REMOVAL OF HEAVY METAL FROM WASTE WATER BY ELECTRO CHEMICAL OXIDATION (COAGULATION) PROCESS

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Abstract : From last several decades Heavy metals pollution has become a more serious environmental problem as a result releasing toxic materials into the environment. There are lot of techniques physical , chemical , biological , advanced oxidation and electrochemical processes were used for the treatment of domestic, industrial and agricultural effluents. Heavy metals from the earth's crust to the environment due to rapid developments and increase in mining and industrial activities. The presence of this toxic metals in environment cause the changes of human exposure to these metals in excess of their natural levels through ingestion, inhalation or skin contact.

Heavy metals are toxic for human health and all watery species depending on their concentrations and bioaccumulation conditions. Specific gravity greater than about 5 or relatively high density or high relative atomic weight is called as heavy metals (especially one i.e. poisonous) one mercury or lead. Heavy metals have density criteria range from above 3.5 g/cm3 to above 7 g/cm3. From the experimental analysis it's clear that the % removal of metal increase with decrease in concentration and the % removal of metal increase with increase in contact time . The optimum value of concentration is 5-10 ppm in which higher % of metal removed after this % reduction of metal is decrease. The optimum value of contact time is 30-90 min . in which higher % of metal removed after this % reduction of metal is constant The % removal of metal increase with increase in pH. The optimum value of pH 5-6 in which higher % of metal removed after this % reduction of metal decrease.

Keywords - ***Electro Chemical Oxidation Process Photo Penton Process, wastewater Treatment, Heavy metals removal , Various Treatment processes.***

I. INTRODUCTION

Due to human activity concerning heavy metals constitutes a major health hazard. In various industrial and agricultural activities many heavy metals used that can be found in waste waters in soluble or insoluble form. Heavy metals is toxic for human health and all watery species depending on their concentrations and bioaccumulation conditions.

Specific gravity greater than about 5 or relatively high density or high relative atomic weight is called as heavy metals (especially one i.e. poisonous) one mercury or lead. Heavy metals has density criteria range from above 3.5 g/cm3 to above 7 g/cm3. **Important sources of heavy metals are**

1. Urban industrial aerosols created by combustion of fuels
2. Metal ore refining
3. Industrial processes
4. Liquid and solid wastes from animals and man
5. Mining wastes
6. Industrial and agricultural chemicals.
7. Leaching processes
8. Chemical conversions
9. Automobile exhausts

Forms of heavy metals

1. Salts
2. Oxides or hydroxides
3. Organic form i.e., alkyl lead or methyl mercury.
4. Inorganic metals to be toxic and they have to be available usually in the dissolved form.

5. Dissolved organic and inorganic ligands
6. Colloids
7. Particulate matter

1.2 Properties of Heavy Metals:

1. Heavy metals occur near the bottom of the periodic table.
2. Heavy metal have high densities.
3. They are toxic in nature.
4. Heavy metals are non-degradable.
5. Density > 5 gm/cc.
6. They have harmful effect on biological systems.
7. Specific gravity of heavy metal are more than 5.
8. They have tendency to accumulate in organisms.
9. They have high relative atomic weight.
10. They are poisonous in nature.

II. LITERATURE REVIEWS

Electrochemical Methods include electro flotation, electrodeposition, direct/indirect electrochemical oxidation. Electrochemical is probably the most versatile method in that various polluting materials, including a wide range of ionic species as well as organic materials such as textile dyes, phenolic compounds and polymer latex can be successfully treated. [10].

Removal of heavy metal ions (Cd^{2+} and Zn^{2+}) by electrochemical was investigated in an acidic condition, which is necessary for re-using or discharging the mediated electrochemical oxidation (MEO) media. Effects of various parameters such as electrolytes, current densities, and electrode materials were examined for a metal-contaminated MEO system using Fe^{2+}/Fe^{3+} pairs as a mediator. It was found that ECG with Al electrodes is greatly affected by the presence of Fe^{2+}. [Cd^{2+}] and [Zn^{2+}] remain constant until [Fe^{2+}] reaches a certain concentration level. [10].

The removal of Ni (II), Pb (II), Cd (II) ions was studied using an assorted electrode sets of aluminum and iron by Khosa et al. Removal of Ni and Cr from tap water was studied with aluminum electrodes by Hernández, et al**.**

By Mansour and Hasieb the removal of nickel and cobalt was also studied using two aluminum plates. [8].

1. Renk R.R., 1989, stated that electrocoagulation has reduced contaminated water volume by 98% and lowered the treatment cost by 90% for bilge water containing heavy metals and oil emulsions. Although electro coagulated water may vary because of the individual chemistry of process waters, a few examples of water treated by electrocoagulation include the reduction of heavy metals in water such as arsenic, cadmium, chromium, lead, nickel, and zinc are generally reduced by 95 to 99% [5].

2. Naomi et al. 1993 concluded that alternating current electrocoagulation treatment achieved approximately 66% removal of lead in the high metals runs, whereas polymer treatment showed a slightly higher removal (71%), while electrocoagulation treatment of slurries with low concentrations of metals yielded the highest lead removal (96%) [3].

3. Gomes et al., 2007 observed the removal efficiency of 99.6 % of arsenic at pH value of 2.4 in case of iron electrode at 60 min treatment time. They also observed 97.5 % removal efficiency of arsenic at pH value of 6 in case of aluminum electrode at 60 min treatment time.

4. Koyba et al., 2011 found the 93.5 % removal efficiency of arsenic at pH value of 6.5 and 98.9 % at pH value of 7, in case of iron and aluminum electrode.

5. Akbal et al., 2010 investigated the chromium removal from metal plating wastewater using iron electrocoagulation. They observed the 99.9 % removal of chromium at pH value of 3, current density of 10 mA/cm2 and treatment time of 20 min.

6. Dermentzis et al., 2011 studied the effect of pH on removal of chromium and zinc using aluminum EC. They observed the complete removal of chromium and zinc from synthetic and real electroplating wastewater in pH range of 4-8, current density of 40 mA/cm2 and treatment time of 60 min.

7. Koyba et al., 2015 observed the optimum conditions of pH 6.4 and treatment time of 50 min at which 99.04 % of zinc is found.

8.Kamaraj et al., 2015 reported the 99.3 % of lead removal at the pH value of 7 and the removal decreased to 82.7 % when pH reduces to 3.

9. Mansoorian et al., 2014 also studied the effect of pH on lead and zinc removal. Low removals are observed at acidic pH (pH = 3) for both the metals, which increases and found maximum at pH value of 4 and 5 for lead and zinc, respectively. It reduces further as the pH increase. [4].

10.**The effect of electrolysis** time on lead and copper removal shows a gradual increase along time, with a maximum removal of 98.7 and 90.2 % respectively occurring in 60 minutes. Lead and copper removal by electrocoagulation over 90 % was obtained for an initial pH up to 5.

11. An increase in copper removal efficiency was observed removal percentage increased up to 99 % for an initial pH value of 7. After 30 minute the amount of lead removed increased from 62 to 83 % as the current density increased from 0.147 to 0.441 mA cm-2.

12. The optimum removal efficiencies were achieved at a current density of 1.029 mA cm-2 and pH of 5. Both lead and copper removal were found rapid at higher current densities. The lead and copper reached a value of 91.4 and 54.1 % respectively. [10].

13. The removal efficiency of zinc, copper, Cr (VI) and nickel reached value as high as 99%, when pH is 7 and be not affected by pH for zinc, copper and nickel, as long as this kept in the range between 7 and 12, in contrast a slightly decrease of the removal efficiency of chromium is observed, when the initial pH is increased above 7.

14. The highest current (1.35 mA/cm2) produced the quickest removal rate, with a 99%, concentrations reduction occurring just after 6.4 min for zinc, copper and chromium and after 9 min for nickel. While the removal rate with 87% and 80% concentration reduction occurring just after 30 min for cadmium and cobalt respectively [6].

III. Treatment Process

3.1 Conventional Methods For Heavy Metal Removal

Several methods have been used for the removal of heavy metals from water and waste water. For removal of heavy metals from contaminated waste water as follows

1. Chemical precipitation
2. Ultra-filtration
3. Ion exchange,
4. Reverse osmosis
5. Electro winning
6. Carbon adsorption

7. Phytoremediation

Following are the electrochemical treatments of wastewater

1. Electro-deposition
2. Electrocoagulation
3. Electro-flotation
4. Electro-oxidation.

Advanced electrochemical oxidation is modification to the electrocoagulation process, where oxidizing agents and catalysts are introduced into wastewater and effluent before it enters the cells. Advanced electrochemical oxidation cells are normally installed in wastewater and effluent treatment plant inline after electrocoagulation cells. Electrochemical treatment of wastewater is environmentally friendly and appropriate for applying to an effluent system.

IV. MATERIAL AND METHODOLOGY

4.1 Materials

1. **Acid or Alkali**

H2SO4 acid or NaOH alkali to be used for pH maintain of waste water. The optimum Value of pH necessary for the Fenton process.

2. **Electrodes**

Iron or Aluminum electrode are used for the electro Fenton process

4.2 Electro Chemical Oxidation (Coagulation Or EC) Process

EC is an electrochemical process with reactive anode and cathode (iron or aluminum electrode). When current is applied to the system by a power supply, metallic ions are dissolved from anode and transferred to the bulk. Afterwards metallic ions combine into larger flocs and can be removed easily. Water molecules are hydrolyzed at the cathode. Two different mechanism proposed for iron electrodes can be seen in the reactions.

Mechanism I

In the anode : $4\,Fe(s) \rightarrow 4\,Fe^{2+}(aq) + 8e^-$

In the cathode : $8\,H^+(aq) + 8\,e^- \rightarrow 4\,H_2(g)$

In the solution : $4\,Fe^{2+}(aq) + 10\,H_2O(l) + O_2(g) \rightarrow 4\,Fe(OH)_3(s) + 8\,H^+(aq)$

Mechanism II

In the anode : $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

In cathode: $2\,H_2O(l) + 2e^- \rightarrow H_2(g) + 2\,OH^-(aq)$

In solution: $Fe^{2+}(aq) + 2\,OH^-(aq) \rightarrow Fe(OH)_2(s)$

Metal ions produced at the anode and hydroxide ions produced at the cathode react in the aqueous media to produce various hydroxides species depending on the pH such as $Fe(OH)_2$, $Fe(OH)_3$, $Fe(OH)^{2+}$, $Fe(OH)^{2+}$ and $Fe(OH)^{4-}$. The iron-hydroxides coagulate and precipitate to the bottom of system.

4.4 Preparation of Synthetic wastewater:

1. Take 5 mg metal powder in crucible then add 5 ml of concentrated nitric acid in to it.
2. Heat it till all brown fumes removed.
3. The remaining blue solution in crucible will dilute in 1000 ml of distilled water.
4. If we take 5 mg solution in 1000 ml water is 5 ppm solution.
5. Similarly we can make 10 L synthetic water of various concentrations solution.
6. For make various ppm solution follows the process steps from 1 – 4 as above mentioned.

4.5 Experimental Procedure

1. Take the 10 L known concentration solution in the vessel.
2. The metal solutions were agitated by agitator for a desired time.

3. The samples were withdrawn from the stirrer at the pre-determined time intervals
4. Analysis the concentration by help of the spectrophotometer.
5. Take the readings at various time of interval 30, 60 , 90 min.
6. Similarly take the reading for various pH, different current like 5 V (1 amp) , 12 V (2 amp) and also for various concentrations.

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V. RESULTS AND DISCUSSION

5.1 Effect of pH on % Removal of Metal

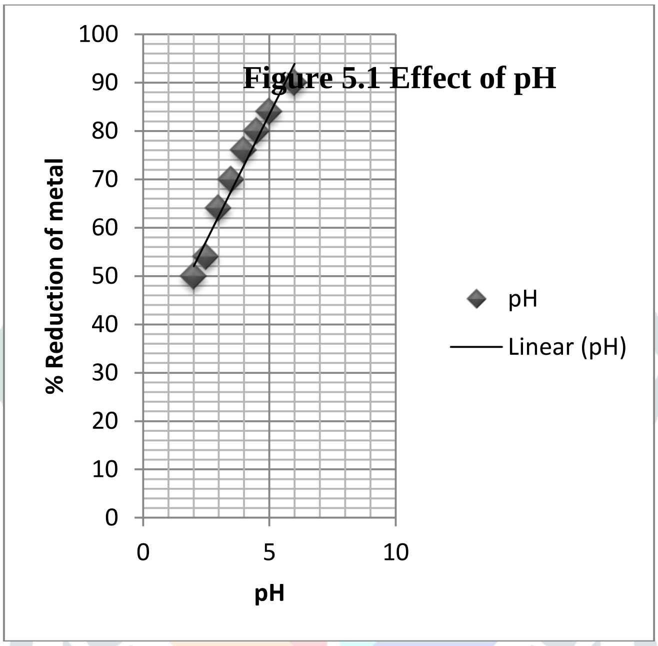

Figure 5.1 Effect of pH

Graph shows the effect of pH on rate of adsorption**.** The percentage of each metal adsorbed increases with the pH. The maximum adsorption of each metal ion occurs at pH range between 5 and 6.

5.2 Effect of contact time on rate of % Removal of Metal

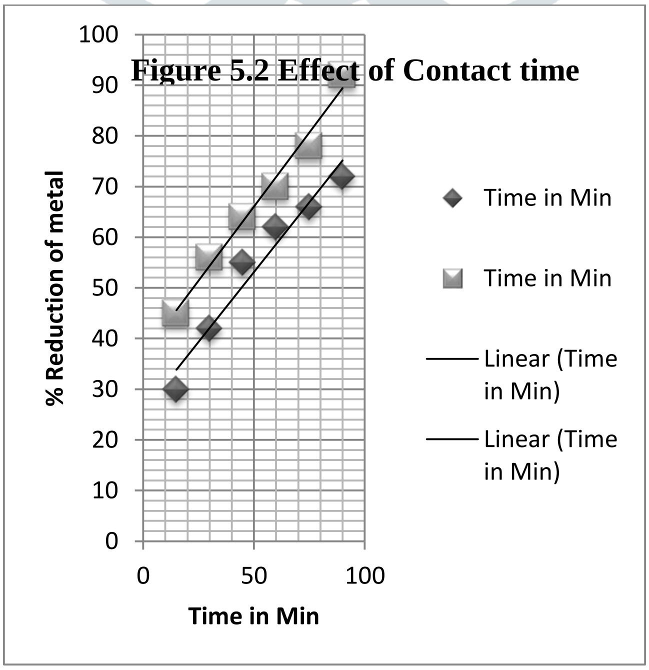

Figure 5.2 Effect of Contact time

From above graph observed that the efficiency of metal ion adsorption is related with the increase of contact time. The maximum adsorption is noticed at contact time of 90 hours for metal removal.

5.3 Effect of Concentration

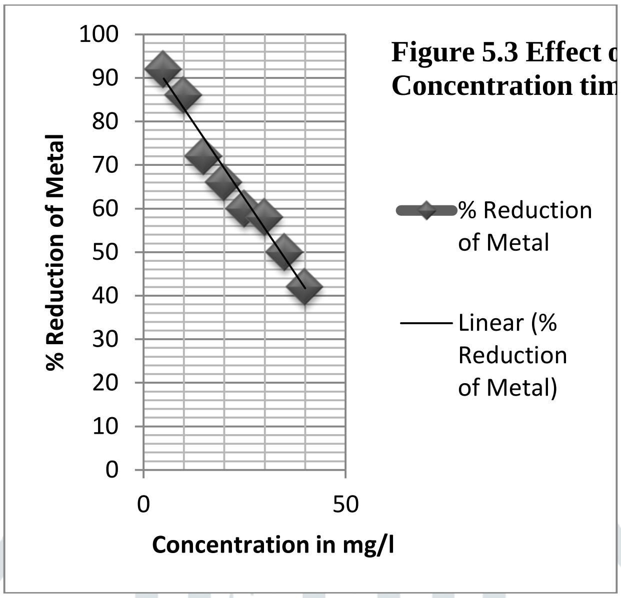

Figure 5.3 Effect of Concentration

Graph shows the Concentration vs % reduction of heavy metal. As concentration increases % removal decrease at particular stage after that rate of removal of heavy metal are constant.

5.4 Effect of Various Parameters on Rate of Adsorption

5.4.1 Effect of pH on the Removal of Metal

Many research tasks on the adsorption of metal ion from aqueous solution showed that the pH of the solution has a great influence on the percentage of metal removal. Low percentage of removal of metal at low value of pH by a competition between the hydronium ions.

The percentage of each metal removed as function of the pH for a 12 V- and 2-Amp DC and a time of contact of two hours. The percentage of each metal removal increases with the pH. The maximum % of metal ion reduction occurs at pH range between 5 and 6.

5.4.2 Effect of Contact time on the of metal removal:

Contact time on the % removal of copper and nickel ions was carried out at pH 5 with 12 V 2 Amp while varying this parameter from 15 – 90 min.

It is observed that the efficiency of metal ion removal is related with the increase of contact time. The maximum metal removal is noticed at contact time of 90 min for heavy metal.

5.4.3 Effect of Concentration

In this experiment concentration vary between 5 – 20 ppm. As concentration increases % removal decrease at particular stage after that rate of metal removal is constant.

5.4.4 Effect of Current

Optimum value of current between 12 - 30 V DC after that rate of removal reduced. Value of DC voltage should be less than 30 V DC supply.

5.4.5 Effect of the distance between the electrodes

Effect of distance between the electrodes on the removal efficiency of metal removal. Distance between the electrodes in this method is selected between 3 cm and 3.5 cm which causes a 4% increase in the removal efficiency and gives rise to energy consumption and operational cost of the method. The minimum distances should be selected.

VI. FUTURE SCOPE AND BENEFITS

Future Scope

•Electro chemical can be adopted to treatment of waste water.

• To improve the efficiency of conventional method.

• Electro chemical can be used as an additional treatment to treat waste water.

• Electro chemical process can make waste water for reusable.

System capabilities:

• Removes heavy metals.
• Removes suspended and colloidal solids.
• Destabilizes oil and other emulsions.
• Removes fats, oils and grease.
• Removes complex organics.
• Destroys and removes bacteria, viruses and cysts.

Benefits:

• Treats multiple contaminants.
• Sludge minimization.
• Capital cost significantly less than conservative technologies.
• Operating cost significantly less than conservative technologies.
• Low power requirements.
• Generally, no chemical additions.
• Low maintenance.
• Minimal operator attention.
• Consistent and reliable results.

VII. CONCLUSION

As per observation, it's clear that Electro Oxidation (Coagulation) has good efficiency of heavy metal removal from the waste water. We study the removal of metal at various pH, Contact Time and the Concentration of metal shows the optimum values of all parameters. Heavy metal can easily adsorb from waste water by Electro Oxidation with low cost and high efficiency. Electro oxidation is the efficient technique of removal of the heavy metal from the various types of waste water. The percentage of each removal of metal as function of the pH and a time of process of 30 – 90 min. The percentage of each metal adsorbed increases with the pH. The high 5 - 6 removal of each metal ion occurs at pH range between 5 and 7. We examine the removal of copper and nickel ions by EO process was carried out at pH 2 – 7 with a with varying contact time from 0.5 to 5 hours. In this experiment concentration vary between 5 – 20 ppm. As concentration increases % removal decrease at particular stage after that rate of metal removal constant.

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