In the last few decades, many precious environmental resources especially water and soil, have loaded with huge amount of pollutants as a result of rapid industrialization, urbanization, population growth and modern agricultural activities. Now a days, a wide variety of contaminants are entering to the aquatic environment, which not only disrupts natural conditions of eco-system but also have toxic impact on living organisms. Heavy metals and fluoride are some of the inorganic contaminants which leads to many health disorders and disfunctions in human and animals. Hence, the remediation of such contaminants is essential for the well-being of the mankind. Expensiveness, ineffectiveness at low concentration, time consumption and sometimes non-eco-friendly nature are the main drawbacks of many of the prevailing remediation techniques available for theses contaminants. Consequently, development of effective, efficient and eco-friendly clean-up methods for the removal or reduction of the toxic contaminants like heavy metal and fluoride from water is necessary, for the protection of human and environmental health.
2.1 Heavy metals related issues and remediation

Among numerous inorganic contaminants in water, contamination and accumulation of heavy metals is a serious problem around the world, because of their persistent, non-biodegradable and bio accumulative nature, abundant sources and high toxicity even at low concentration. Its occurrence in high amount is a potential threat to food safety and have detrimental effects on human and animal health (Hu et al., 2017). Effluents from several industries like electroplating, mining, smelting, tannery, leather, textile, paint, petroleum refining, pigment & dyes, wood processing, photographic film production etc., contains significant quantity of heavy metals. Even though, some heavy metals are extremely essential to living organism, but its concentration beyond the limits suggested by various national and international organization may lead to various physiological disorders (Saha & Paul, 2016).

Verma and Dwivedi (2013) have reported that the metals like zinc (Zn), iron (Fe), copper (Cu) are beneficial for human and animal health in small dosages but beyond the limit it may become toxic. For agriculture purposes, some metals like zinc (Zn), copper (Cu), iron (Fe), manganese (Mn), are applied in prescribed quantities. But, heavy metals like lead (Pb), mercury (Hg), arsenic (As), cadmium (Cd), chromium (Cr) especially hexavalent chromium, nickel (Ni), barium (Ba), cobalt (Co), selenium (Se), vanadium (V), etc. are very toxic, harmful, and poisonous even in at parts per billion level. Tendency of heavy metals to bioaccumulate, i.e., the increase in the heavy metal concentration in a biological organism over time, compared to its concentration in the
environment, makes it more hazardous. In living things, metals are stored sooner than they are broken down or excreted. Its toxicity leads to damaged or reduced mental and central nervous function, damage to blood composition, kidneys, lungs, liver, and other vital organs and lowers the energy levels. While, long-term exposure may have consequences like slowly progressing physical, muscular, and neurological degenerative processes that mimic Parkinson's disease, Alzheimer's disease, muscular dystrophy, and multiple sclerosis. Allergies are also one of its common issues and cancer is the detrimental effect of frequent, long-term contact of some metals or their compounds. Severe mucosal irritation and corrosion, hepatic and renal damage, widespread capillary damage, gastrointestinal irritation, central nervous system disorders followed by depression and possible necrotic changes in the liver and kidney are the impact of excessive intake of Cu in human. The Ni exposure have the effects which vary from skin irritation to damage to the nervous system, lungs, and mucous membranes. Hexavalent chromium, a strong oxidant is highly toxic. The carcinogenicity is a main toxic characteristic of some heavy metals (Argun et al., 2007).

The excessive amounts or imbalances of a metal species exhibits many toxicity symptoms, cellular functioning disorders, long-term devastating disabilities in human beings, and ultimately death. In global context, the pollution by heavy metals is becoming one of the major environment threats. It is a most sever problem in population dense countries particularly like China and India (Dave & Chopda, 2014). The US Environmental Protection Agency (US EPA) and the Agency for Toxic Substances and Disease Registry (ATSDR) enlisted the top 20
hazardous substances which include some heavy metals such as As, Pb, Hg, and Cd (Pandey, 2012). These toxic metals from the environment can be removed by various physicochemical and biological approaches. Majority of the, physicochemical treatment techniques are expensive and not environmentally safe. Chemical precipitation, ion exchange, oxidation/reduction, reverse osmosis, membrane separation, electro dialysis, solvent extraction, sedimentation, filtration, electrochemical techniques, and cation surfactant, etc. are the various treatment methods for heavy metal contaminated water but, some of these approaches are expensive, energy intensive and often linked with generation of toxic by-products (Argun et al., 2007; Tripathi & Ranjan, 2015; Czikkely et al., 2018). So, development of environment friendly, low cost, and effective techniques to remediate toxic heavy metals from water is an obligatory for the wellbeing of mankind and environment. Prevention of transport of toxic metals from soil to water resources can be achieved by proper soil remediation.

Heavy metals can be lethal to human as well as environment even at low concentration. Therefore, effective and efficient remediation strategies are required to reduce or remove the heavy metal contamination. Numerous chemical, physical and biological technical solutions have been utilized and established to remove potential toxic metal from wastewater (Czikkely et al., 2018). Each method has its own merits and demerits. The biological remediation methods are most effective because of its characteristics like natural process, environment friendly nature, inexpensiveness, and high public acceptance. Environmental clean-up using biological agents is termed as bioremediation. Phytoremediation, an
eco-friendly technique has revealed promising results in the decontamination of heavy metals and also been a solution for various emerging environmental issues. The fundamental elements in this technique are plants (terrestrial or aquatic) which plays a vital role for remediation of heavy metal contaminated environments. It is considered as environmentally friendly, efficient, cheap and reliable remediation method for metals (Wani et al., 2017).

Ali et al. (2018) reviewed and stated that phytoremediation involves the usage of plants to remove, transfer, stabilize and/or degrade pollutants in water, soil and sediment. This plant-based technology has increased acceptance in the last ten years as an efficient, cheap and environmentally friendly technology especially for eradicating toxic metals. Currently, in the US alone, 6-8 billion US dollars are expended annually for environmental clean-up and in the worldwide context, it is 25-50 billion US dollars per year. Water hyacinth (*Eichhornia crassipes*), pennywort (*Hydrocotyle umbellata L.*), and duckweed (*Lemna minor L.*) are some important aquatic plants used for the remediation of aquatic ecosystem. More investigations are required in the phytoremediation topic to address technical issues and to find out the geographically appropriate plant species for effective remediation. In phytoremediation process, accumulation of metals by plants is influenced by several factors like variations in plant species, plants growth stage, element characteristics control absorption, accumulation and translocation of heavy metals.

*Eichhornia crassipes* was utilized for heavy metal removal, world widely. Water hyacinth is although considered to be as one of the most
problematic aquatic plants due to its uncontrollable growth in water bodies but its quest for nutrient has provided way for its usage in phytoremediation process. Besides, its use in solving wastewater treatment problems in urban or industrial areas using this plant, various useful by-products can be developed like animal and fish feed, power plant energy (briquette), biogas, ethanol, composting and fiber board making. For the future aspects, the utilization of invasive plants in contamination abatement phyto-technologies can undoubtedly assist for their sustainable management in wastewater treatment (Rezania et al., 2015).

Taiwo et al. (2015) studied that water hyacinth (*E. crassipes*) can be used for phytoremediation of heavy metals (Zn, Cu and Pb) in water samples for the period of 8 weeks. The study conducted with heavy metals solutions in different concentrations. At the end of 8 weeks of treatment study, it was detected that the amount of the metals in the water were below the detection limit but it was accumulated in the plant. Correspondingly, the results of the Bioconcentration factor (BCF) exhibited that the studied plant (*E. crassipes*) hyperaccumulated Zn than other metals. Hence, heavy metal uptake by *E. crassipes* by phytoremediation technology appears to be a prosperous method for the remediation of heavy metal contaminated environment.

*E. crassipes* have the ability to remediate different toxic metals (Zn, Cu, Cr, Cd, Ag, Pb, and Ni) from natural water bodies and/or wastewater polluted with low levels. But, a significant reduction in biomass production was reported in metal treated plants compared to the control. More metals were also accumulated in roots than in shoots.
(Odjega & Fasidi, 2007). To overcome the reduction in biomass under metal contaminated media and for better translocation of metals to plants aerial parts, different technique can be used to assist phytoremediation process.

Song et al. (2011) reported that the performance of laboratory-scale constructed wetlands coupled with micro-electric field (CWMEF) using cannas (*Canna generalis*) for heavy metal contaminated wastewater treatment. They observed, a better performance for heavy metal (HM) removal from wastewater by CWMEF than the ordinary constructed wetlands (CWs). Due to the stimulation of the appropriate voltage and electrical exposure time, the plant (cannas) grown better and in fact, assimilated more metal ions in CWMEF than in CWs. The environmental conditions in constructed wetlands coupled with micro-electric field, like the increased pH by electrolysis of water, the occurrence of aluminum ions by anodizing of aluminum, leads to chemical precipitation, physical adsorption and flocculation of metallic ions. This study suggest that the constructed wetland system coupled with micro-electric field (CWMEF) has much better heavy metal removal capacity than do conventional CWs. Putra et al. (2017) also reported about the Electro Assisted-Phytoremediation (EAPR) to reduce the COD, BOD and heavy metal (Pb and Cu) concentration in the wastewater using water hyacinth. Their result displayed that the EAPR method reduced the COD, BOD, Pb and Cu in the 4 h of EAPR process. Titanium electrode and the combined use of stainless steel U316 rod and net wire were used as an anode and cathode in the experiment. The residual concentrations were within the water quality standard of class IV according to government regulation No. 82/2001 of
the water quality management and water pollution regulation of the Republic of Indonesia.

A combination of phyto - and electroremediation was also attempted by Kubiak et al. (2012) for the arsenic removal using *Lemna minor*. This article presents only the preliminary results of electrically enhanced phyto-remediation, using common duckweed, for the arsenic remediation from spiked surface water. The aquatic phytoremediation process improves when combined with electrochemical process (Putra et al., 2017). Under electrified conditions plant can improve ability to resist adverse circumstances by promoting the synthesis of CHLab, inhibiting MDA synthesis, and catalyzing SOD synthesis. Accordingly, the plant assimilates more metal in electrified phytoremediation process (Song et al., 2011).

Various nanomaterials of different sizes and shapes were fabricated and have employed successfully and safely in various fields such as environmental science, medicine, and food processing, etc. However, their use in agriculture purposes, especially for plant production and protection, is an under-explored area by many research communities. Preliminary studies indicated that some nanomaterials have the potential to improve seed germination and growth, plant protection, pathogen detection, and pesticide/herbicide residue detection (Khot et al., 2012). Morteza et al. (2013) studied the effect of titanium dioxide on plant (corn i.e., *Zea mays* L.). The outcome of their study revealed that nano TiO$_2$ have significant effect on chlorophyll content (a and b), total chlorophyll (a + b), chlorophyll a/b, carotenoids and anthocyanins. The maximum
amount of pigment was recorded in nano TiO$_2$ sprayed plants compared to control. The application of nanoparticles especially TiO$_2$ nanoparticles facilitated the increase in crop yield.

Contamination of groundwater resources through the leaching of heavy metals from soil is also a major environmental concern. Most of the existing conventional soil remedial technologies are expensive and inhibit the soil fertility; subsequently, causes negative influences on the ecosystem. Ghosh and Singh, (2005) discussed in detail about mobility, bioavailability and plant response to presence of soil heavy metals. Several practices to enhance phytoextraction and utilization of by-products have been also elaborated. They also mentioned about the needs of proper disposal of biomass produced during process and its viable management by producing renewable energy.

Qu et al. (2011) discussed about the effect of ammonium molybdate on phytoremediation of heavy metal contaminated soil. It has been used to remove the toxic metals in wastewater by forming precipitates (Pb). However, the application of ammonium molybdate in the remediation of the toxic metals contaminated soils is not a widely studied area. The experiment conducted (1) To find the reaction mechanisms of ammonium molybdate with toxic metals; (2) To investigate the effects of ammonium molybdate on (im)mobilization of the toxic metals in soils; and (3) To understand the effects of ammonium molybdate on uptake toxic metals from soils by alfalfa (*Medicago sativa* L.) plants; aforementioned were the main objectives of their study. The amphoteric-immobilization/mobilization effects of ammonium
molybdate on toxic metals were revealed in the study. The ammonium molybdate can be termed as half-extracting agent, half-chemical stabilization agent, or amphoteric agent. Metals like Pb, Hg, Cr, and Zn can be precipitated with ammonium molybdate and could be stabilized by ammonium molybdate, but metals such as Cd, Ni, Cu can be formed more soluble fractions with ammonium molybdate. The heavy metal contents and BCF values in alfalfa plants were increased after treatment with ammonium molybdate. TF < 1 were also observed. The application of ammonium molybdate increases the acid soluble fractions of Cd, Ni, Cu, and residual fractions of Pb, Hg, Cr, and Zn i.e., the toxicities of Cd, Ni, and Cu to plants in soils increases but, the toxicities of Pb, Hg, Cr, and Zn decreases (Qu et al., 2011; Qu et al., 2016). Ogunkunle et al. (2015) reported the heavy metal accumulation by plant from Amaranthaceae family.

The ease of operation, convenience and simplicity of design, makes the adsorption process a better alternative in water and wastewater treatment. Adsorption processes are applied in many wastewater treatment plants, for the removal of dissolved contaminants and that remain from the subsequent biological phases or after chemical oxidation process. Nowadays, the most commonly adopted adsorbent is the activated carbon. Activated carbon is commonly used for the removal of various contaminants from water such as heavy metals and dyes. However, its widespread usage in wastewater treatment is sometimes limited due to its expensiveness, also further issues such as the adsorbent regeneration capacity or the disposal (Gisi et al., 2016). Tripathi and Ranjan, (2015) has reviewed various low-cost adsorbent for the removal of heavy metal
contamination from wastewater. The removal of toxic heavy metals like Pb, Cd, Zn, Cu, Ni, Hg, Cr etc. using effective agent or adsorbent materials like clay, zeolites, chitin and peat moss were reported. Also, various agricultural waste materials such as rice husk, black gram, neem bark, waste tea, walnut shell, Turkish coffee, etc. were recognized as a potent adsorbent for metal removal. Besides, the technical feasibility to remove toxic metals from polluted water using low-cost industrial by-products like blast furnace sludge, fly ash, waste slurry, iron (III) hydroxide and red mud, lignin, coffee husks, tea factory waste, Areca waste and sugar beet pulp were explored.

Some medicinal plants also have potential to remove heavy metals from water. Rao et al. (2010) have confirmed the biosorption potential of Fennel biomass (*Foeniculum vulgari*), a medicinal herb for the effective elimination of Cd (II) ions. Argun et al. (2007) discussed in detail about the adsorption of heavy metal (Cu, Ni, and Cr) ions from aqueous solutions by oak (*Quercus coccifera*) sawdust modified by means of HCl treatment. As a part of the study, the optimum pH, adsorbent mass, contact time, and shaking speed were determined. The adsorption isotherms were studied using concentrations of the metal ions ranging from 0.1 to 100 mg/L. Their results revealed that, the adsorption process follows pseudo-second-order kinetics, as well as Langmuir and D-R adsorption isotherms. And also, discusses about the thermodynamic parameters of the adsorption (the entropy, enthalpy and Gibbs free energy). The spontaneous and endothermic nature of adsorption process was demonstrated by the results. The maximum removal efficiencies obtained were 93% for Cu (II) at pH 4, 84% for Cr (VI) at pH 3 and 82% for Ni (II) at pH 8. The wood-based
materials increase the COD of water, but by acid modification of the adsorbents decreases this issue. The removal study of cadmium and lead from aqueous solutions using red alga *Ceramium virgatum*, exhibited high sorption capacity. The Fourier transform infrared spectra confirms the carboxyl (– C O), hydroxyl (–OH), and amine (–NH) groups which were responsible for the binding of the metal ions (Hannachi, 2012).

Utilization of iron oxide-based nanomaterials for the removal of heavy metals is well recognized adsorbents. Due to its significant physiochemical property, low-priced method and easy regeneration or separation in the presence of external magnetic field makes them more attractive toward water decontamination. Surface modification strategy of iron oxide nanoparticles is an effective method to increase the efficiency of iron oxide nanoparticles for the removal of the heavy metal ions from the aqueous system (Dave & Chopda, 2014). Al-Saad et al. (2012) investigated the sorption behaviour of the iron oxide (α-Fe₂O₃) nanoparticles and its applicability to purify water from the aluminium, arsenic, cadmium, copper, cobalt, and nickel. The adsorption behaviour of iron oxide nanoparticles towards six metallic ions (Al (III), As (III), Cd (II), Cu (II), Co (II), and Ni (II)) has been investigated by batch experiment under different conditions (pH, concentration of metals, contact time, adsorbent dosage, and temperature).

Dorniani et al. (2014) studied the efficacy of two nanocarriers polyethylene glycol and polyvinyl alcohol magnetic nanoparticles coated with gallic acid (GA) in drug delivery. X-ray diffraction and TEM results showed the formation of pure Fe₃O₄ nanoparticles having spherical shape
with the average size of diameter after coating Fe$_3$O$_4$ nanoparticles with polyethylene glycol-GA (FPEGG) and polyvinyl alcohol-GA (FPVAG). In the study, thermogravimetric analysis was used to prove the thermal stability after coating and fourier transform infrared (FTIR) revealed the successful coating of two polymers (PEG and PVA) and gallic acid on the superparamagnetic iron oxide nanoparticles. Anticancer activity of the two nanocomposites, FPEGG and FPVAG demonstrated its high anticancer effect.

Water quality management and its assessment in light of heavy metal concentration is of prime importance. For water quality management, the overall water quality status and identification of source of origin of heavy metals are essential. The heavy metal pollution index (HPI) and Factor analysis (FA) are most suitable and effective approaches to evaluate the status of water quality and recognizes the source of contaminants (Saha & Paul, 2016). The most appropriate statistical methods to identify the origin of metals and the correlations between heavy metals at a contaminated site are principal component analysis (PCA) and cluster analysis (CA).

2.2 Fluoride contamination in water and its remediation using plant materials

Contamination of water by fluoride is a serious topic across the globe because of its irreversible health threats. During initial stages, fluoride studies were limited to local or regional scale. Because of its serious socioeconomic implications, this problem demands the need for a global perspective. Bhattacharya and Samal (2018) reviewed that fluoride
contamination severely affected around 200 million people of 29 countries including India. Consumption of fluoride beyond the maximum permissible level of 1.5 mg/L recommended by WHO is related with dental and skeletal fluorosis but, lacking of fluoride intake associated with other health issue, dental caries. Weathering of minerals like fluorite/fluorspar, apatite, topaz and mica and some industrial activities (mainly phosphorous fertilizer plants; steel, zinc, aluminium, smelting industries; glass and ceramic industries, etc.) contribute fluoride contamination. Fluoride enters into the food chain by its bioaccumulation nature. Moreover, dental fluorosis is highly endangering the most susceptible group, infants and children. The Nalgonda technique and activated alumina processes are the most widely used defluoridation techniques in water. But it has drawback of residual aluminium after treatment.

Babu et al. (2015) reported that issues associated with excess fluoride ion in groundwater is a serious problem in fluoride endemic areas of the developing countries. In India, a plethora of people are facing severe fluorosis problems as a result of high intake fluoride ion ($F^{-}$) through drinking water and it has been estimated that 62 million people from 19 out of the 32 Indian states are facing dental, skeletal and/or non-skeletal fluorosis. The extent of fluoride contamination in water ranged from 1.0 to 48.0 mg/L.

Fluoride consumption is commonly considered as a double-edged sword. Inadequate amount of fluoride intake in ($<0.5$ mg/L), causes health issues like dental caries, deficiency in formation of dental enamel, and lack of mineralization of bones, predominantly among children. While the
excessive fluoride consumption cause health problems in the young and old. If the fluoride consumption exceeds 4 mg/L, it leads to the dental fluorosis in children while the prolonged consumption of fluoride at higher concentrations i.e., more than 10 mg/L causes dental fluorosis, skeletal fluorosis and crippling skeletal fluorosis, perhaps cancer. In India, majority of the population reliant on groundwater source for drinking purpose. High fluoride content in groundwater has been mainly reported from different areas of Indian states such as Andhra Pradesh, Haryana, Assam, Bihar, Gujarat, Chhattisgarh, Karnataka, Maharashtra, Madhya Pradesh, Rajasthan, Odisha, Tamil Nadu, Telangana, West Bengal, Uttar Pradesh, and Punjab (Annadurai et al., 2014). In 2009, RGNDWM & CGWB enumerated that out of 639 Indian districts the fluoride-affected ones were 229 and 218 respectively. But, in 2012, the number was increased to 267 according to MoWR (Saxena & Sewak, 2015).

As per from literatures, the fluoride ingestion from food is roughly in the ratio of 30 to 40 % and from water, it is 60 to 70 % (Saxena & Sewak, 2015). Hence, to regulator the overall fluoride intake, the only controllable aspect was water. The proper defluoridation technique is a necessary for the socio-economic development of man and community. Several defluoridation technologies have been developed over the years to eradicate fluoride ions from water such as electrocoagulation (Drouiche et al., 2009), chemical precipitation (Pinon-Miramontes et al., 2003), ion exchange (Singh et al., 1999), reverse osmosis (Ndiayea et al., 2005), electrodialysis (Amor et al., 2001) and adsorption (Naohito et al., 2009). Also, aluminium salts-based treatment methods have been widely used.
Among the aforementioned methods, most of the methods are quite expensive, generates secondary effluent and sludge.

Various inexpensive materials have been tried for removing fluoride from drinking water, but these materials cannot be applied because their low fluoride adsorption capacities. Many biomaterials have potential to be used as low-cost sorbents and they are widely accessible and environmentally safe. Some low cost and non-conventional adsorbents include agricultural by-products, wood, nut shells, bone, peat, and coconut shells processed into activated carbons (Singanan, 2013).

Alagumuthu et al. (2010) investigated the fluoride adsorption capacity and its kinetics using the sorbent carbonized ground nut shell (GNSC) impregnated with zirconium oxychloride. The equilibrium data were analyzed using the Langmuir, Freundlich and Redlich-Peterson isotherm by linear methods displayed that the data fitted better with Freundlich model than the other two. Thermodynamic studies exhibited the spontaneous nature of fluoride adsorption with increase of entropy and an endothermic process. The kinetic data obeyed the pseudo-second order model. The zirconium impregnated ground nut shell carbon is a cost-effective adsorbent for the defluoridation problem in the developing countries due its great potential application in the fluoride remediation from water. So, development of effective and low-cost, carbon form adsorbent from easily available plant materials is an effective defluoridation method.