes and fibres, pharmaceuticals, Steel mills, oil and leather. (Shah, Manzoor, & Hashim, 2021) Pakistan lacks the implementation of environmental protection laws, rules and regulations, which is the reason that levels of industrial toxic effluents are rising day by day.

In Pakistan, industrial wastewater is released into the sewer lines, a waterbody, a nearby field or a septic tank. In big cities like Karachi and Islamabad, the wastewater is treated and then released, however, other cities do not treat water before disposing it off. (Amjad et al., 2019)

The industrial sector has led to the production of 250 tonne CO (Carbon monoxide), 378 tonne SO_2 (Sulphur dioxide), 162 tonnes of nitrogen oxides, in addition to more than 3700 tonnes of heavy metals like mercury, cadmium arsenic and other organic contaminants. (Shah et al., 2021)

The reason for the increasing levels of pollution due to the industrial sector is that in Pakistan there is a lack of policies and monitoring systems. (Ali, Zhang, & Yue, 2020) The growth of industries is unplanned and industrialists keep on closing the gap between the general population and various plants, which has led to people getting polluted water to drink, and polluted air to breathe. Many industries have the option of selecting sustainable options for the disposal of wastewater, but they refuse due to lenient laws and ease of use. (I. Rehman et al., 2020)

Anwar & Anwar (2020) conducted a case study on groundwater from Kasur, Kala Shah Kaku and Lahore industrial area and observed that heavy metals were coming from various sources. A total of 40 groundwater samples from various industries, including steel mills, textile, chemical, pharmaceutical and leather were collected. A comprehensive analysis indicated that chromium and copper values were high due to tanneries, steel mills were accountable for zinc, lead and cadmium, and manganese came from the aluminum industries, textile industry increased magnesium in the wastewater. Nickel came from the wastewater discharge of metal factories, powerplants, stainless steel industries and batteries. (Anwar & Anwar, 2020)

1.3.1 Steel

Human civilization could not have developed without iron and steel. It has wide applications like the automotive industry, in the building of machinery and equipment. But its leading application is in the construction industry, which is the reason for almost more than half of the global steel production. Steel is developed from iron. When steel is mixed with other metals, it results in alloys like stainless steel. (Shah et al., 2021)

The production of steel takes six steps. It begins with the mining of the raw materials, processing, reduction of iron ore, air separation, production of ferroalloy and then steel production. The main source of cadmium, nickel and lead were found to be steel industries production(Shah et al., 2021)

A study of two steel mills indicated that samples from the waterbodies around a steel mill had high concentrations of cadmium were due to the untreated industrial waste from these mills. Lead was found to be greater than the permissible levels with the mean value of 0.12 mg/l. (Anwar & Anwar, 2020) The values for zinc also exceeded for one of the mills at 4.50 mg/l. The level of nickel in groundwater is high due to the stainless steel industry, reaching 1.30 mg/l. (Anwar & Anwar, 2020)

1.3.2 Cement industry

Worldwide, 150 countries produce cement. In Pakistan, 5.5 % of all industrial production accounts for cement production, providing 30 billion PKR annually. Pakistan cement production is among the top five exporters, and it is the 14th largest cement producer globally(Zeb, Ali, & Khan, 2018). Pakistan exports to Afghanistan, Russia, India, the UAE, and Iraq. Cement production has increased as the construction activities, residential societies and various other infrastructures have amplified in the last few years. However, it is also responsible for most of the toxic effluents in the environment. 5 % of the CO_2 emissions are due to the cement production processes (Ansari, 2019). These emissions occur during raw material transportation, utilization of electricity, and the processes involving combustion of fossil fuels, in addition to the process involving conversion of limestone to calcium oxide. (Zeb et al., 2018) In Pakistan, the laws regarding industrial effluents exist but are not strictly implemented. People in Pakistan are not aware of the danger various contaminants from the industry pose to the environment, various organisms including humans and their health. In addition, the workers are not usually educated, if any industry needs to implement the laws and treat any kind of solid or wastewater, they would have to train their workers, too. (Ansari, 2019)

Cement is a hydraulic binder requiring water for chemical reactions. Cement production mainly needs to go through three stages, which are extraction and preliminary processing, pyro processing and grinding and mixing. During the production (Gerbens-Leenes et al., 2018) A cement mill, limestone quarry, deposit sites and unpaved roads are the main sources of air pollution, leading to dust and high concentrations of Ca, Fe, Mg, S, limestone, K, and N. (Ansari, 2019) Released into the air, these compounds and heavy metals cause serious adverse effects to the animals, plants and human beings. The cement industry is the leading cause of noise pollution. Most of the times the workers do not wear protective equipment, and the noise level is a lot higher than 85 decibels, the normal range for humans. Constant exposure to the noise level above that causes hearing damage that may be temporary or permanent. (Zeb et al., 2018)

The cement industry remains one of the greatest reasons for water pollution around the areas where the industrial units are situated. A study on soil contamination showed around a cement factory in Bahtar, showed that on average 43.3 mg/l iron, 5.3 mg/l nickel and 1.01 mg/l Chromium was found, compared to the permissible limits, all of these were above them, see Table 4. (Zehra, Abbas, Naz, Hassan, & Idrees, 2017)

1.3.3 Leather industry

The leather industry is the 2nd largest contributor for the economy of Pakistan, providing more than 500,000 people employments. In 2015, the leather industry led to a contribution of 724 million US$ in export, almost 5% of total GDP in Pakistan, from the established leather industries in Sialkot, Kasur, Karachi, Multan, Lahore, Peshawar and Gujranwala. (Hashmi et al., 2017)

Although it is one of the most important industries in Pakistan economically, the waste it is producing is polluting the environment including water. The causes include the byproducts of the tanning process which lead to an increase in total dissolved solids, chemical oxygen demand, sulphates, chlorides and heavy metals. (Hashmi et al., 2017) Exposure to these leads to various disease like cancer, and respiratory tract and eye irritation. An agent in the leather industry, chromium III, has a harmful impact on the environment and is a hazard to human health. (Chen et al., 2019)

The leather industry leads to the hydrogen sulfide, ammonia, sulphur dioxide, carbon dioxide, chloride gas, and formic acid fumes are released into the environment from the leather finishing processes like liming, de-liming, and pickling. (China et al., 2020) The leather-making processes lead to 850 kg of solid wastes out of 1000 kg rawhide. The types of solid waste include pre-fleshing waste, lime fleshing waste, shaving, buffing and trimming wastes. The leather industry is found to be associated with water scarcity as well as water pollution. Approximately 4000 litres are used up for the processing of one ton of skin. Many of the leather industry effluents like chromium slat, formaldehyde, arsenic, toluene, acetene solvents, and benzene are likely to cause lung, bladder, kidney, oral and nasal cancers to the workers coming in direct contact without any protective equipment. (Hashmi et al., 2017) In addition, the water from the industry is pumped out to lakes, ponds and rivers untreated with all the harmful chemicals present in it. One tannery leads to the pollution of groundwater to the extent of almost 7-8 km of the perimeter around it.

The substances that are found in the polluted water around a tannery are calcium, chloride, sodium, magnesium, sulphate ions and Chromium 6 (China et al., 2020) These lead to the water hardness that gives rise to stomach issues, kidney stones, and cardiovascular diseases. The high level of sodium and chloride ions in the water produces unnecessary sodium chloride in the water meant for drinking, which leads to hypertension, cardiac arrest and asthma. (Khalid et al., 2021).

Waterbody in which the leather industry discharges its waste also has germanium and ammonium nitrogen. The high levels of germanium in drinking water can lead to lung cancer, and shrinkage of the nose membrane(China et al., 2020) The rise in the levels of nitrogen can lead to methemoglobinemia, in which babies are affected, Oxygen transport is disturbed due to nitrates. The overall water pH is turned acidic due to the heavy metals binding to sulfhydryl functional group in amino acids, which inhibits enzymes, and corrodes the intestine and mucosal membranes. (Khalid et al., 2021)

Khalid et al (2021) studied the metal concentrations in the environment due to the leather industry in Sialkot, revealed that all the metals were found to have elevated levels. Tanneries and their subprocesses lead to around 215,036.1 gallons of effluents in the city of Sialkot, which leads to polluted The pH of the water taken from five different sites is on average acidic due to toxicity from hydrogen sulfide from the tanneries (Khalid et al., 2021). The high concentrations of Mg, K, Mn, Na, and Ca are a consequence of the different salts of these elements utilized for the preliminary processing and basification in tanning. In one site, the EC was found to be 10.2 dSm^{-1} and TDS was 8,160 mgL^{-1} (Khalid et al., 2021). These off the chart's values were attributed to the saline nature of the effluents. Arsenic was discovered in very high concentrations of 119.1 mg kg-1 at one of the sites near a tannery (Khalid et al., 2021).

1.3.4 Marble industry

The marble industry plays an important role socioeconomically in Pakistan. However, when water is disposed of from the marble industry it contains more than 70% of the mineral utilized during the mining, processing and final polishing steps. Most of the times it is released into the environment without any treatment. (Ahmad, Khan, Ali, Fatima, & Ali, 2019)

Noreen et al (2019) studied how the marble industries in the urban area of Chitral in the district Mardan, effect the water bodies nearby. Water samples, in addition to the industry workers' blood samples, were collected from twelve different marble industries. The levels of copper, manganese, zinc, and arsenic were observed to be more than the acceptable levels of NEQs in all of the water samples, in addition, all of these were significantly bioaccumulated in the blood of the workers as well. (Noreen et al., 2019)

1.3.5 Impacts of Heavy Metals

A case study in Kasur quantified the heavy metals in water, soil, and vegetables,to evaluate the health impact of heavy metals on people. Kasur is located in Punjab. It has many industrial setups. Drain Rohi is used for disposing of the wastewater of all these industries. 48 groundwater samples, 48 soil samples were collected, in addition to one kilogram of the edible part of the vegetables (Ashraf, Ahmad, Sharif, Altaf, & Teng, 2021) The pH was mostly alkaline for all the samples, 7.93 to 8.17. the heavy metal concentration was calculated, and the results indicated that most of the toxic metals were present as shown in Table 5. All the heavy metals exceeded the permissible levels by NEQs.

This study evaluated the Hazard Index, which was the collective effect of the intake of the toxic elements from consuming the plants. The HI for adults was 9.10 for Tomato, 10.30 for Brinjal, 16.36 for Cabbage and 9.00 for Okra. All the values are higher than the permissible HI of 1.

In addition, this research studied the target cancer risk (TCR) TCR is the approximation of the predictability of cancer. If values are $\leq 10^{-6}$, it means that the risk of cancer is low, between 10^{-5} and 10^{-4}, means the risk is moderate and between 10^{-3} and 10^{-1}, means high risk of cancer. The result showed that the TCR values for Ni for all vegetables indicated a high risk for cancer. The TCR of chromium in cabbage also indicated high risk. The remaining metals showed a value for moderate risk, for all the vegetables (Ashraf et al., 2021)

Table 5 Highest concentrations of heavy metals in the case study of Kasur Source (Ashraf et al., 2021)

Metal	Highest Concentration mg/L
Arsenic	0.04
Cadmium	0.03
Cobalt	0.38

Chromium	1.09
Copper	2.17
Iron	0.54
Mercury	0.04
Manganese	0.31
Nickel	0.02
Lead	0.02
Zinc	3.4

1.4 Treatment of Wastewater

1.4.1 Conventional Techniques to Remove Heavy Metals

There are many ways to eliminate the heavy and toxic metals from the water before it is released into the environment including iron extraction, chemical precipitation, membrane separation, surface complexation, adsorption and electrolysis. (Abdel-Raouf & Abdul-Raheim, 2017) One of the most used techniques among these is adsorption in terms of being inexpensive, highly efficient, simple and still flexible (Niu, Li, Cao, Wang, & Wang, 2020)

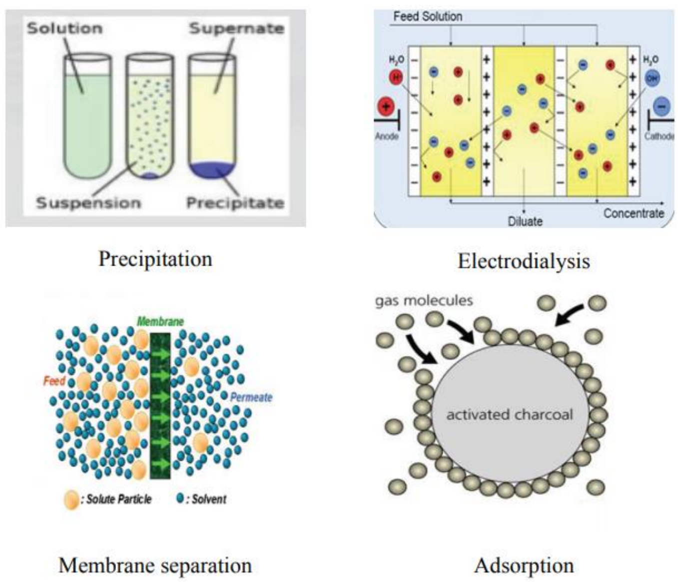


Figure 5 Techniques for removing heavy metals from wastewater Source:

1.5 Problem Statement

Because of the increased pollution problems in industrialized society, the study of contaminants in water, especially heavy metals, has become a major field in research. Due of their toxic properties, heavy metals are classified as major contaminants. Constant elevated exposure to heavy metals that include, but are not limited to, arsenic, mercury, zinc, and cadmium is likely to damage the essential organs of the people living near the source. These metals have entered the atmosphere as a result of their deposition in lakes and rivers. When eaten by humans, they can cause poisoning due to their toxicity.

Rivers are the most important resource of any country—especially one that is currently developing and is agriculturally dependent—because they provide irrigation for agriculture as well as drinking water. For an agricultural country such as Pakistan this issue is of the utmost pertinence. Industrialization has resulted in the discharge of different effluents into these bodies of water.

Environmental regulations mandate the elimination of hazardous chemicals such as heavy metals from wastewater using traditional processes, which may be physical, chemical, or biological. Sedimentation, membrane isolation, screening, and filtration are examples of physical processes. Coagulation, adsorption, and solvent extraction are some examples of chemical processes that have been employed in the past. To comply with environmental regulations and to have a clear idea of the impact of these pollutants, it is crucial to first understand the composition of the pollutants.

The corpus of this project aims to classify the waste products of the three major industries of Pakistan—cement, leather, and steel—to identify the processes that directly produce these pollutants, and to analyze these effluents is to characterize them according to their properties. Finally, we tested the effectiveness of the prototype adsorption unit in reducing the content of pollutants from the waste water samples.

We have also proposed a design to bring the prototype adsorption unit to the site of the discharge. This will allow the industries to treat the waste before it is released into the bodies of water. The unit will treat the water and a clean, safe effluent can be discharged.

1.6 Research Objectives

We have collected water samples from three of the major industries of Pakistan, namely the cement, the leather, and the steel industries in order to classify the major pollutants found in their discharge.

The main objectives of this study are:

- To enlist harmful industrial effluent discharges.
- To characterize the harmful elements found in the effluent discharge.
- To analyze the efficacy of the prototype adsorption unit in dealing with the harmful content of the discharge, i.e., to perform pre-adsorption and post-adsorption analyses.

1.7 Scope of Study

The scope of our research is limited to the three main industries that we have mentioned: cement, leather, and steel. Samples of waste water have been collected from each of these three industries. The sample size from each is kept to roughly 4.5 liters, collected in three bottles of 1.5 liter capacity.

The source of the waste in terms of the direct industrial process is identified, along with the major pollutants. The techniques used for the characterization of the samples include UV spectrometry. The analysis is done twice for samples from each industry: once before the treatment with the prototype adsorption unit and once after the samples have been treated.

Essentially, a pre-treatment and post-treatment analysis is done to check for the efficacy of the prototype adsorption unit, such that its feasibility for field usability may be ascertained.

Finally, efficacy of the proposed design as a portable, on-site adsorption unit to treat the discharge at its source, is analyzed.

Chapter 2 Literature Review

2.1 Types of Wastewaters.

Broadly wastewater covers three types and these are domestic sewage, commercial or industrial sewage and third form is storm or hurricane sewage, further they contain few sub types.

2.1.1 Domestic Wastewater.

Domestic sewage or home sewage comprise of water from residential blocks, towns and populated areas containing minor and major markets, schools and prayer places like mosque and churches.

2.1.2 Industrial Wastewater.

Industrial or commercial waste is the major concern for professionals of wastewater technology, it broadly covers wastewater from major economic zones and industrial zones, vast variety in composition of industrial wastewater depending upon nature of industry, as wholesome it is the bye product of industries, it can be organic or inorganic these two sub categories different type of attention.

2.1.2.1 Organic Industrial Waste.

Organic industrial waste is much more fatal than inorganic for living organisms, organic pollution is created by the following chemicals.

- Phenols
- Chlorinated phenols
- Pesticides
- Agriculture industrial waste

Agriculture industrial waste is further divide into two main categories and these are

a. Agriculture Residues. Residues consist of further two more sub categories Field residue and Process Residue

   1) Field Residue. Residue left after cutting of crops or during storm season old parts of trees separated from trees due to thrust of air and be part of field residue
   2) Process Residue. Residue resulting from agriculture process

b. Industrial Residue. Residue is resultant of fruits processing.

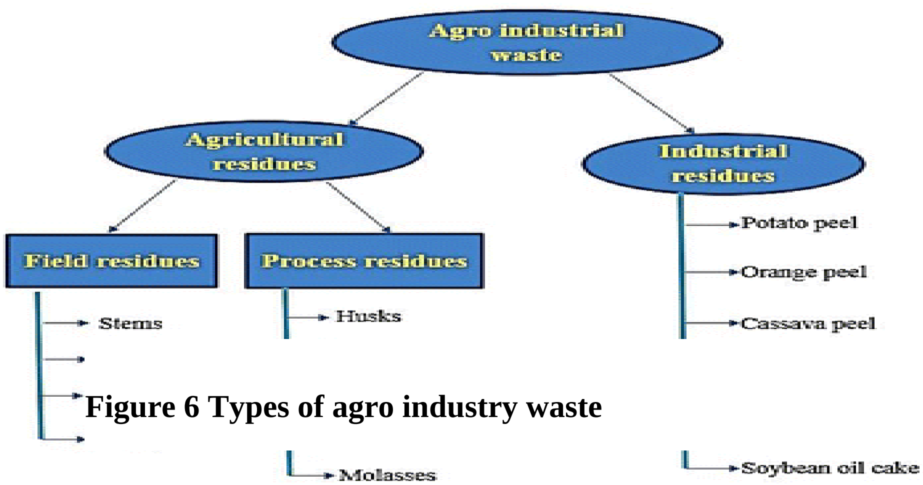


Figure 6 Types of agro industry waste

2.1.2.2 Inorganic Industrial Waste.

Inorganic industrial waste is comparatively less fatal than organic industrial waste inorganic, industrial waste composed of heavy poisonous metals including cadmium, chromium, arsenic, lead and mercury.

2.1.3 Storm Wastewater.

Storm waste water is in actual a pure water but got polluted when flow on ground surface, it mixes with sewerage, source of storm water is precipitation, storm water is capable of infiltrating into ground surface it could additionally be amassed at the floor in the shape of ponds and puddles.

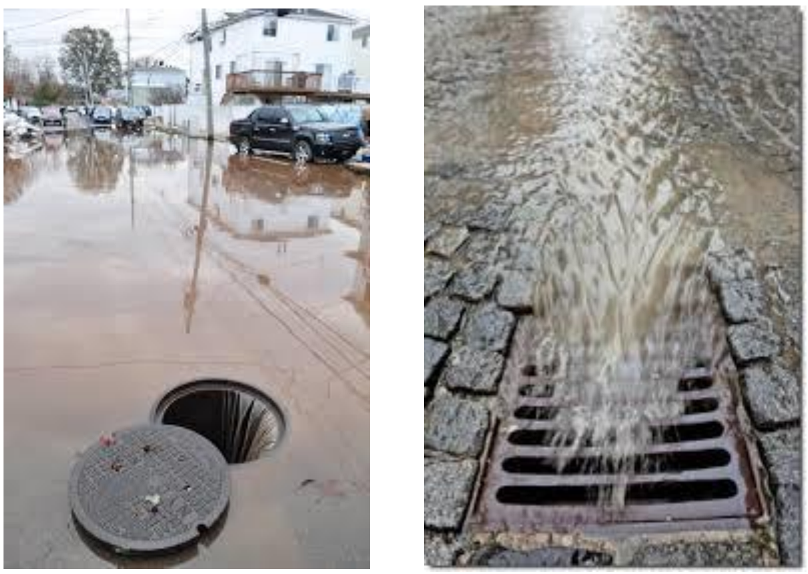


Figure 7 Storm waste water

2.2 Wastewater Treatment Method.

Due to globalization, developments of economic zones, urbanization and industrialization wastewater treatment becomes a major concern for scientists. The accurately use of present water assets and remedy of polluted water assets inside inexpensive approach and reasonably-priced technology is the point of interest for professionals. Treatment of wastewater is obligatory for important reason and this is water supply shortage. During purification process, number one remedy called primary wastewater treatment consists of three important steps, and these are

a) Preliminary,
b) Bodily
c) Chemical purification

Primary wastewater treatment involves mainly screening; secondary remedy relies upon biochemical decomposition of natural solids to inorganic. Third and final step referred to as tertiary remedy process, in which wastewater is transformed into useable water, which may utilized for the purpose of drinking or in healthcare. At the end of this step, nearly most pollutants are being eliminated from water. In order to acquire a very good quality of water, these three steps must be mixed together or performed simultaneously, however financial constraints continue to be a critical problem.

2.2.1 Primary Treatment Methods.

Method involves easy steps which can be performed at home for storm water gathered or ponded but if they have to be performed on large scale it require a schematic way, it helps in casting off suspended solids and organic matters the preliminary step is performed at initial level in this step visible dirt is removed, bodily step is performed to remove minor suspended solids, boiling at home is the example of bodily step and chemical purification involves addition of chemicals like at home chlorine has been added in waste water to kill germs.

2.2.1.1 Screening Separation Method.

Method is generally the first step performed to eliminate solids and minor suspended solids it can be performed at home, pieces of wood, laundry wastes, torn pieces of cloths, plastic, hairs and fecal solids are the example of things that can be removed at screening level, Screening result entirely depends upon the size of sieve or filter, number of sizes of filter s are available at market, size of sieve depends upon the desired result and financial limitations, finer debris and minor suspended solids can also be removed but it requires a minor size sieve.

2.2.1.2 **Filtration Method**.

This method involves using a roughly 0.1–0.5 mm pore diameter (Xuan-Thanh Bui, Chart Chiemchaisri, Takahiro Fujioka, & Sunita Varjani, 2019) in filtration separation technique. Furthermore, the water is passed through a membrane, membrane have pores which liquid to pass through diameter of membrane pore is dictated by the desired results, vast variety is available in membranes is available at market, cartridge is one of the example that can be used in membrane filtration technique cartridge is useful in casting off greases and lubricant thick in density from wastewater, which is the key rationale of the filtration method is casting off minute solids and oil, water treated through membrane filtration is appropriate for further treatments part of tertiary steps like ion exchange method and adsorption method, this technique is in place at biotechnological industries filtered water through filtration method is directly with chemicals at biotech industries.

2.2.1.3 **Centrifugal Separation Method.**

Method works on the principle of centrifugal forces, wastewater is treated in the machine heavier weight particles are separated from lighter during process for greases and lubricants density is the main parameter which decides the sizes and capacity of machine, centrifugal gadgets with different sizes are available at market. .

2.2.1.4 **Sedimentation and gravity separation method**.

Gravitational force is the principle of this method. It is used in removing all the solids, pebbles and silts from the solution. As suspended stable solids settle down due gravitational forces, density dictates the time factor in sedimentation gravity separation method, few chemicals has been added to accelerate the process, water available in result of sedimentation and gravity it can remove nearly half of the suspended solids.

2.2.1.5 **Coagulation processes.**

Due to globalization number of trade ships has been increased and water sources are being polluted with oil coagulation process is suitable for removal of oil emulsion and has been typically applied to lakes, ocean and river water to make it appropriate for domestic use, it is commonly applied after sedimentation and gravity technique suspended solids left after sedimentation process are treated with chemical compound there are a few herbal coagulants including starch, alum, iron substances, and aluminum slats in addition to aluminum salts. This system may be controlled by the elements of how high the temperature is, how acidic or basic the water is or how much is the contact time.

2.2.1.6 **Floatation Method**.

To cast off suspended stable solid along with oil, grease, and organic solids from wastewater, the method preferred is the flotation separation technique. In this technique, suspended solids are eliminated by processing with both air and gas. Various chemical compounds like alum and activated silica are used to assist flotation separation technique. For paper and refinery industries, flotation separation technique is a powerful technique for wastewater treatment (as much as 75–99%) (Xuan-Thanh Bui, Chart Chiemchaisri, Takahiro Fujioka, & Sunita Varjani, 2019), to separate mixed plastic is too difficult using gravity separation; therefore, for wastewater treatment and recycling purposes, plastic flotation method has been used as most effectively.

2.2.2 **Secondary Treatment Method**.

Secondary treatment methods performed to remove all suspended particles either soluble or insoluble, purpose of secondary treatment process is to convert or transform natural/organic or inorganic solids to fluid form which can further be treated in tertiary process it can be performed after primary or directly but for better results it should be performed after primary step. Any sample that may have quite high concentration of microorganisms, like fungi or bacteria, should undergo treatments that come under the secondary treatment methods. This is because the transformation of any kind will gain the microorganisms help, as they convert many organic and inorganic substances as well. During the process most of the toxic pollutants will also be eliminated.

2.2.2.1 **Aerobic Separation Method.**

Biologic strength of organic elements present in water is lowered to remarkable level by treating water with bacteria, process mainly depends upon heat, oxygen desired and availability of oxygen, and the very important is biological activities of the bacteria. If bacterial growth is exaggerated by addition of some chemicals to the solution, the organic pollutant oxidation rate will also be enhanced. Aerobic treatment techniques are the most effective method for removing suspended, volatile, and dissolved organics. Due to production of a huge amount of bio solids, aerobic treatment techniques have a big disadvantage; however, the biodegradable organic amount can be reduced substantially (up to 90%) (Xuan-Thanh Bui, Chart Chiemchaisri, Takahiro Fujioka, & Sunita Varjani, 2019) using this method.

2.2.2.2 **Anaerobic Separation Method.**

This method utilizes the principle behind the process of anaerobic decomposition, which is called putrefaction, it happens when dissolved oxygen is not existing in wastewater, and the procedure is called as anaerobic treatment procedure. The facultative and anaerobic bacteria help in transforming the organic matter into sulfur and carbon. The treatment method consists of two stages, which are known as methanogenic and acid-genic stages. Many gases are exhausted during this process which included ammonia, nitrogen and methane. This technique helped in reducing the biological load of the water to be treated,

2.2.3 Tertiary Treatment Method.

This is the third stage aimed to produce safe water for drinking after tertiary treatment all the germs are removed and water is considered safe for all purpose.

2.2.3.1 **The crystallization method**.

Pollution level is first raised to certain level to achieve crystallization point and crystallization method is considered powerful method for obtaining pure water, technique is beneficial for disposing dissolved solids this system is generally suitable to wastewater from industries like paper enterprise, crystallization system may be used for the reason to manipulate PH.

2.2.3.2 **Solvent Extraction Method.**

Method liquefy pollution and solid with the help of naturally available solvents, acetone and methanol are examples of solvent used in solvent extraction method in this method, few natural solvents are brought to the wastewater to facilitate particles removal. The method may be very beneficial to eliminate oils, and numerous organics elements. However, this method is frequently used for extraction of heavy metals lead and cobalt is the example of such metals.

2.2.3.3 **Ion exchange technique.**

Very common in use because of the reasons, easy, technically smooth and allows handy removal of even traces of heavy particles, extraordinary purification ability and performance, speedy comparative to other methods, professionals prefer it for commercial waste. Ion exchangers are natural or synthetic resins. Synthetic resins are widely desired because of their effectiveness on heavy metals from wastewater. To dispose of hazardous ions from wastewater, some resins are used in conjunction with zeolites, sodium silicates, and acrylic and metha-acrylic resins. Using this method, natural and inorganic pollution may be decreased approximately to 95%, however pretreatment is required if the wastewater includes oil or grease

2.2.3.4 **Adsorption separation method.**

Adsorption separation approach is an effective and useful way because of the reality it can be carried out without technical experts to wastewater, it contains flexibility and overall performance. When in evaluation with distinct strategies, it appears superior to others. Some factors which have an impact on adsorption overall performance together with the shape of adsorbents are pollutant, adsorbent particle diameter, pH, contact time, and temperature, pretreatment needs to be effectively followed. To take away pollutants mainly heavy metals from wastewater, various adsorbents such as activated carbons from unique substances, carbon nanotubes, and masses of bio absorbents are utilized. However, novel, and effective adsorbents with close by availability are financially suitable.

2.3 Wastewater treatment plants in the world.

Table 6 List of largest wastewater treatment plants

Ser	**Plant Name**	**Country**	**City**	**Nature**
1	Jean R Marcotte	Canada	Montreal	Uses Secondary treatment planned
2	Detroit Wastewater Treatment Plan	United States	Detroit	Secondary treatment plant
3	Deer Island Wastewater Treatment Plant	United States	Boston	Full secondary treatment established in1995
4	Blue Plains Advance waste	United States	Washington DC	Secondary treatment

	Treatment Plant			established in1959
5	Hyperion Water Reclamation Capacity	United States	LA	Misty-weather secondary treatment
6	Kuryanovo wastewater treatment facilities	Russia	Moscow	Secondary Treatment Plant
7	Lyuberetskiye wastewater treatment facilities	Russia	Moscow	Secondary Treatment Plant
8	Seine Aval Wastewater Treatment Plant	France	Paris	Secondary Treatment Plant
9	Beijing Huaifang Treatment Plant	China	Beijing	Built Under Ground

2.4 Wastewater treatment Plants in Pakistan

Pakistan focus on wastewater treatment is comparatively less than that of developed countries only 1% wastewater receives treatment.

2.4.1 Islamabad.

According to the Pakistan Water Situational Analysis, there are three wastewater treatment center in capital city, out of these three one is functional

2.4.2 Karachi.

Trickling filters are functional at Karachi in korangi districts.

2.4.3 Peshawar.

The four wastewater treatment plants are at outer edge regions of the town, along Ring Road, Charsadda Road, Warsak Road and in Hayatabad. Only the sewage plant mounted on Warsak Road is presently operational.

2.4.4 Lahore.

City has some screening and grit removal systems, but they are hardly functional.

2.4.5 Kasur.

Tannery Pollution Control Project is one of the marvel achieved in the last decade the Government of Pakistan and United Nations Development Program mutually inked Kasur tannery pollutants Control venture in 1996. (KTWMA, 2010).

1. Leather Sector is amongst pinnacle sales producing industries of Pakistan, tanning enterprises are concentrated in Korangi, Kasur, Lahore, Multan, Gujranwala, and Sialkot. Kasur town is fifty five km far from the provincial capital Lahore and majority of the populace is affiliated with Leather Industry, because of tanning waste Kasur becomes a well-known location for carrying studies on Tannery industry wastewater.
2. This waste effected 327 acres of lands completely and similarly 311 acres of land in monsoon season.
3. Plant is now treating 13000 cubic meters of wastewater, Dumping sites have been constructed in Kasur.

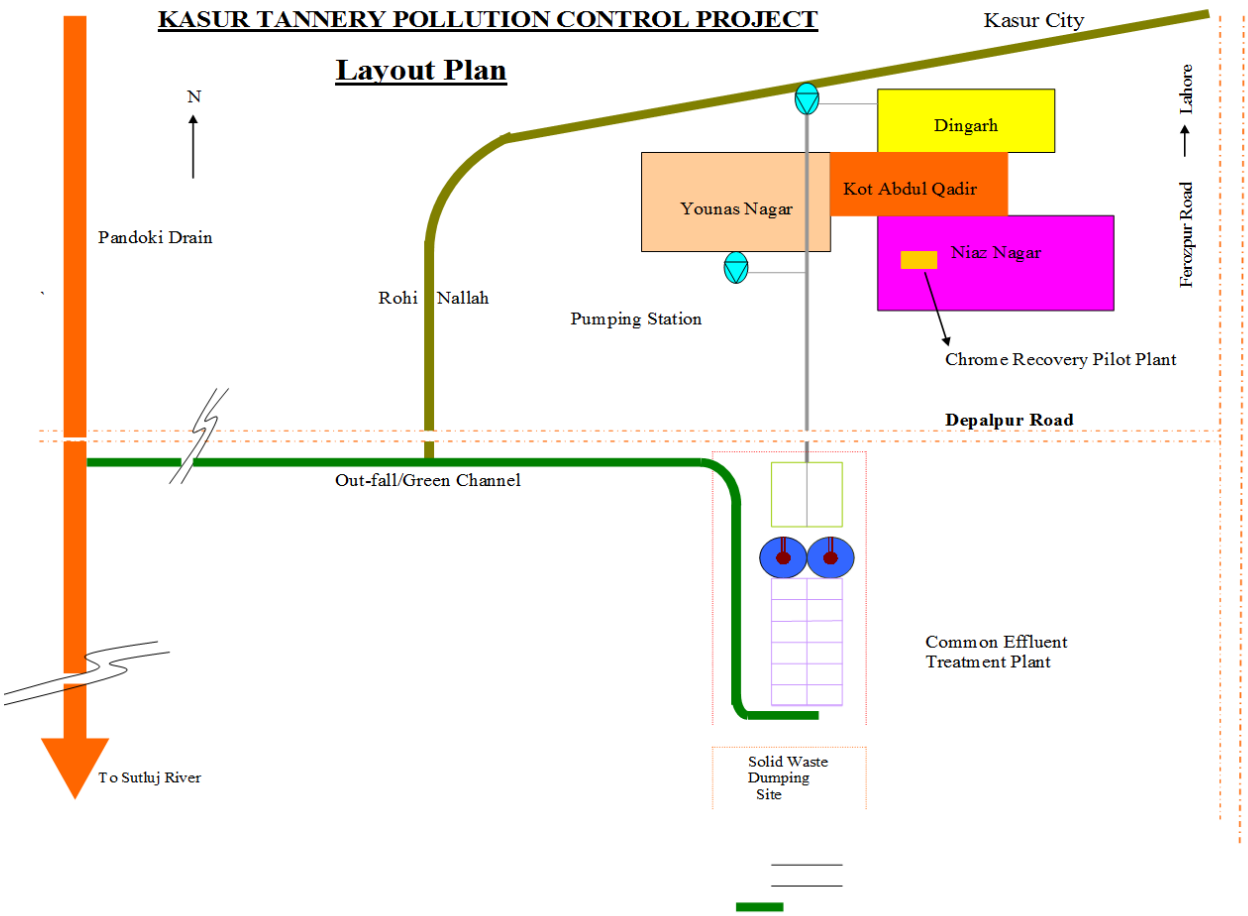


Figure 8 Layout plan of Kasur tannery pollution control project

2.4.6 Faisalabad.

There is a wastewater treatment plant, wherein wastewater gets primary treatment. There isn't any wastewater treatment plant on Eastern extent of Faisalabad at present. Untreated wastewater is amassed and carried thru open hurricane water channels to Madhuana Drain which eventually discharges into River Ravi. It is unsafe for the population dwelling alongside the river aside from being a prime purpose of environmental degradation. At western extent, there is a small wastewater treatment plant of 20 MGD potential, which covers 10% of general home wastewater. Proposed wastewater treatment plant is under construction with general potential of a hundred and fifty MGD. (CEO Kashif Raza Awan, 2020)

2.4.6 Rural Areas

In rural areas, wastewater treatment is nonexistent, leading to pollution of surface and groundwater.

Chapter 3 Methodology

3.1 Introduction

Industrial effluents are discharges from various industries and various organic/inorganic pollutants have been found in these effluents. These pollutants may also include metals like mercury, chromium, cadmium ,copper, lead etc. These metals are toxic and once in access ,they can affect human health and environment very badly.

3.2 Development of a Prototype adsorption unit for the treatment of Industrial Effluent

Prototype adsorption unit is small portable setup developed for the treatment of wastewater. Efficacy and benefits of using carbon adsorbents has been sufficiently explained in previous section. Here we will focus on the construction and operating mechanism of the adsorption unit which we used while carrying out this study.

Prototype was primarily prepared by National Centre of Physics (NCP); preparation of adsorbent i:e modified charcoal at nano level goes well beyond the scope of this study.

Basic concepts being employed in its preparation are discussed the following paragraphs. Purpose of this design is to develop a portable adsorption unit for the removal of toxic and harmful materials (with focus on access and harmful heavy metals) from industrial waste (that is then discharged into the environment). This unit must take polluted water and process it to such an extent that released water is harmless when discharged into a sewer, river or a stream.

3.2.1 Definition of Basic System Requirements

1) Portability: This unit has to be used at different sites so it must be of such size that it is manageable by one or two operators.

2) Capacity: The unit should finally i:e upscaled version, be able to process spills of up to 200 liters and of varying concentrations at any one time, to the desired treatment objective. Presently the capacity will not be the guiding element as it is being experimented for the desired outcome i:e efficacy. Capacity can later be enhanced once it gives the desired outputs.

3) Adsorbent: Absorbents such as Granular Activated Carbon can absorb most of toxic pollutants found in our waters because of agrarian nature of our economy. Its cost is low and also is readily available.

3.2.2 General Overview

Prototype consists of two distinct bodies i: e suction pump and the modified funnel.

3.2.2.1 Modified Funnel

It is designed to constitute a series of materials arranged in a specific sequence (as per treatability of each item). Column of materials in funnel starting from the top are.

- Cotton layer
- Sand
- Adsorbent
- Cotton bed

Effluent passes through all these layers and depending upon various factors like contact time, quality of materials etc. expels the desired impurities into these materials. Resultantly we obtain treated liquid at the bottom.

3.2.2.2 Suction pump

It is an auxiliary attachment that is used to create sufficient suction that would allow and facilitate the flow of liquid from the column at required rate. It is attached to the liquid collecting beaker (at bottom)

Detailed Description: To understand the complete operating mechanism, we have divided the procedure into following main parts.

1. Contacting System

2. Flow Configuration

3. Fluid Handling and Control

3.2.2.2.1 Contacting System:

One of the primary factors that impacts the efficacy of adsorption is the contact time permitted/ available between effluent and different parts of column i:e with cotton, sand and adsorbent. Among these contact times the most crucial is Carbon contact time. As a general note; more is the contact of effluent and carbon adsorbent better will be the purification of effluent. There are varying factors which govern the contact time of effluent with carbon adsorbent. The availability of solute molecules to pores of the adsorbent particle determines the rate of adsorption, i.e infusibility. As Diffusion is affected by the size of the solute molecule and shape, size and number of adsorbent pores available.

The size range of the particles should be as narrow as possible; the largest particles control the rate and give the lowest adsorption performance, while the smallest particles control the pressure drop.

Brief description (of various contacts) along with diagrammatic representation has been shown in subsequent paragraphs.

3.2.2.3 **Cotton Layer:**

Cotton is used for filtration, i.e. separating liquid and solid particles from a mixture. It is used to separate dirt particles from water to purify water.

- In the context to prototype, cotton layer in the beginning acts as a purifier i: e to remove most of solid impurities. It forms a part of layered defense, with its focus to contain maximum contaminants from reaching the next layers. Cotton layer obviously does not remove the impurities at micro level but preventing the main solid impurities from going ahead in the column, it not only aids the efficiency but also enhances the life of adsorbent / complete prototype.

- Similar is the function of cotton layer deposited at lower end of prototype. It mainly acts as a safeguard, to remove any accidentally missed out impurity. Few advantages of cotton that over rules its usage as compared to other such materials available in market include.

  - Availability in local market
  - Cheap
  - Washability

3.2.2.4 Sand layer

Sand filtration removes of suspended, floating and sinkable matter by the process of percolation through sand bed. Wastewater flows through a fine bed of grit and sand or either of them.

Types of sand filtration;
- **Rapid sand filters:** They have to be cleaned often by back washing, done by reversing the water direction.
- **Semi-rapid** sand filters
- **Slow** sand filters.

Rapid and semi-rapid sand filters require pumps and chemicals. But slow sand filters use a natural biological process. This process takes place in normal atmospheric pressure. They reduce the amount of bacteria, viruses, microbes, etc. present in water without using chemicals. It is a natural way to get rid of micro-organisms and prevents water-borne diseases. This method was also used in 19^{th} century to treat flowing bodies of water like streams and rivers.

Sand layer in prototype performs the functions mentioned in the above paragraphs. It also acts as a second line of defense. Its functionality may differ, but its purpose is almost similar to that of the initial layer of cotton. Thus, it enhances the life and efficiency of portable prototype.

Thickness of the layer may vary as per

- Quantity of water that is to be treated.
- Capacity of funnel/designed equipment .
- The level/degree of visible impurities.

The layer used here is 20 to 30 cm thick.

3.2.2.4.1 Adsorbent:

Attractive forces between solute, solvent and sorbent molecules cause adsorption. In adsorption, intermolecular forces act only on the surface of adsorbent, while in absorption they act on bulk phase molecules.

Activated carbon is made by treating any amorphous form of carbon such as wood, coal, pulp mill and petroleum-based residues and char, to give high adsorption capacities. These amorphous forms of carbon are heated to leave a carbon residue. Partial oxidation using steam, carbon dioxide, or oxygen in air then activates it. Activation increases carbon's surface area by adding pores and adds some active functional groups onto the surface.

Carbon attracts solutes that are less polar, have high molecular mass and lower degree of ionization, therefore it readily removes such pollutants from the waste stream. There are two forms of activated carbon:

- Granular activated carbon (G.A.C.)
- Powdered activated carbon (P.A.C.)

G.A.C. can remove heavy metals such as mercury, cyanide and chromium from electroplating wastes.

For the present experiment, Carbon adsorbent that is used has been prepared by treating modified charcoal at nano level. It possesses all the above-mentioned properties and thus stands suitable for testing the removal of Heavy Metals from industrial wastes. One of the main reasons that lead to selection of charcoal was its cheap price and ease of availability in local market. Further details involved in preparation of these carbon adsorbent fall beyond the scope of study.

Amount of effluent that can be passed through adsorbent to get it filled i:e maximum capacity ,has yet not been calculated. Once it reaches the limit it can either be changed or it can be cleaned and re used.

Characteristics of Adsorbent. Ideally, the adsorbent should satisfy four requirements:

1. Reasonably high surface area or micro pore volume to achieve a high adsorption capacity.

2. The pore diameter must be sufficiently large appropriate to the size of the adsorbate molecule.

3. The appropriate surface functional groups to attract the adsorbate molecule (or the large surface area may become of secondary importance).

4. A relatively large porous network providing access to the internal surface area

Following flow chart/diagram depicts the sequential arrangement of various elements of contact column.

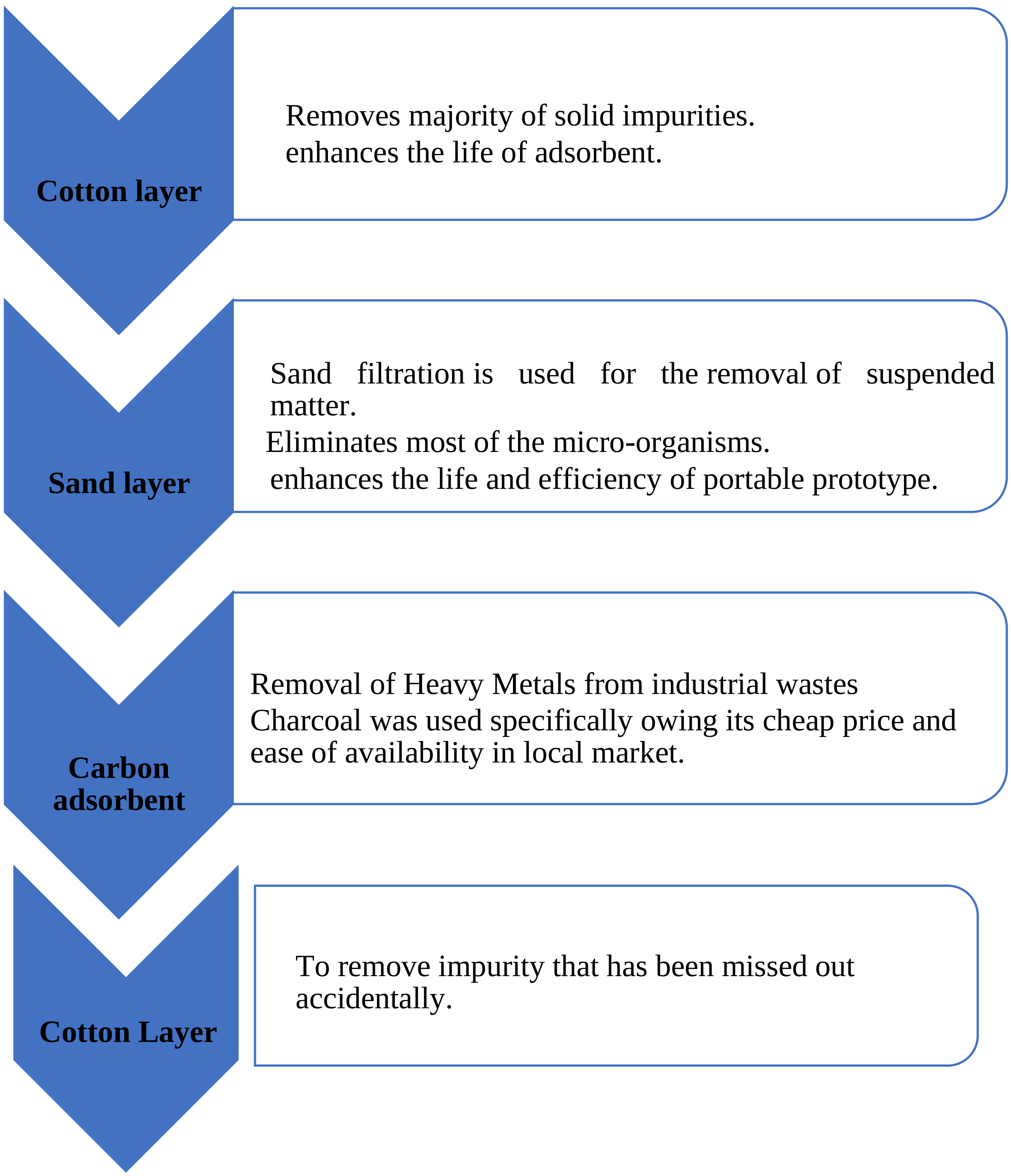


Figure 9 Flow diagram of the various steps in the elements of contact

3.2.3 Flow Configuration

Fixed Bed adsorbers work with the fluid flow via column either being up or being down:

- Down-flow system; gravity helps with the down-flow system, but it makes the contact between the carbon and the influent less effective. Large volumes of Industrial Wastes can be treated quickly and efficiently by down-flow system because high velocity of down-flow system makes it suitable for large volumes.
- The up-flow system*:* It removes more pollutants than the down-flow system in a given time. It requires lesser pre-treatment conditions and also has little head losses because contact between the influent and carbon is far better.

Keeping in view the above-mentioned pros and cons of both configurations and variation in the degree of purification (removal of heavy metals), we opted for down flow configuration.

3.2.3.1 Fluid Handling and Control

3.2.3.1.1 Fluid handling:

There are no instruments strictly specific for fluid handling less the funnel that has the complete column.

- Different beakers can be used to pour in the effluent from the top. Any beaker or lab equipment that permits smooth pouring of water and gives a measurement of liquid placed in it may be used. We used simple Lab Beaker

- Modified Flask is used to collect that effluent after it has passed through the prototype. Flask is such that it has a valve that connects vacuum pump to it. Flask once filled, process is halted and liquid from flask emptied in a specific container.

3.2.3.1.2 Fluid Control:

- Fluid Control is done manually by keeping an eye on the filled column above the top of first cotton layer and on the flask placed at the bottom

- Beside this, Fluid flow is enhanced by suction of vacuum through vacuum pump. Vacuum pump increases the speed of process, but care needs to be taken regarding this; over speeding needs to be avoided as it would reduce the degree of impurity removal / heavy metal removal.

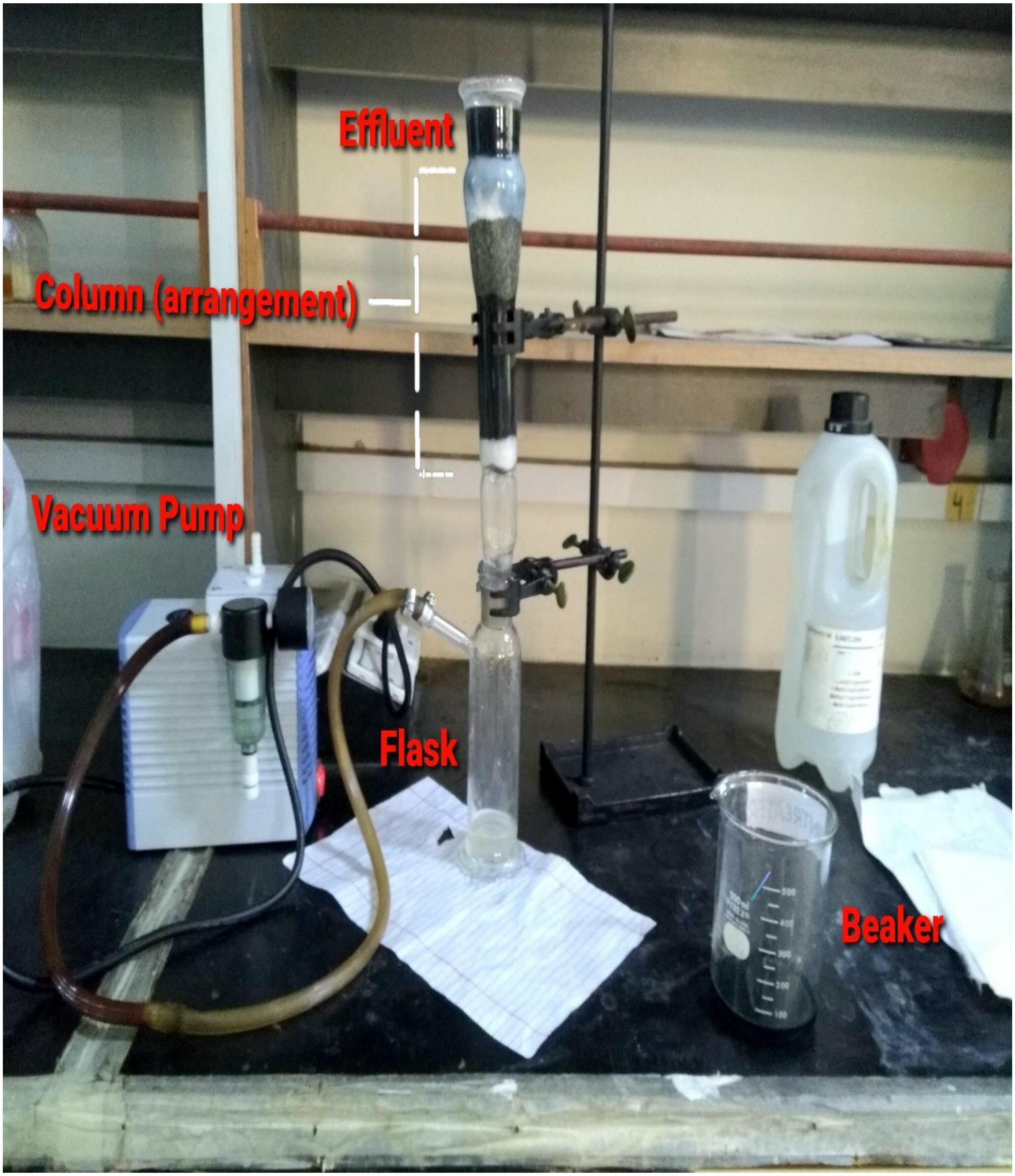


Figure 10 Components of prototype

Figure 11 Components of Contact column

3.3 Procedural details

3.3.1 Sample Collection

In order to check the efficacy of prototype in removal of heavy metals we used samples that were collected from three industries i:e Cement Manufacturing Industry, Steel industry and Leather Industry. In the subsequent paragraphs, details regarding the collection of samples from each industry are explained.

3.3.1.1 Cement Manufacturing Industry

Many industries have made all kinds of waterbodies their dumping reservoirs for the all the waste they produce. Cement industry is one of the most essential sectors in the development of Pakistan. Cement industry is responsible for many of the industrial effluents that are dumped in the rivers and later become a serious hazard for environment and flora and fauna around it.

Major pollutants from cement industries include particulates produced in the rotary Kiln and from crushing and grinding, blending, moving materials to silos and packing. Generally, the effluents produce is composed of waste heat, dissolved solids, which may include potassium and sodium hydroxide, chlorides, and sulphates, in addition to suspended solids and processed water. These effluents are mainly discharged into water bodies owing to the lack of check and balance by environmental agencies.

Samples of cement industry wastewater, collected in our case were from 3 vertical roller mills i:e Coal mill, Raw mill and cement mill. All the samples were collected at the same time from three different places of discharge. To cut long story short, wastewater (collected by us) is used in various Vertical Roller Mills, primarily to cool the heated lubricants. Shell and Tube heat exchangers are used for this purpose. Samples were collected from all three mills.

Total of 4.5 liters sample was collected i:e 1.5 Liters from each place.

Figure 12 Cement industry sample

3.3.1.2 Leather Industry

Tanning industry goes far back in our history. It produces various highly detrimental toxic chemicals in the process. Such wastes must be treated properly before releasing them in the environment. Its wastewater has a large variety of toxic heavy metals like cobalt, lead, chromium, nickel, cadmium, selenium, arsenic. The waste produced is either of these three things: leather fibers, particulate matter dust and effluents. The effluents contain more than 40 different chemicals including different types of acids, dyes and heavy metals; therefore, it is considered primary environmental pollutant.

Pakistan has big tanning industry; it is the third largest export earning for Pakistan. In Punjab, Kasur is the second largest producer of leather. Effluent Samples were collected from a leather industry based in Kasur i:e Yousuf Tannery. Samples have been extracted from the effluent that was being discharged into the environment. All the samples were collected at the same time from three different places of discharge. Total of 4.5 liters sample was collected i:e 1.5 Liters from each place.

Figure 13 Leather Industry Sample

3.3.1.3 Steel Industry

A large amount of water is required in steel industries for transport of waste materials (ash, sludge, and scale etc.), suppressing dust, cleaning, controlling temperature (heat treatment), and other usages. Therefore, a large amount of water has to be released which contain toxic chemicals and pollutants. Each kind of usage pollutes water differently and there for we get different quality of water after each usage. Difference in quality depends on type of metal and quality of scrap in the effluent (depending upon the processes). Wastewater that was being used for casting was selected considering maximum possibility of having heavy metals .In casting water is used in the initial stages of solidification for cooling the mold, and under the mold it directly comes in contact with the newly solidified metal surface.

Effluent Samples were collected from a Steel mill based in Islamabad i:e **Fazal Steel Mill.** Samples have been extracted from the effluent that was being discharged into the environment. All the samples were collected at the same time from three different places of discharge. Total of 4.5 liters sample was collected i:e 1.5 Liters from each place.

Figure 14 Steel Industry Sample

3.3.2 General Procedure

3.3.2.1 Visual Analyzation:

All the samples were initially analyzed for the degree of concentration of impurities like dyes, mud etc. in order to determine the pretreatment required prior to the treatment in prototype. Samples from Steel and cement industry appeared fair enough through naked eye examination and were considered viable to be directly processed through prototype. In case of Leather Industry Sample, it was highly concentrated, as depicted in the picture above. High concentration of dyes in effluent demanded an additional treatment prior to the treatment in prototype.

3.2.1.2 Pretreatment:

- pH value of Leather sample came out to be 3.5. i:e highly acidic. Major suspended solids were removed through filtration (using simple filter paper).

- Filtered solution was checked for concentration using UV spectroscopy i:e Ultraviolet Spectroscopy. Concentration/Adsorption should have been below 1, so that it could be treated by prepared carbon adsorbent. Concentration came out to be higher (as depicted in the following figure).

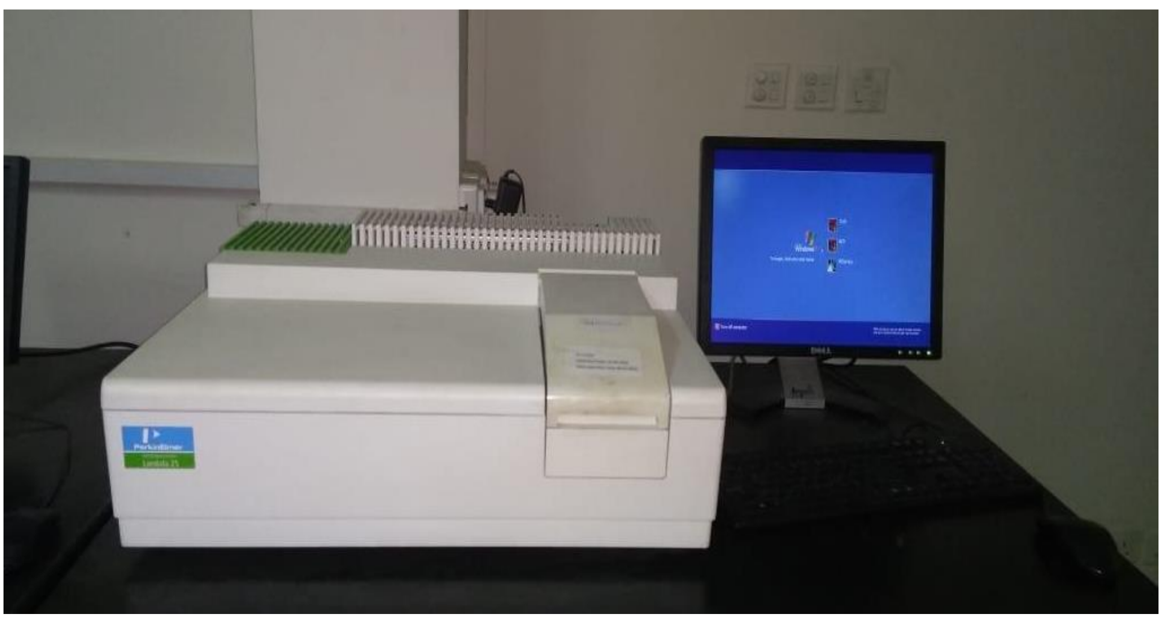


Figure 15 UV spectrometer

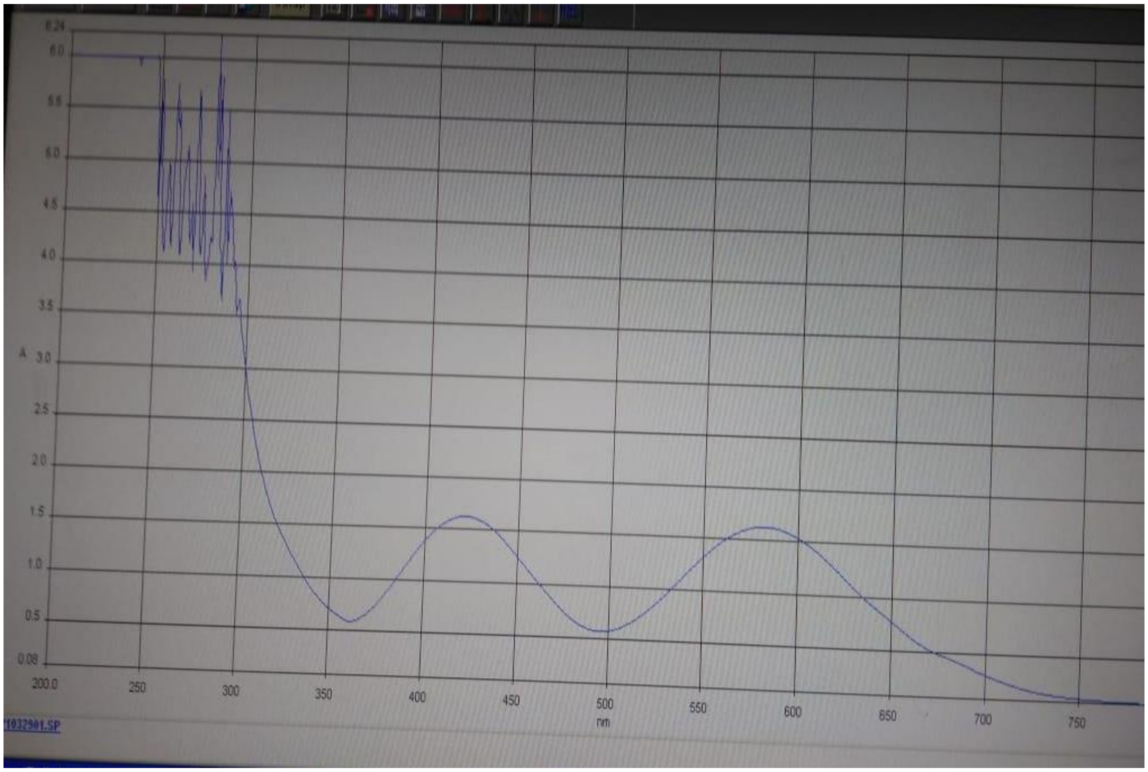
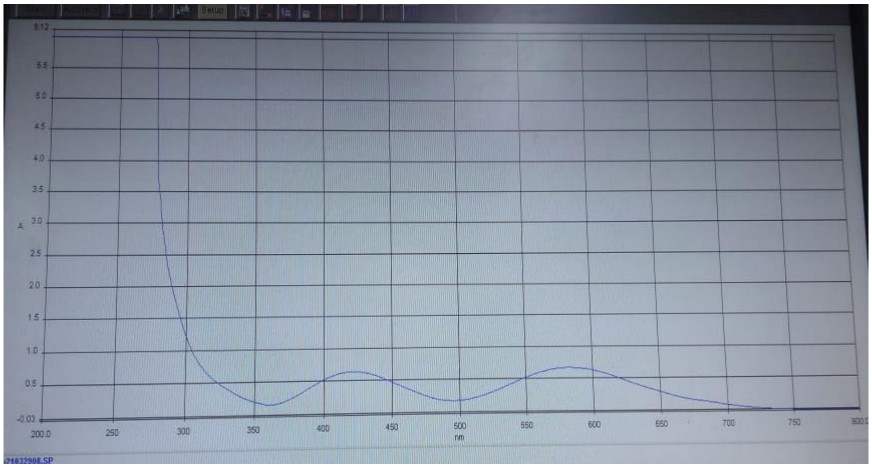


Figure 16 Leather industry Effluent adsorption value

- Based on the experience of Lab staff and on results of two trials, Leather Industry Effluent sample was diluted by 2:2 (effluent: distilled water). After this it was retested for adsorption by UV spectrometer. Adsorption value now was below 1 (as shown in the diagram), thus now it was ready to be treated by carbon adsorbent.



3.2.1.3 Pre-Adsorption Analysis:

Figure 17 :adsorption after diluting the effluent by 2:2

Half of the quantity from each sample was collected and was deposited to PCRWR (Pakistan Council of Research in Water Resources) for atomic adsorption analysis, prior to adsorption.

3.2.1.4 Adsorption using prototype:

For the remaining half of each sample test was performed using prototype. Each sample was passed through complete contact column and collected in clean bottles. Cotton, Carbon Adsorbent had to be cleaned after passing each sample. At an average it took 6,7 working hours for performing test on each sample. Special precautions had to be guaranteed to prevent breakage of any instrument and to prevent mixing of samples. Samples were deliberately labeled in order to prevent mixing. Extended time was taken because of small effluent carrying capacity of prototype. This capacity can be easily enhanced by varying (increasing) the size of the container used for preparing prototype. This will obviously be done once the experiment yields the desired or aimed outcomes.

3.2.1.5 Post Adsorption Analysis:

These clean Bottles containing the processed samples i:e after passing through prototype, were duly labeled and again deposited with PCRWR for Atomic Adsorption Analysis post adsorption.

3.2.1.6 Results

Results were obtained from PCRWR and subsequent analysis was done. This portion has been highlighted in next section. Based on this analysis it was deduced that whether this arrangement is viable for removal of heavy metals from industrial effluent or not.

.

Chapter 4 Results and Discussion

4.1 Result

- As stated previously, half of all collected sample i:e 2.25 liters from each industrial wastewater was submitted in PCRWR for pre adsorption atomic analysis. This was necessary as to determine the percentage efficiency of our protype against each heavy metal. This result has been shown in the column “Initial Concentration”.
- Similarly, remaining half of each sample i:e post adsorption, was submitted in PCRWR . This result has been shown in the Column “Final Concentration”.
- Efficiency of removal of each heavy metal has been shown in separate column.

Results obtained have been discussed in subsequent paragraphs.

4.1.1 Cement industry:

Results obtained after atomic adsorption from PCRWR had serious errors and demanded re testing. Tests could not be repeated amid Covid-19 limitations.

4.1.2 Steel Industry:

As mentioned previously , atomic adsorption was performed on half of the sample prior to adsorption (initial concentration) and on remaining half of the sample it was performed once it had undergone adsorption(final concentration).Following table shows these results as well as the removal efficiency of each heavy metal.

Table 7 Percentage efficacy

Heavy Metals (Industry A)	Initial Concentration (µg/L)	Final Concentration (µg/L)	Removal Efficiency (%)
Pb	5	BDL	99.5
Ba	938	8.77	99.06
Mn	840	40.9	95.15
Cr	240.58	50.19	79.13
Cu	2450	520	78.77
Al	145	43.7	69.86
Co	16.96	5.81	65.74

Cd	8.74	3.19	63.50
Sr	1240.3	462	62.74
Ni	48.44	23.17	52.17

4.2 Discussion:

In order to obtain better visualization of the comparison of pre adsorption composition and post adsorption composition, following bar chart has been shown.

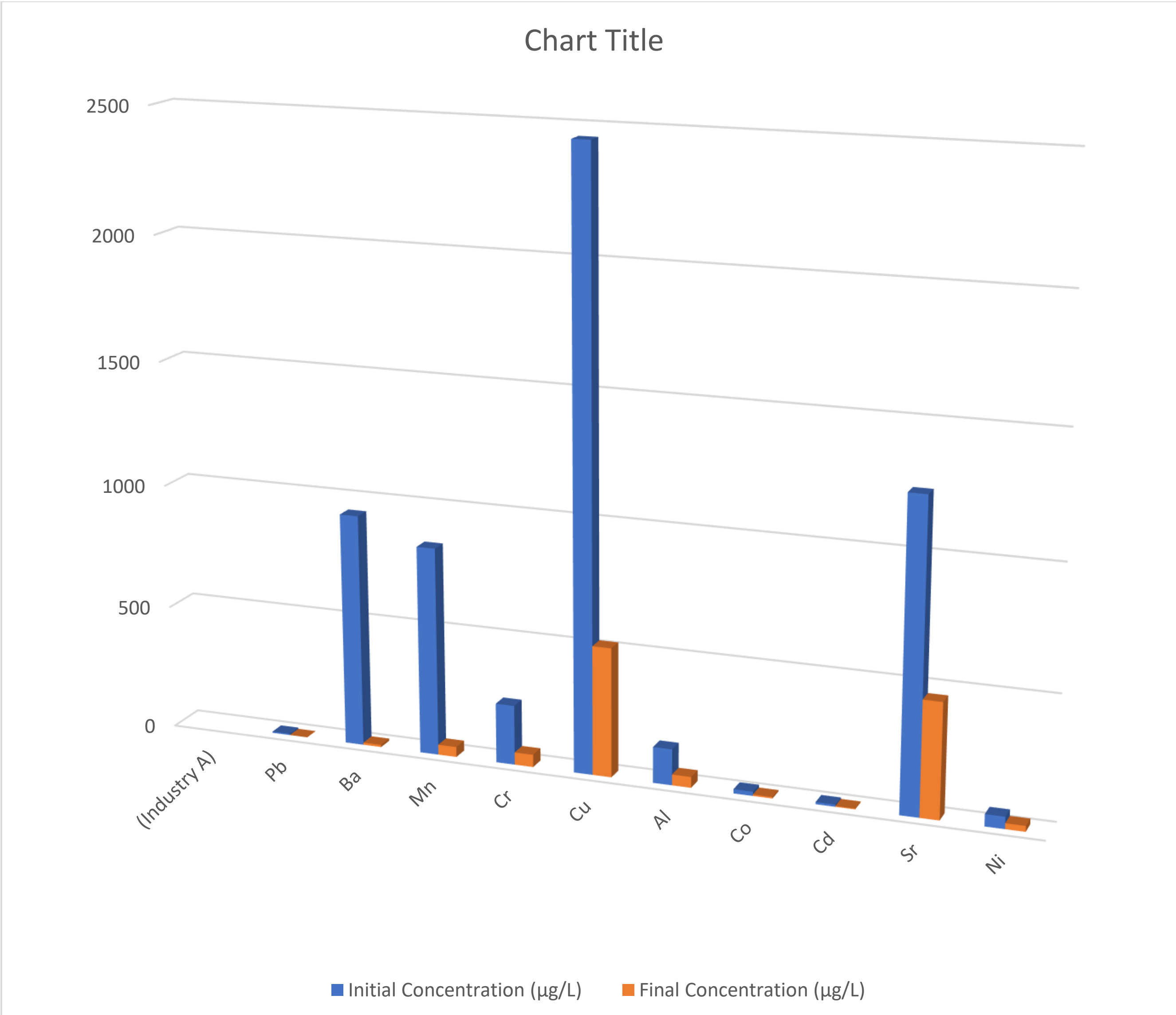


Figure 18 Comparison of pre adsorption & post adsorption

Comparative analysis shows a varying percentage of removal of different heavy metals. Highest removal percentage is of Lead i:e 95.5% and lowest removal efficiency is of Nickel i:e 52.17%. Almost half of the nickel content has passed without being adsorbed. Percentage removal of Nickel is low enough and thus seeks attention. Overall heavy metals adsorption percentage for all 10 elements comes out to be 76.562% .This percentage is fine enough to cause a valuable decrease in the detrimental effects caused through excessive heavy metals in Steel industry waste.

In order to ascertain practicality of removal of heavy metals from steel industry effluent we must compare the obtained final concentration with allowable concentrations (it has been shown in fig 4).Following table shows above mentioned analysis.

Table 8 comparison with permissible limits

Heavy Metals	Final Concentration (µg/L)	Allowable Concentration (µg/L)
Steel industry		
Pb	0	500
Ba	8.77	1500
Mn	40.9	1500
Cr	50.19	1000
Cu	520	1000
Al	43.7	200

Co	5.81	10
Cd	3.19	100
Sr	462	4000
Ni	23.17	1000

All the obtained concentrations are far below the minimum permissible limits of heavy metals in industrial effluents; thus, it goes without saying that as regards to its efficacy prototype has proved to be practicable.

4.2.1 Leather Industry:

Pre adsorption results as well as post adsorption tests could not be performed in PCRWR amid Covid-19 restriction

Chapter 5 Conclusion & Proposed Future Work

5.1 Conclusion

In order to minimize the rapid contamination of water in economy centered world, much needs to be done. Else the day is not that far that clean water would turn so scarce that in struggle to get its availability ,nations would go to war. Presently most of the industrial effluents in developing countries is discharged unchecked into the environment because of lack of effectiveness environmental agencies. Industries hesitate using wastewater treatment plants owing to the high cost of such systems. These norms hold primarily good for Pakistan where even today wastewater treatment remains a neglected concern.

In the same very regard, an effort has been placed to reduce the contamination of natural water resources through prevention/removal of excessive heavy metals from industrial effluents; using a cheaply made prototype. This prototype uses an adsorbent made by treating charcoal (at atomic level) as main heavy metal removing agent. Preparation of activated carbon adsorbent remains well beyond the scope of this study and thus has not been discussed. Local availability of charcoal at lower price makes it cheap/easy to use and develop. Efficacy of this prototype in removal of heavy metals from industrial waste was the main concern and has been amply answered by the above stated results. Samples of three diverse industries i:e cement, steel and leather were used thus majority of the possible heavy metals that any industrial waste may contain were encountered. Consequently, the results obtained can be easily claimed to stand productive for maximum industries.

Main purpose of this study was to inspect the efficacy of this lab-based prototype in removal of heavy metals from industrial waste up to a level that they remain un harmful to environment . Now once it has produced desired results, upscaling of this sample prototype into a wastewater treatment plant, to meet the requirements of high industrial discharge remains an immediate requirement. Production of adsorbent at mass scale as well as development of other supporting equipment/components would remain a demanding task.

5.2 Proposed Future Work

As described previously, scope of this study alone does not stand enough to bring this prototype/adsorbent into practical usage. However, by resolving the main task i:e effectiveness in removal of heavy metals, it has opened a broad space for further studies. Following tasks demand deliberate research and analysis to bring this prototype into its practical life.

- Discharge that is permitted to flow through the upscaled prototype version along with its viability to handle average industrial discharge.
- What is percentage reduction in the efficiency of adsorbent (in removal of heavy metals), as it keeps getting filled with adsorbed impurities(heavy metals)?
- Which option is more viable; either to remove the adsorbent and clean it or to replace it once it reaches some threshold limit , in context to adsorbed impurities(heavy metals)?
- A detailed design of upscaled water treatment plant ,with various detailed calculations e.g., suction capacity of the suction pump. Configuration of the contacting system may vary for upscaled version.
- Increasing the efficacy of adsorbent against specific metals like Nickel, where the results have not appeared to be very promising.

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ENVIRONEMNTAL APPLICATION OF NANO-TECHNOLOGY FOR TREATMENT OF INDUSTRIAL WASTE WATER

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