Review paper on removal of heavy metal ions from industrial waste water effluent

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Abstract- Heavy metal ions is a major key of pollutions and it is one of the big environment issue today. To overcome this problem the handling of metal ions is necessary. In recent research, there are various techniques that has been used to examine the metals ions and overview the methods also. The technologies involves are- ion-exchanging, chemical precipitation, flotation, adsorption, membrane filtration, electro-chemical, coagulation-flocculation methods. It is find from experimental and literature survey article that membrane filtration, ion-exchange and adsorption are most common techniques used for the discourse of removal of metal ions from waste water effluent.

Keywords- Heavy metal ions, adsorption, waste water, removal, effluent.

INTRODUCTION- Environmental pollution has many forms like the water we use to drink, the air we use to breath, the ground where we cultivate our plants these are all contribute to health problems, and the major role plays heavy metals which are present in waste water. Atomic weight of heavy metal elements in between 63.8 to 200.5 and specific gravity is higher than 5.0 [1]. Here some of the common examples of metals including chromium (Cr), iron(Fe), copper(Cu), lead(Pb), zinc(Zn), mercury(Hg), nickle(Ni), cadmium(Cd), copper(Cu), thallium(Tl), and arsenic(Ar),cobalt(Co). These heavy metals are characterise into major 3 groups: harmful metals ( Pb, Hg, Zn, Cr, Ni, As, Cu, Sn, Cd, Co) useful metals ( As, Pd Ag, Pt, Au) and radio metals ( such as Ra, Th, U) [2]. Discharge from industry contains different organic and inorganic pollutants among these a huge amount of toxic metal ions are found and which are hainful to human health and when it is discharge into aquatic area it also causes problem to flora and fauna [3] With the speedy development of industries like mining operations, paper industries, metal plating, fertilizer company, batteries, etc. these pollutants knowingly or unknowingly discharge into surrounding increasingly and as we know that heavy toxic metals are non- biodegradable & carcinogenic in nature. Heavy toxic metals are very harmful because this tends to bio-accumulate which sence that concentrations of chemical increase in an organism over time. Harmful metals is concern in examine of waste water effluent especially mercury, nickel, zinc, lead, copper [4]. For human health Zinc is essential but in very small quantity.

Zinc is a trace element and is essential for physiological operations of alive tissue & also perform biochemical functions. Excess of zinc causes health issues like stomach cramps, anemia, skin diseases, nausea and vomating[5].

Cu (copper) perform important metabolic work in animals body but extreme intake of Cu brings a serious issues concern like cramps, convulsions, vomiting, sometimes it causes unproductive death also [6]. Ni (Nickel) increases its extreme level brings dangerous conditions of kidney & lung problems and also gastrointestinal distress, skin problem and pulmonary Fibrosis [7]. Hg (Mercury) is neurotoxin that distroy central nervous system. Excess amount of Hg affects the kidney function, impairment of pulmonary, chest pain and dyspnea[8]. A known environmental calamity with heavy metals is Minamata disease and which is due to Mercury(Hg) pollution in Japan.
Lead damages the Central Nervous System. Pb also affects liver, reproductive system and kidney and also brain function and cellular processes. Symptoms be like extreme headache, weakness of muscles, insomina, anemia, dizziness, renal damage, irritation [9]. Chromium present in two states in aquatic environment that are Cr(III), Cr(VI). But we find that Cr(VI) is extreme dangerous to Cr(III). Cr(VI) damages human physiology and accumulate in the food and causes health issues and the symptoms are skin dermatitis and lung caecinoma [10].

TECHNOLOGIES ARE USED FOR TREATMENT OF HEAVY METAL IONS

1. Chemical Precipitation

This process is most efficient & common process used in companies [11] due to its simple techniques and inexpensiveness for operation. In Chemical precipitation – precipitates are formed when chemicals are combine with toxic metals ion. With the help of two process first one is filtration and second one is sedimentation the insoluble precipitates are separated. Hydroxide and sulfide chemical precipitation are the two process which comes in conventional precipitation.

![Diagram](image)

**Figure 1.** Removal of sludge from contaminated water by chemical precipitation.

1.1 Hydroxide chemical precipitation. The hydroxide precipitation is most common techniques used in chemical precipitation because of its control pH value and much low cost [12]. A different amount of hydroxides has used to find precipitation of toxic ions from contaminated water because of its low
cost and simple handling, lime is best suited choice for hydroxide chemical precipitation in companies [13].

Hydroxide chemical precipitation method takes Ca(OH)2 & NaOH for eliminating Cr(VI) & Cu(II) ions from contaminated water [14]. To increase the property of lime precipitation, the seed material we used is fly ash [15]. This carbonation treatment enhance the size of particle and gives better efficiency of toxic metals ion elimination. Although this process is large in use but it also has some major drawback first one is it creates disposal & dewatering problem because HCP gives high volume & small density muck [16] and the second thing is some hydroxide metals are amphoteric and compound metal cause some problems.

1.2 **Sulfide precipitation**-The most widely used method is Sulphide chemical precipitation, it is very effective for heavy metal ions treatment. The biggest advantage of this process is that its solubilities is lower than HCP process and it is not amphoteric in nature. So that’s why it removal efficiency of heavy metal ions is much more than hydroxide chemical precipitation. Ozverdi and Erdem (2006) examine for removal of Cd2+, Pb2+ and Cu2+ pyrite sulfide iron is used. Chemical precipitation exist when its pH is smaller than 3.0 because of H2S formation (Equ (a) and (b)) and adsorption process occurs when pH varies from range(3.1-6.0).

>[17] Dr. Mahmood M. Brbootl et al., used hydroxide precipitation for the removal of Iron (III), chromium (III), copper (II), Lead(II), Cadmium(II) and Nickel (II) from the aqu solution with the help of jar tester magnesia used as a precipitator.

>[18] The pH value range is 9.6 – 10 with MgO precipitant

The optimum value of MgO precipitant is 1.6 – 3.0 g/l.

**2.0 Ion- exchange**

Considering too much advantage second method is ion-exchange. This is widely used method for the treatment of industrial wastewater effluent. These advantages are its removal efficiency, treatment capacity is high, and high kinetics[19]. Resin of ion-exchange method, either natural solid or synthetic resin. It possesses some special capacity to replace its cations to the metal ions in the contaminated water. Synthetic resin is best used materials among all the material take part in ion-exchange method because it is very effective to eliminate the toxic metal ions from effluent [20].

The cation exchanger are acidic group of sulfonic (-SO3H ) with strong acidic group and acidic group of carboxyl (-COOH ) with week acidic resin. Heavy metals present in the solution are go through the cations col where heavy metal-ions are replaces for the H+ on the resins with below reaction process:

\[ nR - SO3H + M^+ \rightarrow (R- SO3^-)n M^+ + nH^+ \] (a)
\[ nR - COOH + M^+ \rightarrow (R- COOH^-)n M^+ + nH^+ \] (b)

Lots of researcher find that Zeolite possesses strong cation replace capability for toxic ions under variant circumstances [21]. In recent work studies some researcher also find that for better exchange capability of clinoptilolite the surface of it surrounded with amorphous iron-oxide [22]. Research
studies shows that for eliminating metal ions an ion exchange resin is used as zeolities and montmorillonites. But as compared to synthetic resins they are small in stock.

> [23] Alyuz and Veli initially well defined a most efficient techniques for the removal of unwanted metal ions from the contaminated water and that is ion-exchange method with a better efficiency.

> [24] Zagorodni describes the ion-exchange method for the elimination of heavy metal ions with the use of inorganic ion-exchanger material that is zeolite

> [25] Rathor et al., describes metal sulphide used as ion-exchanger for the better efficiency in removing heavy metal ions from the waste water effluent.

> [26] Fathima and Pandith et al describes hybrid techniques in which organic and inorganic are hybrid for high potential of removing heavy metal ions from the waste water effluent.

3.0 Adsorption

Considering economic technique for removal of heavy metal ions we go through the adsorption process, it is very effective method for treatment of wastewater effluent. The use of this technique is very flexible in nature. Sometimes adsorption is a reversible process, and for the desorptions process the adsorbent can be re-generated and here there are several adsorbents present for removal of heavy metal ions

3.1 Activated carbon adsorbents- The most common adsorbent used for removal of heavy metal ions is activated carbon adsorbents (ACA). It contains large volume of mesopore and micropore which gives large surface area this is the main advantage of this adsorbent. Many researchers find that activated carbon is the best adsorbent for eliminating toxic metal ions [27]. Due to exhaustion of coal the price of AC is increased so without affecting this factor we will use activated carbon composite and additives in place of ACA, Tannic acid[28], surfactants [29], additives of alginate [30], magnesium [31] and most important activated carbon composite can be effectively absorbents for heavy metal contaminants. Due to expensive source of AC adsorbent there is conversion of carbonaceous material into activated carbon for heavy metal removal.

3.2 Carbon nanotube adsorbents- In 1991 Iijima discovered CNT (carbon nanotube). He describes the properties of CNTs and also give basic idea of its application. Carbon nanotube gives the best results for eliminating toxic metal ions like cadmium [32], copper [33], lead [34], chromium [35], nickel [36] from the contaminated water. And carbon nanotube adsorption gives the excellent result of removal of these heavy metals. Carbon nanotubes are characterized into two groups (a) SWCNT single walled carbon nanotubes adsorbent & (b) MWCNT (multi walled carbon nanotubes adsorbent [37]. The procedure of carbon nanotube adsorbent are very complex in nature so the mechanism go through the chemical-interaction, electrostatic-attraction and sorption precipitation in-between the surface of functional-group and the heavy metal ions of the carbon nanotubes adsorbents [38]. Due to low capacity of sorption of metals it oxidized through KMnO4, HNO3 and NaClO solution to increase its capacities of removing toxic metal ions [39].

3.3 Low cost adsorbents- From the research it is found that instead of being expensiveness of activated carbon it is widely used adsorbent for removing metal ions. So, the researcher continue
studied to find the low cost adsorbent. More than hundreds of articles has been published for the low cost adsorbent and they are by-product of industrial waste, natural material and agricultural waste for the treatment of toxic metal ions. In 2008 Gupta & Bhattachar survey the two kaolinite and montmorillonite adsorbent for eliminating the toxic metal ions. Also in 2008 Sud et al. survey that agricultural byproduct waste is used as adsorbent for treatment of heavy metal ions through aqueous solutions. In 2008 Wan Ngah & Hanafiah survey that chemically plant waste used as adsorbent for eliminating of toxic metal ions. Many researchers examine that by product of industrial waste like diatomite (40), lignite (41), natural-zeolite (42), lignin (43), clino pyrrhotite (44), peat (45), aragonite-shells (46), kaolinite (47). In 2010 a researcher Jiang examine that from Longyan we find the kaolinite-clay and it is used for elimination of toxic metals from the contaminated water and the time is approx. 29-30 minutes was observed. In 2009 the two researcher Navia & Agoubordea investigated that sediments & saw-dust and sometimes the mix of both material used as adsorbent for the eliminations of Zn & Cu from the aqu soln. The adsorption capacities are 4.84, 2.57 & 5.58 mg per grm for Zn and for Cu it is 4.70, 2.30, 4.32 mg per gram.

3.4 Bio-adsorbents: The very new adsorbent is discovered for removal of toxic metals from aqu solu is bioadsorbent and the process is known as bioadsorption. This adsorbent is inexpensive in comparison to other adsorbents and it is highly effective for removal of metal ions these are the advantages of this adsorbent. It is best suitable adsorbent for the treatment of contaminated water. Bio-adsorbent are basically divided into three groups (48) they are; (a) microbial biomass { such as yeast, bacteria, fungi }, (b) non-living biomass { such as squid, shrimp, bark, krill, lignin, crab shell etc } and (c) alga biomass. There are different in-expensive bioadsorbents are sawdust [49], egg-shell [50], coffee-husk[51], citrus peel [52], potato peel [53], black gram husk [54], seed shells [55] and sugar beet pectin gels [56] etc for removal of heavy toxic metal ions. Algae is a renewable biomass which present in large amount in the earth zone which is used naturally for the treatment of waste water effluent. This low cost adsorbent possesses a lot of advantages like it is widely available in nature secondly it is low cost in nature and have high metal ions sorption capability [57]. Removal of heavy metal ions through bacteria from aqu solutions are Pseudomonas aeruginosa [58] and Escherichia coil [59] etc. Fungi & Yeast produces large biomass and they are easy to grow. Fungi bio-adsorbents are saccharomyces cerevisiae [60], Rhizopus arrhizus [61], Lentinus edodes [62], Lentinus edodes [63]. Renu, Madhu Agarwal et al., describes that for the removal of toxic metal ions the best suitable method is adsorption and the characterised it into two different parts that is (1) commercial adsorbent (2) bioadsorbent for removing copper, chromium, and cadmium.

> [64] In 2011 Fu and Wang discovered the most efficient techniques used for removing heavy metal ions that is adsorbton.

> [65] Gopalakrishnan et al., in 2015 describes the quality of nanomaterial which possesses the functional group, surface area is high and enhance active site due to these qualities the removing of heavy and unwanted metals ions can remove easily.

> [66] Renu et al., in 2017 describes adsorption techniques for the removal of toxic metal ions with the use of commercial adsorbent and bio-adsorbent which increase the removing capacity.

> [67] Sabry M. Shaheen et al., discover that with the help of zeolite in adsorption techniques the elimination of heavy metal ions will take place with better efficiency.
K. Singh et al., found that adsorbent like composite of carbon nanotubes, alumina, graphene sand composite, eggshell and many more are used to eliminate the toxic metal ions like copper, chromium, cadmium from the waste water effluent.

**More Case Study Related To Adsorptions**

Laxmipriya Panda et al., do excellent work towards removal of heavy metal ions with the use of waste ash from the industry and utilizes in the elimination of Cd$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Pb$^{2+}$. And that ash is dolomitic which generates the geopolymer due to its volume and size enhancement it gives total 99% removal by archiving temperature = 343.3 K, ph = 7.9 and ion concentration = 9.9-10 ppm.

Bao-Lin Zhang gives knowledge about two adsorbent that is MoFs MIL-100(Fe) and second is Fe-BTc which works on removal of Cd and Pb. The performance rate of MoFs is higher than Fe-BTc with ph change from 2-7. These two adsorbent removes Pb more than 99.5% and Cd approx 99.2%. The noticeable thing is that here endothermic phenomena take place that is spontaneously change in entropy.

Researcher review here for the removal of Cr(VI) metal ions because of its high toxicity with the use of activated carbon such as Bentonite which plays excellent work towards removal of Cr(VI) and gives result like equilibrium time rate was 119-120 min with temperature rate is 35-40 degree celcius and ph is 2. Here concentration of chromium (VI) was found 200 mg/L.

**4.0 Membrane filtration**

Membrane filtration method have different types of membrane for treatment of waste water effluent. It is easy to operate with space saving and also possess high efficiency of metal removal. The membrane which used to eliminate ions from the contaminated water are reverse osmosis, electrodialysis, ultra-filtration, nano-filtration.

![Figure 2. Filtration of contaminated water through membrane filtration](image)

4.1 **Electrodialysis**- ED is the type of membrane filtration for the ions separation from solution by electric discharge through solu. Ion exchange membrane is used in electrodialysis process. The two exchanger works here one is anion exchanger and second one is cation exchanger. For the purpose of
drinking water and process-water from the sea-water and briny water electro-dialysis is widely used. Electrodialysis gives good result for separation of useful metal ions from the waste effluent and sea water [72]. Electrodialysis also gives the effectively result for the treatment of toxic metal ions removal. In 2007 the researcher Nataraj gives a working model for elimination of hexa-valent Cr ions by electrodialysis method using ion exchanger membrane, and the outcome gives the satisfactory result. In 2009 the researcher Cifuentes discover that electrodialysis is very effective for the elimination of copper and iron from the aqua solution. From a lot of experience were performed and then after researcher found that for improving the performance of cell the temperature and voltage will be increased and it is also find that with increase of flow rate the separation percentage will be decreased.

4.2 Reverse Osmosis - In this process the solution which is being purified will pass through the semi permeable membrane via eliminating the unwanted materials. Reverse osmosis is useful techniques for eliminates a large quantity of dissolved contaminants from water. 20 percent of universe desalination capacity is performed by reverse osmosis[73].

In 2009 the two researcher Dialynas & Diamadopoulos studied that efficiencies of elimination metal ions will increase when reverse osmosis is combine with bio-reactor membrane. But it has some disadvantages also like it consume high power because of pressure of pumping and second thing is its membrane restoration.

4.3 Nanofiltration - Between Reverse Osmosis and Ultra-Filteration the in-between process happens and that we known as NF (Nano-filtration). Nano-filtration is a worthfull techniques for the elimination of toxic metal ions like Cr[74], As [75], Ni [76], and Co [77] from contaminated water. Nanofiltration possess a lot of advantages like it consumes less power supply, its efficiency of eliminating toxic metal ions is comparatively high with other filtration process, it is easy to operate and more reliable in nature[78].

In 2010 a researcher Figoli reviewed that with the help of 2-commercial nano-filtration membranes {NF90 & N30F} the elimination of pentavalent As from the synthetic water occurs. And at the same time they found that pH is increases while temperature of operation is decrease gradually. Murthy & Chaudhari takes a year to examine the elimination process of toxic ions with the help of nano-filtration method and they reported the use of polyamide nano-filtration membrane for the removal of Ni ions from aqua solution of contaminated water [79]. and they also observe that the max removal of Ni ions is 97.9% and 92.0% for feed-concentration of 6 and 249 mg per L respectively and they also research on Cd and Ni rejection capability using nano-filtration membrane for removal of toxic heavy metal ions [80]. The outcome for the Cd and Ni rejection are 98.93% and 82.68% respectively for feed-concentration of 5.0 mg per L.

4.4 Ultrafiltration - For the rejection of colloidal and dissolved material from aqua solution a membrane techniques work on low trans-membrane pressure and that is known as UF (ultra-filtration). For obtaining high efficiency of metal removal the MEUF (micellar en-hanced ultra-filtration) and second one is PEUF (polymer en-hanced ultra-filtration) was come.

In 1980s a researcher Scamehorn et al., was initially discovered Micellar enhanced ultrafiltration for the treatment of dissolved and multi-valent toxic metal ions from aqua solution [81]. Efficiency of
metal rejection through micellar enhanced ultrafiltration totally dependent on the following parameters like concentration of metals to surfactants, pH of solution, ionic-strength and terms synchronize to membrane operation.

> [82] Hani Abu-Qudais use the part of membrane filtration that is reverse osmosis and nanofiltration for the removal of cadmium and copper from the waste water effluent.

> [83] Blocher, Dorda J et al., describes the hybrid techniques of separation of heavy metal ions from the contaminated water.

5.0 Flotation

Extensively used method for the removal of waste water treatment is flotation.

For the separation of toxic ions from the aqua solution with the help of attachment of bubble, mineral originated process we use flotation techniques. The main process of flotation are dissolved air-flotation, ion-flotation and precipitation are used for the treatment for waste water effluent.

Dissolved air flotation permit to bubbles of air to stuck on suspended-particle in the aqua solution, making a thin film of low density than solution where the toxic metal ions eliminate as a sludge formation [84]. dissolved air flotation proves that for the removal of ions it is the widest used techniques in 1990s [85].

Ion- flotation method is also very effective for the removal of metal ions from the contaminated water. Ion flotation process totally depend on im-parting metal ions in contaminated hydrophobic with the help of surfactants and through air bubbles these ion-metals eliminates from the contaminated solutions [86].

In 2008 the researcher Yuan et al., examined the capacity of ion-flotation to eliminate the cd, cu and pb from the dilute aqua soltn from the bio-derived tea (saponin). The max elimination of cu2+, pb2+ and cd2+ are 81.12%, 89.94% and 71.16% respectively.

Another process that is used for the removal of metal ions from the waste water effluent is Precipitate flotation it is type of flotation process with the help of air bubbles in the formation of precipitate. Under the observation of metal soltn concentration the formation of metal hydro-oxide occurs due to precipitation formation [87]. Elimination of Cr (III) from the dil aqua solution is carried because of precipitation flotation process and here ethanol is used as an-ionic collector [88]. And the excellent result come with accuracy of ph 7.99 and max removal of metal ions is 96.1%.

> [89] Mavrov V et al., discover the hybrid of flotation process for the removing of cadmium and copper toxic metal ions from the waste water effluent.

> [90] Blocher et al. in 2003 has also given the hybrid theory for removal process in which he combine the flotation and membrane filtration for the removal of zinc, copper, nickel from the waste water effluent.

> [91] In 2002 Rubio et al., used collector such as SOS and MIBC for the removal of cadmium and it gives result from 89.3% to 97.6%.
6.0 Electrochemical Treatment

In this method on a cathode surface the metallic ions are spread and by this procedure useful metals are recover in elemental state. But it has major disadvantages like it is very expensive techniques due to large electric consumptions. So, this process is not more in use but from last 2 decades it is widely used because of its modify basic properties [92]. And here we studied that different form of this technologies such as electrofloation (EF), electro-coagulation(EC) and electro-deposition (ED).

EC takes electrodes of AL or Fe to generate coagulate by mixing electrically either Al or Fe [93]. At the anode side there is generation of ions of metal take place and at the cathode side there is formation of hydrogen ion take place and these hydrogen gas (ions) help to flush out the flocculated particles from the aqua [94]. In 2008 the two researcher Heidmann and Calmano studied and examine the removing capability of Zn2+ , Ni2+ , Cu2+ , Ag+ with the help of electro-coagulation. For the examination of Hg2+ concentration of synthetic solution the electro-flotation method is also used [95]. The removing efficiency is greater than 99.7% when the gap between the electrode is nearly 3 cm and the current density varies from 2.6 to 3.123 Adm-2 and pH value of mercury ions varies from 3.1 to varies accordingly [96].

David Hasson et al., describes the removal techniques of phosphate with the use of electrochemical treatment is also described calcium and magnesium hardness. Electrochemical techniques is known for its high potential for the elimination of hard metal from the industrial wastewater.

Chaloempan Petsriprasit et al., describes electrochemical process with lots of advantage and disadvantage, it is the best suitable process for the removal of heavy metal ions from the industrial waste water effluent.

7.0 Electroflotation

EF (electro-flotation) is a process of liquid/solid separation in which pollutant comes at the surface of water solution in the form of gas bubbles of oxygen and hydrogen. Electro-flotation gives the good result in the removal process of toxic metal ions. The researcher survey the electro-flotation techniques with the help of Al electrode for the waste water treatment [98]. Using this method the metal ions like Ni , Zn , Fe , Co , pb can easily removes from waste water. And it gives 99.9% removal rate which is actually a excellent result of removal. In electro-flotation process with the use of hybrid electrode of Fe and with the use of micro- filtration , filter-paper and ultra-filtration test operate for increasing efficiency of Ni with or without use of any external source of oxygen [99].

Electro-deosition is a method which is used for the recovery of useful metal ions from contaminated water and it is totally different process. In this method there is no extra residue added for the separation of metal ions so, researcher say that it is very clean process for metal recovery [100]. The researcher found that ED is very useful technique for the recovery of useful metal ions from the waste water effluent [101].

8.0 Coagulation & Flocculation
Involving two processes: sedimentation & filtration to eliminate metal ions from contaminated water and the whole process is known as Coagulation and Flocculation method. The main work of coagulation is disturbing the colloid particles by making the forces neutral which keep them apart. There are examples of some coagulants like ferrous sulphate, aluminium and ferric chloride which give the excellent work of removing impurities and metal ions from waste water effluent and also form the precipitate of amorphous metal of hydroxide. In a research it is found that when coagulants like poly-aluminium chloride and ferric chloride mix with impure water of industries then this coagulants removes the impurities and toxic metal ions from the effluent [102].

![Flocculation Diagram]

**Figure 3.** Removal of heavy metal ions from waste water effluent through flocculation

Coagulation is very effective process for the removal of metal ions from the contaminated sources, suspended particle and hydrophobic collides are the major two objective of the coagulations. Sodium xanthogenate group works effectively in the eliminations of metal ions from waste water effluent [103]. The turbidity decreases and Ni2+ removal increases when the pH of water sample is increases.

Flocculation is a process in which we add attorney and due to this impurities which are present in aqua solution comes out in the form of flocs. When the suspended-particles are flocculated into big particle then the elimination of these large particle can be easily performed by a various techniques like flotation, filtration, straining. There are a lot of flocculants are available and they are macromolecule, polyaluminium chloride, poly-acrylamide, poly-ferric sulphate are most common used for the
elimination of toxic metal ions from the waste water effluent. A research is performed in which a new macro-molecule flocculent (mercaptoacetyl-chitosan) is invented through which not only turbidity remove but also metal ions also remove when this chitosan is react with mercaptoacetic acid [104]. The flocculants are formed to remove metal ions from contaminated water and they are ; N-carboxy-ethylated Chitosns two new { derivate of poly- ampholyte-chitosan} [105] and the second one is co-sodium xanthate { derivate of poly-acrylamide} [106]. A new method flocculation techniques comes in which without any additional process like filtration and centrifugation to separate the metal ions from effluent with the use of thermosenstive polymer [107]. And a new tannic type flocculant has been discovered for the elimination of metal ions [108].

From a research it is find that heavy metal ions are not completely eliminate from the wastewater through coagulation and flocculation method [109]. So, there is need of some other techniques to removes metal ions completely and that can be precipitation , flocculation and coagulation process to eliminate tungsten from the industrial waste water using ferric chloride as a agent [110]. With the use of aluminium composite ( micro-alloyed) for the spontaneous reduction process take place and it also give the good result for removal of metal ions [111]

**Summary of treatment of heavy metal ions removal**

As we can see at the above techniques there is many different process which is used for removal of useless metal ions and impurities with many advantages and contain limitations also.

When the removal of metal ions from aqua solution then we go through the chemical precipitation process because of its easy operation and also low cost but this process is useful only for high concentration waste water and it is not effective for low concentration of waste water. Due to non-economical property of chemical precipitation it generates large amount of sludge which causes difficulties in metal removal process.

Ion-exchange is another techniques which is also used for the removal of impurities which is present in waste water but it can not properly work when the water concentration is low . It is expensive in nature and also cause pollution because of additional of resins so it is not used in large scale purpose.

Adsorption is widely used method for the removal of toxic metal ions from industrial waste water effluent. There are many varieties of low cost adsorbent present in market through which removal techniques may be performed in better way. It is very important point that what type of adsorbent is used for the removal process because the efficiency of removal process is totally depend upon the type of adsorbent is used. In adsorption method there is new type of adsorbent is introduce and that is bio-adsorbent.

Membrane-filtration is useful for high efficiency removal of metal ions but it consist of high cost, complexity in operation and sometimes generate a large amount of flux so their use is in liminated for removal process of metal ions.

Electro-chemical process take forward with the use of chemicals due to this agent it working properties improves and it does not produce sludges . It is very useful for the removal of heavy metal ions but it is not well developed technologies because it capital cost is high and consumes a large power capacity.
Flotation is also used for the elimination of toxic metal ions from the waste water effluent but it consists a lot of advantages like low detention time, efficiency of removal is high comparative to other techniques, metal sensitivity is high, overflow rate is high and operating cost is low but the more concentrated sludge is formed [112]. And also consist some disadvantage like high initial cost, maintenance cost is also high and operational cost is also high. Go through the coagulation-flocculation process for the removal of heavy metal ions the sludge produced in this process is good sludge and is useful for the elimination of metal ions using chemical consputions. Although all the process is used for the removal of metal ions from the contaminated water. The selection of process depends upon the following parameters like first check what is the concentration of solutions, what is the initial cost of method and what is the capital-investment of the process some more parameters like flexibility and reliability of the plant and the last one which is more important to know what is the environmental impact and considering all these things then after a suitable technique is used for the removal of toxic metal ions [113].

Conclusions

As we can see that day by day there is increase in environmental pollution and one of the reason is heavy metal ions pollution of waste water effluent. To overcome with these environment problem we adopt removal techniques like membrane filtration, ion-exchange, chemical precipitation, adsorption, flotation, coagulation-flocculation for the elimination of toxic metal ions from the contaminated water sources. But it is observe that adsorption process is the best suitable method among all the above techniques and it is examine under 180-200 articles survey. Adsorbent of low cost and bio-adsorbent is also very useful for the removal of heavy metal ions, adsorption is very effective and less expensive as compare to other process, it is more economical method for low concentration of treatment of waste water. Adsorption process gives 98-99.8% removal rate of heavy metal ions with maintain ph value and appropriate temperature rate.

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