Chapter 1

INTRODUCTION

1. INTRODUCTION

Water is requisite for life forms present on this earth. It is presents on the Earth before any life form existed. Since the development of life on Earth, it plays a crucial role in biochemical and physiological processes involved in maintenance of living organisms (Franks 2000).There are only few life forms in some ecosystems on earth like Hydrothermal vents that do not require water for their sustenance. The importance of water can be known from the fact that 70 % of the Earth is covered with water. But, out of it only 2.5 % is fresh water and rest is salty water. Further only 1% of fresh water is accessible for direct human use (Michigan 2000).Water in use is liable to be contaminated physically, biologically, chemically and radiologically (USEPA 2015). Contamination of water further reduces the availability of water for its requisite use.

Annual precipitation in India is 4000 km^3 out of which ca. 75 % gets precipitated during monsoon season itself (Bansil 2004). Natural annual run off in rivers is 1869 km^3.1132 km^3 of estimated run off of this natural run off is usable (Singh and Shrivastava 2006). In addition to this, per capita availability of water since independence is reduced to 1820 m^3 from 5000 m^3 and further projected is 1341 m^3 by 2025 (Government of India 2011). Overexploitation of water resource along with population pressure further aggravated this problem. The current picture looks quite alarming for the survival of upcoming descendants of humans. In addition to declination in quantity of water, declination in quality is also of concern. Water quality declination further aggravates the problem. Water quality declination occurred both by anthropogenic and natural activities. Anthropogenic reasons include physical, biological and chemical contamination. This depleting state of water further creates a situation of exigency in some water deficient areas of the country. Heavy metal contamination of water is one of the anthropogenic pollutants. It makes water unfit for human consumption. Geological weathering of rocks is natural source of metal contamination of water. The areas having metal-bearing formations shows elevated levels of heavy metals in water of the region (Förstner and Wittmann 1983).

1.1. Heavy metals in the aquatic system

Two groups of materials have a profound effect on aquatic system i.e. nutrients and pollutants. The first class of compounds promotes biological growth and second one causes adverse effects on the aquatic ecosystem (Förstner and Wittmann 1983). Among various pollutants, heavy metals cause harmful effects on the humans and the environment. Like organic pollutants, metals are not degraded by natural processes. Metals are accumulated in sediments of river; afterwards they find their way into the biological organism through ecological processes. On reaching into humans they have adverse effects on them.

1.2. Effects of heavy metal on fauna flora and human beings

Heavy metals cause enzyme inactivation, disrupt the structure of organelle, cause carcinogenicity, effect nervous, endocrine and respiratory systems. The enzyme inhibition occurs due to interaction between metal and –SH (sulphydryl) group on the enzyme or displacement of co-factor of enzyme. The carcinogenic nature of the heavy metal is thought to be due to interaction with DNA. Kidney is the principal excretory organ of the body, so it is a common target for toxicity due to metal (Hodgson 2010).The neurotoxicity is majorly caused due to lipid soluble nature of forms of metallic contaminants (Hodgson 2010). Lipid solubility of methyl mercury helps in transport across blood brain barrier and then enters nervous system. However, inorganic mercury is water soluble and cannot cross the blood brain barrier and primarily affects excretory system. The toxicity of heavy metals depends on their bioavailability and intracellular transport. Metal toxicity can be exerted, when it crosses the membrane and enters the cell.

1.3. The heavy metals selected for study

Chromium and cadmium were the two heavy metals selected for removal from aqueous solution. The chromium and cadmium are selected due to their widespread contamination of water sources across the world and their toxic nature.

1.4. Global chromium contamination

All continents along with country contaminated with chromium pollution are presented in following table:

Table 1.1 List of countries with chromium contamination

Europe		
Countries	**Contamination part**	**References**
Albania	Butrinti Lagoon	(Topi *et al.* 2012)
Armenia	Arak basin Rivers water	(Nalbandyan 2011)
Azerbaijan	River water	(Suleymanov *et al.* 2010)
Belarus	Waste water	(Yasoveev *et al.* 2013)
Bosnia and Herzegovina	Klinje reservoir and Musnica river	(Banjak and Nikolić 2012)
Bulgaria	Surface water of Dam	(Atanasov *et al.* 2012)
Croatia	Fish pond	(Matasin *et al.* 2011)
Czech republic	Ground water	(Novak *et al.* 2014)
France	Roof run off	(Lamprea and Ruban 2008)
Greece	Malakasa basin	(Linos *et al.* 2011)
Greece	Drinking water	(Kaprara *et al.* 2015)
Iceland	Surface water	(Stefánsson *et al.* 2015)
Ireland	Surface water	(O'Neill *et al.* 2015)
Italy	Tap water	(Accornero *et al.* 2005)
Kosovo	Spring water	(Avdullahi *et al.* 2013;Faiku *et al.* 2014)
Malta	Drinking water	(Bugeja and Shoemake 2015)
Norway	Tunnel wash water	(Meland *et al.* 2010)
Poland	Lake	(Daniszewski and Konieczny 2013)
Portugal	Sediment of Ave river basin	(Alves *et al.* 2009)
Sweden	Headwater stream and bottled water	(Huser *et al.* 2012;Rosborg *et al.* 2005)
United Kingdom	Estuary	(Bryan and Langston 1992)
South America		
Argentina	Groundwater	(Fernández *et al.* 2014)
Bolivia	River water	(Rojas and Vandecasteele 2007)

Brazil	River water	(Alves *et al.* 2014)
Chile	River water	(Pizarro *et al.* 2010)
Paraguay	Sediments of river	(Facetti-Masulli and Kump 2010)
Venezuela	Surface water	(García *et al.* 2011)
	North America	
Haiti	Groundwater	(Broadaway *et al.* 2013)
Jamaica	Surface water	(Knight *et al.* 1997)
Mexico	River water	(Páez-Osuna *et al.* 2015)
	Australia	
Fiji	Ground water	(Singh and Mosley 2003)
	Asia	
Armenia	River water	(Nalbandyan 2011)
Azerbaijan	River water	(Suleymanov *et al.* 2010)
Bangladesh	River water	(Rahman *et al.* 2012)
Cambodia	Groundwater	(Irvine *et al.* 2006)
China	River water	(Liu *et al.* 2013)
India	Lake	(Kamala-Kannan *et al.* 2008)
Indonesia	Stream water	(Palapa and Maramis 2015)
Iran	Irrigation water	(Maleki *et al.* 2014)
Iraq	River water	(Al Obaidy *et al.* 2014)
Japan	River water	(Mohiuddin *et al.* 2010)
Lebanon	Bottled water	(Semerjian 2011)
Jordan	Drinking water	(Alomary 2013)
Malaysia	Gombak and Penchula river	(Ismail *et al.* 2013)
Mongolia	River water	(Hofmann *et al.* 2015)
Nepal	Lake water	(Sharma *et al.* 2015)
Oman	Sea water	(Bazzi 2014)
Pakistan	Surface water	(Muhammad *et al.* 2011)
Palestine	Harvested rain water	(Malassa *et al.* 2014)
Philippines	Sea water	(Su *et al.* 2009)
Russia	River water	(Leslie *et al.* 1999)
Saudi Arabia	Ground water	(Zabin *et al.* 2008)
Srilanka	Lagoon water	(Chandrasekara *et al.* 2014)
Taiwan	Sea water	(Lin *et al.* 2013)
Thailand	Ground water	(Wongsasuluk *et al.* 2014)

Turkey	River water	(Akbal *et al.* 2011)
United Arab Emirates	Ground water	(Al-Alawi 2014)
Uzbekistan	River water	(Kulmatov *et al.* 2013)
Vietnam	River and canal	(Wilbers *et al.* 2014)
Yemen	Sea water	(Al-Shiwafi *et al.* 2005)
	Africa	
Algeria	River water	(Leghouchi *et al.* 2009)
Burkina Faso	Ground water	(Nikiema *et al.* 2013)
Chad	River water	(Hisseien *et al.* 2015)
Cote d’lvoire	Groundwater	(Loko *et al.* 2013)
Democratic republic of Congo	Groundwater	(Ngelinkoto *et al.* 2014)
Egypt	Lake water	(Ali and Fishar 2005)
Ethiopia	Lake water	(Dsikowitzky *et al.* 2013)
Ghana	Ground water	(Odonkor and Addo 2013)
Kenya	Lake water	(Oyoo-Okoth *et al.* 2013)
Malawi	River water	(Ullberg 2015)
Rwanda	Ground water	(Nsengimana *et al.* 2012)
Swaziland	River water	(Kowalkowski *et al.* 2007)
Tanzania	Lake water	(Öztürk *et al.* 2009)
Zimbabwe	River water	(Nhiwatiwa *et al.* 2011)

Chromium has been reported to affect the major regions of the world. The chromium levels in groundwater of Greece central region (Thiva Basin) was ca. 100 mg L^{-1} which was several times higher than permissible limit (Tziritis *et al.* 2012). Chromium was found in larvae of *Odonata* insect (0.64 to 0.72 mg kg^{-1}) in Brazil’s Monte alegre stream (Corbi *et al.* 2011). Chromium contamination is also found in rivers (Udy and Lopan) at Russian-Ukraine border (Vystavna *et al.* 2012).It is also reported in geochemical in composition of flood plain soil profile along central Elbe river , Germany (Shaheen and Rinklebe 2014). Chromium was also found in the muscle, hepatic cells of eel (*Anguilla anguilla*) of France (Ribeiro *et al.* 2005). Elevated levels of chromium were found in soil of Danube river at Romanian, Hungary, Serbia and Bulgaria sector (Pavlović *et al.* 2016).

1.5. Source of chromium contamination

Chromium has been mined mostly from Odisha in India. Chromite is the most common chromium ore (Rakhunde *et al.* 2011). Approximately 95% of Chromium resources exist in South Africa (Rakhunde *et al.* 2011). Chromium is used in several industries, including metallurgy, refractory, pigments, electroplating, tanning, pulp production, milling, mining and wood preservation (Gowd and Govil 2008;Rakhunde *et al.* 2011). Chromium and its salts are used in the manufacture of catalysts, leather tanning industry, ceramic and glass industry (Rakhunde *et al.* 2011).The aqueous effluents from these industries find their way into the environment. Boron, manganese, nickel and molybdenum can be used as substitutes for chromium. The substitutes are held back due to economic viability reasons.

1.6. Chromium contamination in India

Chromium contamination has been reported to affect the natural water systems in our country also. Ground water (Sharma *et al.* 2012), lotic (Chatterjee *et al.* 2010;Gupta *et al.* 2009;Sehgal *et al.* 2012) and lentic water system (Purushothaman and Chakrapani 2012) are reported to be contaminated by the chromium. Chromium concentration was reported to be above the permissible limit in several states like Andhra Pradesh (Reddy and Gunasekar 2013), Maharashtra (Singare *et al.* 2011), Uttar Pradesh (Sharma *et al.* 2012), Punjab (Verma *et al.* 2013), Karnataka (Tharannum *et al.* 2011), Maharashtra (Lokhande *et al.* 2011) and Tamil Nadu (Gowd and Govil 2008).Table1.2 provides drinking water standards of India, WHO and USEPA.

Table 1.2 Chromium standards for drinking water

S.No.	**Country/ organization**	**Maximum limit of chromium (mgL^{-1})**	**References**
1	India	0.05	(Mohan *et al.* 2011)
2	WHO	0.05	(Rakhunde *et al.* 2011).
3	USEPA	0.1	(Gupta *et al.* 2011)

1.7. Adverse effects of chromium on human health

Chromium exists in two forms, + 3 and +6 in the environment (Rakhunde *et al.* 2011). The hexavalent form is more toxic as it crosses the cell membrane. Inside the cell, it reduces to +3 forms and interacts with macromolecules and genetic material water (Squadrone *et al.* 2013;Tokar *et al.* 2013). National Toxicology Program (NTP), IARC(International Agency for Research on cancer), USEPA(United states Environment Protection Agency) and OEHHA(Office of Environmental Health Hazard Assessment) have categorized chromium as a human carcinogen (Rakhunde *et al.* 2011). Apart from a human carcinogen, it causes skin rashes, abdominal pain, respiratory problems, weak immune system, kidney and liver damage, lung cancer and ultimately death of humans (Momodu and Anyakora 2010;Rakhunde *et al.* 2011).

1.8. Global cadmium contamination

All continents habitated by human have been reported to be contaminated with cadmium. Table 1.3 presents the list of countries contaminated with cadmium.

Table 1.3 List of countries with cadmium contamination

Continent Europe		
Countries	**Contamination part**	**References**
Germany	Ground water	(Sridhar *et al.* 2000)
Crotia	Krka river	(Cukrov *et al.* 2008)
France	Ground water and Riou Mort river	(Coynel *et al.* 2007)
Turkey	Kucuk river	(Turgut 2003)
Greece	Artificial reservoir	(Gikas *et al.* 2009)
Spain	Ebro river water and sediment	(Ramos *et al.* 1999)
Romania	Groundwater	(Bird *et al.* 2009)
Czech republic	Odra river	(Rybicka *et al.* 2005)
Croatia	Plitvice lakes national park	(Vukosav *et al.* 2014)
Bosnia and Herzegovina	Fish gonads	(Has-Schön *et al.* 2008)
South America		

Brazil	Pardo river	(Alves *et al.* 2014)
Argentina	Yenicaga lake	(Saygı and Yiğit 2012)
Peru	Blanco river	(Méndez 2005)
Bolivia	Poopo basin	(García *et al.* 2005)
Venezuela	Surface water	(García *et al.* 2011)
North America		
Mexico	Santiago river	(Rizo-Decelis and Andreo 2015)
Canada	Athabaca river	(Headley *et al.* 2005)
Cuba	Almendras river	(Graham *et al.* 2011)
Gulf of panama	Oceanic water	(Greaney 2005)
Haiti	Urban storm water	(Fifi *et al.* 2010)
Dominician republic	Yuna river	(Sadio)
Australia		
Australia	Vegetables	(Kachenko and Singh 2006)
Australia	Lake Macquarie	(Alquezar *et al.* 2006)
Papua new guinea	Oceanic water	(Sherwood *et al.* 2009)
New Zealand	Soil	(Schipper *et al.* 2011)
Asia		
Malaysia	Freshwater lake	(Ebrahimpour and Mushrifah 2008)
China	Longjiang River	(Miao *et al.* 2015)
India	Hindon river	(Suthar *et al.* 2009)
Java	River water	(Sikder *et al.* 2013)
Bangladesh	Buriganga River	(Sikder *et al.* 2013)
Japan	Shiribetsu River	(Sikder *et al.* 2013)
Pakistan	Groundwater and lake	(Kazi *et al.* 2009) (Azizullah *et al.* 2011)
Philippines	Suspended solids of Agusan river.	(Appleton *et al.* 2006)
Thailand	Phayao lake	(Tupwongse *et al.* 2007)
Turkey	Dipsiz stream water	(Demirak *et al.* 2006)
Vietnam	Wastewater of fish fed pond	(Marcussen *et al.* 2012)
Iran	Kowsar dam	(Boustani 2011)
Iraq	Euphrates river	(Khethi and Kadhim 2013)

Africa		
Burkina Faso	Ground water	(Nikiema *et al.* 2013)
Democratic republic of Congo	Groundwater	(Ngelinkoto *et al.* 2014)
Egypt	Lake water	(Ali and Fishar 2005)
Ethiopia	Lake water	(Dsikowitzky *et al.* 2013)
Ghana	Ground water	(Odonkor and Addo 2013)
Kenya	Lake water	(Oyoo-Okoth *et al.* 2013)
Morocco	Fez and Sebou river	(Koukal *et al.* 2004)
Nigeria	Ground water	(Momodu and Anyakora 2010)
Zimbabwe	River water	(Nhiwatiwa *et al.* 2011)

Groundwater (Momodu and Anyakora 2010), river water (Miao *et al.* 2015), lake (Ebrahimpour and Mushrifah 2008) and urban wastewater (Fifi *et al.* 2010) are reported to be contaminated with cadmium. A few manmade structures like dams are also contaminated with cadmium (Boustani 2011). Cadmium concentration varies with season, as it is increased with a dry season (Alves *et al.* 2014).

1.9. Source of cadmium contamination

Cadmium is used in industries like paints, electroplating, phosphate fertilizers (Ali *et al.* 2013) mining and alloy industries (Corami *et al.* 2008). The waste water from these industries contaminates the aquatic bodies.

1.10. Cadmium contamination in India

Cadmium is significantly present in various rivers of the country like Hindon (Suthar *et al.* 2009), and lakes in Andhra Pradesh (Vasudevan and Lakshmi 2011). Many areas of the country contaminated with cadmium are Assam (Dhemaji district) (Buragohain *et al.* 2010) and Karnataka (below WHO permissible limit) (Rajappa *et al.* 2010). The groundwater of Loni (Ghaziabad, U.P) (below BIS permissible limit) (Singh *et al.* 2012) and Assam (Chakrabarty and Sarma 2011) and water of G.B. Pant Sagar Lake (U.P.) (Rai 2010) is also reported to be contaminated with cadmium. Soil of urban area of Guwahati, Assam (Mahanta and Bhattacharyya 2011) and sediments of Sunderbans (Jonathan *et al.* 2010) also contain cadmium in larger amounts. So, the regulators and the public must remain vigilant in conserving current water sources; finding new sources of water and raising enough capital to build the appropriate treatment and distribution facilities. The future will pose many challenges to keep water safe and secure. The standards of cadmium for drinking water have been given in Table 1.4.

Table 1.4 Cadmium standards for drinking water

S.No.	Country/ organization	Maximum limit of chromium (mg L^{-1})	References
1	India	0.005	(Vasudevan and Lakshmi 2011).
2	WHO	0.005	(WHO 2004)
3	USEPA	0.005	(USEPA 2016)

1.11. Adverse human health effects of cadmium in water

Cadmium is a well known carcinogen and teratogen. There is no known function of cadmium in the human biological system. Renal dysfunction and neuropsychological impairments occurred due to chronic occupational exposure (Post *et al.* 2010).Cadmium accumulated in rice developed itai-itai disease. In addition to this, it also led to proteinuria and glucosuria. Cadmium also affects respiratory organs and causes lung insufficiency (Vasudevan and Lakshmi 2011). It also affects the bone and causes its degradation in humans. Cadmium is associated with Alzheimer's and Parkinson disease (Momodu and Anyakora 2010). Chronic renal failure e.g. renal failure epidemic among farmers in Srilanka due to cadmium contaminated irrigation water has been reported.

1.12. Objective of the present study

The present study is to present a solution to chromium and cadmium contamination of aqueous contaminants. With the objective of finding the solution, following targets were focussed:

i. Synthesis and characterization of nano crystalline zirconia and nano crystalline iron oxide/hydroxide for removal of chromium and cadmium from aqueous solutions

ii. Determination of isotherm and kinetic parameters for removal of chromium and cadmium from aqueous solution

iii. Evaluation of thermodynamic parameters for removal of chromium and cadmium from aqueous solution

iv. Optimization of removal (%) by collective variation of input variables using response surface methodology

1.13. Scope

The contamination of water with heavy metal causes a lot of health disorders. To deal with contamination of heavy metal i.e. chromium and cadmium adsorption process is applied. In the current study nano crystalline zirconia and nano crystalline iron oxide/hydroxide were used as adsorbents. The optimum adsorption parameters were estimated by using response surface methodology. The isotherm parameters were estimated by comparison between linear and non linear curve fitting of the data.

1.14. Problem statement

The contamination of chromium and cadmium is tried to abate by application of nano crystalline zirconia and iron oxide/hydroxide.