

Today, water availability both in terms of quality and quantity is a problem all over the world. Mainly water stressed developing countries are experiencing the worse of this problem as the world population and industrialization is increasing and climate change is affecting water resources (EPA, 2000). As far as quantity is concerned, many countries have conflicts and others undergone bilateral/multilateral agreements for water sharing and distribution (Flint, 2004; Rai, 2012). With the enactment of several water legislations and guidelines worldwide coupled with the need for environmental sustainability has necessitated the need for several stringent regulations for drinking water supply and wastewater discharge. Wastewater discharges are causing eutrophication and water borne diseases. The situation is getting worse with rapid urbanization where adequate sanitation and wastewater treatment facilities are lacking. Industrialization has contaminated the environments with heavy metals, particularly, in developing countries of the world, where advance treatment technologies are neither available nor affordable (Hooda, 2007)

Since Middle Ages due to human activities, natural aquatic ecosystems, particularly the estuaries and freshwater systems, are not only being polluted to varying degrees, but are also condemned to fairly long-term pollution due to metals deposited in sediments. The heavy metal load from domestic wastewater and sewage alone signifies that this will be a continuing problem for science and humankind. Water in rivers and lakes can become heavily polluted, depending on the volume flow and its proximity to point sources. Toxic metal contamination of aqueous water streams and groundwater poses a major environmental and health problem that is still in need of an effective and affordable technological solution. To achieve unpolluted drinking water and management of water sources, several technologies and processes for the removal of persistent inorganic toxicants including nitrate, ammonia, phosphates and heavy metals are currently in use. These methods include ion exchange, chemical precipitation, disinfection, adsorption by activated

carbons, reverse osmosis, nano-filtration and sewage treatment plant (STPs) processes. Most of these methods are expensive, require high energy and are not able to completely remove the heavy metals (Memon and Schroden, 2009) and excessive nutrients (Manuela *et al.*, 2010), but merely transfer the pollutants from the wastewater to a sludge residue which is disposed of by land filling (Tolu and Atoke, 2012) whereby the pollutants eventually find their way to fresh water supplies there by contaminating it and thus, do not provide acceptable solution to pollution problem. From an ecological and economic point of view, the need for an alternative ecofriendly and cost-effective technology is recommended as the cleanup of hazardous wastes by conventional technologies is projected to cost at least \$400 billion in the United States alone, (Salt *et al.*, 1995). Methods using living wetland plants to remove metals from water appear to be an alternative. Plants that have a high metal-bioaccumulation capacity and a good tolerance to high metal concentrations over long periods of time are necessary.

Over the past fifteen years phytoremediation technology became an effective method of environment clearing due to the plants ability to accumulate the contaminants at the concentration level thousands times higher than background one. The plants are capable to remove many toxic substances from reservoirs, acquiring the pollutants from waters as food elements, basically through root system using the products of decomposition for their viability (Watai *et al.* 2004). Water plants actively accumulate Pb, Cd, Cu, Fe, Mn, Zn, Cr, As, Ni etc., and other elements and substances. The plants are more tolerant to the inorganic contaminants as they have differential capacity to assimilate or scavenge degradable and non-biodegradable inorganic contaminants. These potentials of plants have emerged as a major area of phytotechnological studies and they have been studied for the phytoremediation potential for removal of toxic contaminants from contaminated soil and

water (Rai, 2010; Tolu and Atoke, 2012; Rawat *et al.*, 2012; Baudhh and Singh, 2012, Brazini et al., 2012; Vymazal and Svehla, 2013).

### **2.1. Pollution of Heavy metals in the environment and their toxicity to the living organisms**

Heavy metals in surface water systems can come from natural or anthropogenic sources. Currently, anthropogenic sources of metal pollution exceed the natural inputs. Main sources of metal pollution are the burning of fossil fuels, mining and smelting of metalliferous ores, municipal wastes, sewage, pesticides, and fertilizers. Energy-production technology and environmental pollution are intimately linked with each other. Energy-intensive processes and chlor-alkali industries for the manufacture of agrochemicals deteriorate the water quality of lakes and reservoirs due to the discharge of various pollutants; especially a range of heavy metals (Rai *et al.*, 2007). Heavy metals constitute a heterogeneous group of elements; having a specific gravity greater than 4.0 and a relatively high density (approximately 5 g/cm<sup>3</sup>) as their common characteristics (Clijsters et al., 1999). From a general biological as well as plant physiological point of view, essential and non-essential heavy metals can be distinguished. Living organisms require trace amount of some heavy metals, these includes cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), strontium (Sr), vanadium (V) and Zinc (Zn), and they are referred to as essential heavy metals. Non-essential heavy metals of particular concern in the environment include cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), and silver (Ag), (Kennish, 1992). Essential heavy metals play essential roles as components of metalloproteins, as cofactors in enzymatic catalysis, and in a wide array of other cellular processes. At supra-optimal concentration however, they become phytotoxic, induce leaf chlorosis, and reduce growth. At least 20 metals are classified as toxic with half of them emitted into environment in concentrations that pose great risks to human health. The common heavy metals that have

been identified in polluted water include arsenic, copper, cadmium, lead, chromium, nickel, mercury and zinc. The danger of heavy metal pollutants in water lies in two aspects of their impact. Firstly, heavy metals have the ability to persist in natural ecosystems for an extended period. Secondly, they have the ability to accumulate in successive levels of the biological chain, thereby causing acute and chronic diseases. For example, cadmium and zinc can lead to acute gastrointestinal and respiratory damages to brain, heart and kidney damages (Nomanbhay and Palanisamy, 2005; Lone et al., 2008). The use of domestic and industrial effluents, which may contain high concentrations of heavy metals on agricultural lands, is a common practice in some parts of the world. These toxic metals, when concentrated on plant tissues can have damaging effects on the plants themselves and may also pose health hazards to man and animals (Athar and Ahmad, 2002). Episodes of the metal pollution such as Minamata Episode due to Methyl mercury, Itai- itai or Ouch Ouch due to Cadmium have taken toll on human populations. Another reason that toxic heavy metals are causing potential concern is that the metals may be transferred and accumulated in the bodies of animals or human beings through the food chain, which potentially causes DNA damage and carcinogenic effects caused by their mutagenic ability (Knasmuller *et al.*, 1998). Examples include Cd, Cr, and Cu, which have been associated with health effects ranging from dermatitis to various types of cancer (Das, Samantaray, and Rout, 1997; McLaughlin, Parker, and Clark, 1999). In addition, some metals occur in the environment as radioactive isotopes (*e.g.*, U238, Cs137, Pt239, and Sr90), which can greatly increase the health risk (Pilon-Smits and Pilon, 2002)

Table 2.1 lists some of the toxic heavy metals with their harmful effects. (Wang et al., 2004; Johnson and Hallberg, 2005; Gardea-Torresdey et al., 2005 Silvia et al., 2006; Baldisserotto et al., 2007 Lon et al., 2008; Singh et al., 2009; Rawat et al., 2009, 2012 ; Apkor and Muchie, 2010, Kumar, 2013).

**Table 2.1. Effect of more toxic heavy metals reported in aquatic ecosystem on human health and plants**

Heavy metal	Effect on Man	Effect on Plants
Cadmium	Damage to brain, Gastrointestinal and respiratory problems, Kidney and Liver damage	Decreases seed germination, lipid content, and plant growth; induces phytochelatin production
Arsenic	Cutaneous and Visceral Malignancies, Black Foot Disease, Severe Vomiting, Diarrhoea	Biochemical dysfunction at cellular level, damage to proteins and lipids.
Lead	Kidney damage, Heart ailments, Reproductive problems, Bone weakness	Reduces chlorophyll production and plant growth; increases superoxide dismutase
Mercury	Foetal Brain damage, Damage to Kidney, Lungs, Heart, Neurological problems	Decreases photosynthetic activity, water uptake and antioxidant enzymes; accumulates phenol and proline
Chromium	Haemolysis, renal and liver failure, Allergies, Dermatitis, Foetal deaths, Lung cancers	Decreases enzyme activity and plant growth; produces membrane damage, chlorosis and root Damage
Copper	Gastrointestinal distress, Liver or kidney damage (Long term exposure)	Inhibits photosynthesis, plant growth and reproductive process; decreases thylakoid surface area
Iron	Increased pulse rates and respiration, hypertension, drowsiness, congestion of blood vessels	
Zinc	Vomiting, renal damage, cramps	Reduces Ni toxicity and seed germination; increases plant growth and ATP/chlorophyll ratio
Nickel		Reduces seed germination, dry mass accumulation, protein production, chlorophylls and enzymes; increases free amino acids
Manganese	Growth retardation, fever, sexual impotence, muscles fatigue, eye blindness.	Brown spots on mature leaves, interveinal chlorosis and necrosis, deformation of young leaves and growth retardation

Since heavy metal pollution affects the quality of drinking water supply and wastewater discharge, there by affecting both human and plant lives, great efforts have been made in the last two decades to reduce pollution sources and remedy polluted water resources. Though various technological advancements have been made to remove pollutants from water but certain drawbacks and limitations are associated with them. Table 2, lists the advantages and disadvantages of conventional methods of water treatment (Rai, 2009, Apkor and Muchie, 2010, Barkat, 2011).

**Table 2.2 Conventional Methods of Water Treatment**

Methods	Advantages	Disadvantages
Chemical precipitation	Convenient, self-operation, low maintenance, low capital cost	Replenishment of chemicals, requirement of extra coagulation and flocculation, toxic sludge generation
Coagulation- flocculation	Settlement of suspended solids in less time, improved sludge settling	Extra operational cost for sludge disposal
Ion exchange	Less time consuming, no sludge generation, high metal removal efficiency, better performance in acidic pH range	Less suitable as few metals are not exchangeable through ion exchange resins, high capital cost
Reverse osmosis	Greater ionic species removal, can also operate at high temperatures, reduces the concentration of dissolved organic compounds	Expensive to procure and operate, elevated pressure makes the technique costly and sensitive to operating conditions
Nanofiltration	Operates at low pressures than reverse osmosis	Costly, membrane fouling

**2.2. Phytoremediation of Aquatic ecosystems: A novel, cost effective and ecofriendly technique.**

Phytoremediation, the use of plants to remove pollutants from the environment, is a growing field of research in environmental studies because of the advantages of its environmental friendliness, cost effectiveness and the possibility of harvesting the plants for the extraction of absorbed contaminants such as metals that cannot be easily biodegraded for recycling

among others (Maine et al., 2004, Skinner et al., 2007, Malik, 2007 ). Over the last two decades, phytoremediation has become an increasingly recognized pathway for contaminant removal from water and shallow soils and is an aesthetically pleasing, solar-driven, passive technique useful for remediation of shallow plumes with low to moderate levels of contamination (EPA, 2001, Wang et al., 2011). Aquatic macrophytes, which play important roles in aquatic ecosystems, have shown great potential to sequester selected heavy metals and nutrients through their root systems and by uptake through their plant bodies. It has been reported that these plants can accumulate heavy metals 100,000 times greater than in the associated water (Mishra and Tripathi, 2008). Therefore, they have been used for heavy metal and nutrient removal from a variety of sources (Hassan *et al.*, 2007; Mishra and Tripathi 2008; Rai, 2010, 2012, Rawat and Singh, 2012). Phytoremediation exploits plant's innate biological mechanisms for the removal of contaminants from the environment for human benefit. The phytoremediation technique relies upon the following processes:

### **2.3. Phytodegradation**

Phytodegradation mainly removes the organic contaminants in the environment by internal and external metabolic processes driven by the plant. It involves the use of plants to uptake, store and degrade contaminants within its tissue. In this process plants metabolize and destroy contaminants within their tissues. Plant enzymes play a significant role in the breakdown of organic pollutants (Newman and Reynolds, 2004). During phytodegradation, the plants are able to take-up metal contaminants directly from the soil/water or release exudates that help to degrade pollutants via co-metabolism in the rhizosphere.

### **2.4. Phytoextraction**

This method is used primarily for wastes containing metals whereby plant roots absorb, translocate and store contaminants along with other nutrients and water. Metal compounds that have been successfully phytoextracted include, zinc, copper, nickel, lead, cadmium,

arsenic, chromium. The process of phytoextraction is known to occur either continuously (natural) using hyper-accumulators or induced through the addition of chelates such as EDTA to increase the bioavailability of metals (Utmazian and Wenzel, 2006). Researchers have also realized that phytoextraction can be used for the recovery of precious metals such as gold, silver, platinum, and palladium, which indicates the wide possibilities of the phytoremediation technology with regards to mining (Gardea -Torresdey et al., 2005).

### **2.5. Rhizofiltration**

Usually aquatic plants perform this process. The hyperaccumulating aquatic plants adsorb and absorb pollutants from aquatic environments i.e., water and wastewater (Rahman and Hasegawa, 2011). A suitable plant for rhizofiltration applications can remove toxic metals from solution over an extended period of time with its rapid-growth root system. A variety of plant species have been found to be effective in removing toxic metals such as As, Cu, Cd, Cr, Ni, Pb and Zn from aqueous solutions (EPA, 2001; Rai, 2012.,).

### **2.6. Phytovolatilization**

This phytoremediation technique is the plants ability to take up toxic metals from the growth matrix and subsequently transform and volatilize them into the atmosphere through its leaves. There is the transformation of pollutants within the plant body, as the water travels along the plant's vascular system from the roots to the leaves, whereby the contaminants evaporate or volatilize into the air surrounding the plant. Some of these contaminants can pass through the plants to the leaves and volatilize into the atmosphere at comparatively low concentrations (Ghosh and Singh, 2005).

### **2.7. Phytostabilization**

Phytostabilization, also referred to as in-place inactivation, is primarily used for the remediation of soil, sediment, and sludges (EPA, 2000). The process of phytostabilization depends on the tolerance ability of a plant to a contaminant. It is the use of plant roots to limit

metal mobility and bioavailability in the soil. During the process, contaminant are absorbed and accumulated by roots, adsorbed onto the roots, or precipitated in the rhizosphere. When this happens, there is the prevention of mobility of the contaminants, hence reducing their availability in the food chain (Lasat, 2000; Jada and Fulekar, 2009).

### **2.8. Role of Constructed wetlands in phytoremediation of polluted water**

The Ramsar Convention on Wetlands, 1997 defines wetlands as the areas of marsh, fen, peat land or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water the depth of which at low tide does not exceed six meters. Wetlands encompass a broad range of ecosystems, from submerged coastal grass beds to salt marshes, swamp forests, and boggy meadows. In general, the term “wetlands” refers to transition zones between terrestrial and aquatic systems with soil saturated with water for at least part of the year or covered by shallow water along with characteristic wetland plant species (Kalff, 2002). Wetland ecosystems act as natural filters and have been effectively used for the treating wastewater; and removing toxic chemicals and heavy metals through absorption by plants. Certain wetlands are being engineered and have been designed and constructed to utilize natural processes involving wetland vegetation, soil, and the associated microbial assemblages to assist in treating wastewaters. They are designed to take advantage of many of the same processes that occur in natural wetlands, but do so within a more controlled environment. They are referred to as constructed wetlands. The use of constructed wetland system is a reasonable option for treating contaminated water by simulating natural wetlands, owing to lower cost, fewer operation and maintenance requirements, and little reliance on energy inputs (Varnell et al., 2009). Constructed wetland (CW) is a biogeochemical and highly efficient system to treat polluted waters generating from different sources such as domestic, highways, mining and industrial sectors and offer an effective alternative for traditional wastewater treatment

systems (Khan et al., 2009). Constructed wetlands have been used for a variety of purposes, from rehabilitating areas where wetlands were previously located, to serving very specific functions such as wastewater treatment (Hawkins et al., 1997). This system has been found to be able to remove various pollutants and nutrients from wastewater (J. Vymazal 2007, Bindu et al., 2008) and has also been successfully used to treat wastewater with high concentrations of nutrients (Gottschall et al., 2007, Haiming et al., 2011). Much interest has been focused on constructed wetlands for removing toxic metals from wastewater and drinking water sources in recent years (Hadad et al., 2006; Maine et al., 2006; Jayaweera et al., 2008). The CW system contains natural processes of aquatic macrophytes that not only accumulate pollutants directly into their tissues but also act as catalysts for purification reactions usually occur in the rhizosphere of the plants (Jenssen et al., 1993). In constructed wetlands, substrate interactions remove most metals from contaminated water (Walker et al., 2002, Liu et al., 2007). The permanent or temporarily anoxic condition in wetland soil helps to create an environment for immobilization of heavy metals in the highly reduced sulfite or metallic form and plants may play an important role in metal removal through filtration, adsorption, cation exchange, and root-induced chemical changes in the rhizosphere (Jainguo et al., 2007, Liu et al., 2007). Numerous factors including pH of water and sediment, mobilization and uptake from the soil, compartmentalization and sequestration within the root, efficiency of xylem loading and transport (transfer factors), distribution between metal sinks in the aerial parts, sequestration and storage in leaf cells, and plant growing and transpiration rates can also effect the remediation processes of the contaminated sites (Hadad et al., 2006; Khan et al., 2006). Most constructed wetlands for wastewater treatment are planted with emergent macrophytes but the design of the systems in terms of media as well as the flow regime varies. The most common systems are designed with a horizontal subsurface flow (HF constructed wetlands), but vertical flow (VF constructed wetlands)

systems are becoming more popular (Vymazal, 2005). Among the different types of CWs, Horizontal Sub-surface Flow Constructed Wetlands (HSSFCWs) are most widely used and became low-impact alternatives to more conventional wastewater treatment processes. In a typical HSSFCW, wastewater is maintained at a constant depth and flows horizontally below the surface of the bed has been proven to be efficient in removing pollutants, organic matter and pathogens. Table 3.3 lists some common aquatic macrophytes used for heavy metal removal from aquatic ecosystems. (Liao and Chang, 2004; Prasad *et al.*, 2005; Hadad *et al.*, 2006; Rai, 2007; Rai and Tripathi, 2007a, 2009; Rehman *et al.*, 2008; Zhang *et al.*, 2009; Dilshad *et al.*, 2010; Abida and Hari, 2010; Amin Mojiri, 2011; Usman *et al.*, 2011; Hamizah Mokhtar *et al.*, 2011; Hegazy *et al.*, 2011).

**Table 2.3 Some common heavy metal accumulating aquatic macrophytes**

Aquatic Macrophytes	Heavy Metal Accumulation
<i>Azolla filiculoids</i>	Cr, Ni, Zn, Fe, Pb, As, Hg, Cd
<i>Azolla pinnata</i>	Cd, Cu, Zn, Hg
<i>Ceratophyllum demersum</i>	Cu, Cr, Pb, Hg, Fe, Mn, Zn, Ni
<i>Eichhornia crassipes</i>	Cd, Pb, Cu, As, Ni, Cr, Zn, Hg, Co, Al
<i>Hydrilla verticillata</i>	Cu, Hg, Fe, Ni, Pb
<i>Lemna spp.</i>	Pb, Mn, Cu, Cd, Cr, Hg, Ni, Fe
<i>Mentha aquatica</i>	Cd, Zn, Cu, Fe, Hg
<i>Nymphaea alba</i>	Cr, Cd, Pb, Ni, Zn, Mn, Fe, Co
<i>Phragmites australis</i>	Fe, Mn, Zn, Cu
<i>Potamogeton crispus</i>	Cu, Pb, Mn, Fe, Cd
<i>Salvinia spp</i>	Cu, Fe, Ni, Zn
<i>Spirodela polyrrhiza</i>	As, Hg
<i>Typha domingensis</i>	Fe, Mn, Zn, Al, Ni
<i>Wolfia globosa</i>	As