Electrocoagulation Methodology as an Effective Tool for the Treatment of $Pb^{+2/+4}/Cd^{+2}/Cr^{+2/+3/+6}$ in Wastewaters – A Review

Rakhi Baghel[1], Ashok Sharma[2], Sarita Sharma[3] , Sanjay Verma4, Mahesh Patidar[5]

[1]M. tech Research Scholar, Department of Chemical Engineering, Ujjain Engineering College Ujjain (M.P).

[2,3,4,5] Department of Chemical Engineering, Ujjain Engineering College, Ujjain (M.P), 456010, India*

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Abstract - *Heavy metal presence within the aquatic ecosystem has become an environmental issue that is disturbing the ecosystem globally. Effluent from industries is responsible for affecting toxin of groundwater bodies similarly ponds, rivers, including lakes which in turn pollutes the underground water owing to percolation and transportation. Heavy metals such as Al, Fe, and Na are needed for impressive metabolism of alive plants however the excess amount is objectionable and the water containing heavy metals beyond their permissible is considered polluted water due to its hazardous nature. Among hazardous heavy metals, heavy metals such as arsenic, lead, cadmium, and chromium are observed to be highly toxic since they have lethal effects on living beings, even the slightest increase in the quantity of these heavy metals can cause serious illness or death. Various methodologies and techniques like adsorption, membrane separation, etc. are usually adapted for the treatment of these heavy metals but these treatment technologies are economically unfit as well as the disposal of by-product is a major issue. Electrocoagulation-assisted treatment methodology for the treatment of heavy metals in aqueous solution, is immerged as a remedy to this because it is economic, feasible as well as production of sludge is also minimal. The objective of this study is to review the effectiveness of the electrocoagulation technique based on various factors such as pH, current density, and treatment time.*

Key Words*: *Heavy Metals Removal, Wastewater Treatment Technology, Electrocoagulation, Cadmium, Chromium, Lead

1. INTRODUCTION

It has been reported that the presence of heavy metal is causing great danger to Mother Nature and cannot be decomposed by the action of the microorganisms [1]. Contamination of water due to the presence of these heavy metals is a globally recognized problem of the 21st century [2]. As the presence of heavy metals being lead, cadmium, as well as chromium in the water, can cause various diseases even at a very low concentration, these heavy metals can disturbed the environment. These heavy metals can pollute the environment in either direct contact with surface water as effluent or through indirect contact as solid waste. Among of the heavy metals, Cadmium is the most dangerous as even a trace of it can cause renal disorder and disturb metabolism. Even essential minerals like Zn and Mn can cause disorder in a living being, if exceed its permissible limit. These heavy metals can easily enter into the food chain as these heavy metals are water-soluble and can accumulate inside the living cell [4]. It has also been reported that metals such as 'As', Cd and Pb are highly poisonous for the quality of any water body quality. Few heavy metals such as Pb, Cd, and Cr are further briefly discussed for their harmful effects on human beings.

1.1 Lead ($Pb^{+2/+4}$)

1 The excess amount of lead extant in being atmosphere can cause long-term damage to the ecosystem as well as human health. Lead is also an industrial pollutant that can readily arrive at the ecosystem through water, air, soil and it can result in kidney malfunction, tissue harm of the mind, anemia, and even passing away in high dosage amounts as it is highly toxic[5]. In 2019 Lead was the second most dangerous heavy metal this rank given by the 'The Agency for Toxic Substances and Disease Registry'. The high amount of lead in wastewater would harm living organisms and the ecosystem. It can affect the mental condition, liver, kidney, basic cellular processes, and reproductive system of human body [6].

1.2 Cadmium (Cd^{+2})

Cadmium is one of the heavy metals which is highly toxic and can generally be found in the wastewater of many industries [9]. Application of Cd and its compounds are in dye industries, as an antioxidant for steel, electroplating, and the production of fertilizers. Cadmium is poisonous and progressively reported as a poisonous substance by many authors [10]. There are two problems associated with the presence of Cd in the environment, (1) it is extremely toxic even at a lower concentration, and (2) It is a non-biodegradable element. It has been reported by WHO that Cd is undesirable in food materials and proper checking needs to be carried out before the consumption/marketing of food and it is also present in the list of 12 world hazardous elements [8,43]. The permissible limit imposed by WHO for the presence of Cd in drinking water is 0.03 mg/L [7].

1.3 Chromium ($Cr^{+2/+3/+6}$)

Chromium is also one of the most toxic metals because of its high solubility and mobility [11] as it can create environmental pollution [12]. Cr is present in oxidative states or structures in the environment, (1) Hexavalent structure of Cr(vi) (2) trivalent structure of Cr(iii). In both of them, Cr(vi) can impart 500 times serious health issues as compared to Cr(iii). The same removal of Cd from wastewater is at most important in view of environmental safety and sustainability [13]. Table 1 presents the major discharge sources of heavy metals and Table 2 presents permissible limits of $Pb^{+2/+4}/Cd^{+2}/Cr^{+2/+3/+6}$ (mg/L) imposed by WHO in different water bodies such as inland surface water, public sewers, and Irrigation fields.

Table -1: major discharge sources of $Pb^{+2/+4}/Cd^{+2}/Cr^{+2/+3/+6}$

S.no	Metal	Source	Reference
1	$Pb^{+2/+4}$	Paint and ceramic products and naturally orientated in the form of bluish-gray substance under the earth's crust and can come out during mining, manufacturing, agriculture, and even during construction work	**[15]**
2	Cd^{+2}	Textile industries, Paint industries, Fertilizers and pesticide industries, Electronics and Electrical industries, Thermal power plants, steel plants, and domestic solid waste and wastewaters	[14]
3	$Cr^{+2/+3/+6}$	Oil refineries, Paper industries, Electroplating Industries, pesticides, and fertilizers industries	[16]

Table – 2: Permissible limit of pollutant concentration according to WHO & Indian Standards [17, 18, 44]

S.no	Metal	Permeable limit			Maximum permeable limit (mg/L)
		Inland surface water (mg/L)	Public sewers (mg/L)	Irrigation fields (mg/L)	
1		0.10	0.10	0.10	0.01
2		2.0	1.0	-	0.003
3		0.10	2.0	-	0.05

2. Treatment Methods for Heavy Metals Removal

Dissimilar treatment technologies have been adopted for the removal of heavy metals from wastewater just as adsorption, coagulation, ion exchange, chemical precipitation, reverse osmosis, etc. The applicability of the different treatment methodologies strongly depends on the physical (such as initial concentration of pollutant) and chemical (such as hexavalent or trivalent bonds) parameters of subjected pollutant.

2.1 Adsorption method

Adsorption is the phenomenon that takes place when there is a strong opposite charge that develops between the adsorbent and the adsorbate. It is a surface phenomenon hence adsorption can be defined as the deposition of opposite ions of the adsorbate on the opposite ions-wise oriented adsorbent surface. Characterization techniques such as zeta potential are used for the determination of the strength of these charges at different pH and the greater the charge the better adsorption could take place [19,20]. Adsorbents such as activated charcoal impregnated activated resigns and cellulose is commonly used adsorbents. Green adsorbents such the one developed from waste such as marble powder, hydroxyapatite and CaO synthesized from eggshells are also in use for the treatment of wastewater.

2.2 Reverse osmosis process

In reverse osmosis, inlet feed wastewater is subjected to high pressure owing to which selective ions from feed passed through the membrane to the other side of the setup. Tremendous performance is reported i.e., 93 percent, 95%, and 95% for the removal of Pb, Cr, and Cd ions [21, 22] but at the expense of non-economic conditions.

2.3 Ion Exchange Method

In this process, wastewater is passed through storage tanks containing chemicals that can transfer desirable ions from them and can take undesirable ions from wastewater. Two types of ion exchange methods are used first cationic exchange and second is anionic exchange [23,26]. Reported effective pH is from 2-6 for the removal of ions of heavy metals. For the same reason, pre-treatment is required which added cost for the treatment process and as a result, the cost of the treatment plant becomes high.

2.4 Chemical Precipitation

Precipitating the impurities from under the effect of a chemical such as alum or alkali is known as chemical precipitation wastewater treatment methodology. Even heavy metal ions such as Cd or Cr can be precipitate down into solid particulates through this method. Post-treatment is required as the separation needs to be down, generally gravity settling, filtration, centrifuging and sedimentation is applied for separating these solid insoluble particulate [24,27]. The generation of a huge amount of sludge is the main cause of the downfall of chemical precipitation wastewater treatment technology.

The above-stated treatment methodologies are not only uneconomic but also generates huge amount of sludge. For dealing with the same problem electrocoagulation is being used and reported as is an economically viable wastewater/water methodology.

3. Electrocoagulation

In Electroplating coagulation of heavy metals takes place due to the oxidation of anode, when subjected to an external electric supply. Commonly use anodes are made up of aluminum and iron. As the electric current flows through the anode, oxidation and ion formation of the anode takes place [25, 28-29]. On cathode, H_2 gas and OH^- are formed. As the OH^- is negatively charged it started moving towards the positively charged anode. In electrocoagulation, a DC supply is used as an electric source across the electrodes while treating water/wastewater as an electrolyte. Mechanisms representing the electrocoagulation process are presented from Eq. (1) - (8) (where metal is used as anode i.e. Fe is represented by 'A_0') and the electrocoagulation setup is shown in Fig. 1

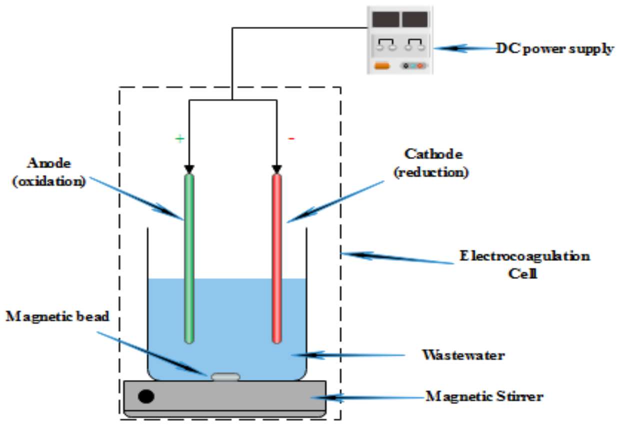

Fig -1: Electrocoagulation Setup

Mechanism 1:

Anode: $A_{0(s)} \rightarrow A_0^{+2}{}_{(aq)} + 2e^-$ ....(1)

$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$ ....(2)

Cathode: $A_0^{+2}{}_{(aq)} + 2HO^- \rightarrow A_0(OH)_{2(s)}$ ....(3)

Overall: $A_{0(s)} + 2H_2O \rightarrow A_0(OH)_{2(s)} + H_{2(g)}$ ....(4)

Mechanism 2:

Anode : $4A_{0(s)} \rightarrow 4A_0^{+2}{}_{(aq)} + 8e^-$ ....(5)

$8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)}$ ....(6)

Cathode : $4A_0^{+2}{}_{(aq)} + H_2O + O_{2(s)} \rightarrow 4A_0(OH)_{3(g)} + 8H^+_{(aq)}$ ....(7)

Overall : $4A_{0(s)} + 10H_2O + O_{2(s)} \rightarrow 4A_0(OH)_{3(g)} + 4H_{2(s)}$ ....(8)

3.1 Operating Parameters effect on Performance of EC process

Effective wastewater treatment by electrocoagulation procedure depends on numerous parameters like form of electrode material, current density, inter-electrode distance, initial pH, treatment time, appearances of water, etc. Whereas the major parameters over which the removal efficiency depends are solution pH, current density, and treatment time and for the same reason, are discussed below.

3.1.1 Effect of pH

According to the reported articles, pH is one of the most important factors that can alter the removal efficiency of the technique [34]. Sadegi et al., 2013 reported that the improvement was done by removing hexavalent chromium by polyaluminum chloride as a coagulant. It was reported that 99.3% chromium at pH 5 by 8.33 mA/cm^2 current density in 40 min treatment time was obtained [35]. Mansoorian et al., 2014 reported that, by DC, remarkable removal of lead and zinc using iron electrodes was obtained. According to the author, a 97.2% and 95.5% removal of lead and zinc at pH 5-4 by 6 mA/cm^2 current density in 40 min treatment time was achieved [36]. Vasudevan et al., 2011 investigated that, 97.5% of Cd removal by AC and 96.2% of Cd removal by DC source was obtained for the same 0.2 A/dm^2 current density and pH 7.0 on aluminum alloy electrode [37]. Kamaraj et al., 2015 observed that 99.3% of Pb removal can be obtained for an optimum pH 7[47].

3.1.2 Effect of current density

Current density can directly affect the Electrocoagulation wastewater treatment methodology and this can be attributed to the fact that it can directly regulates both coagulant dose and rate of bubble generation. Current density can also affect both, mass transfer on the electrodes and mixing in the electrolyte. Mohammad et al., 2010 reported the variation of current density from 0.915-5.49 mA/cm^2 for the removal of Pb(ii) by aluminum and stainless-steel electrode and was reported that the maximum removal of Pb(ii) i.e., 99% was recorded at the optimum current density of 5.49 mA/cm^2 in 20 min treatment time.[30] Genawi et al., 2020 found that 100% removal of chromium was obtained at the optimum current density of 13 mA/cm^2 at pH 7(**31**). Sharma et al., 2018 present the effect of current density on the electrocoagulation process and reported the removal of chromium(vi) under the influence of Fe electrodes. A current density of 73.5A/m^2 and pH 3.5 were found to be optimum due to the high percentage removal i.e., 91.7% Cr(vi) removal and 91.3% removal of Pb was obtained in 90 min [32] Vasudevan et al., 2012 observed that 98.1 and 97.3% % with the energy consumption of 0.734 and 1.413 kWh/kL were achieved at a cadmium removal was completed for the current density of 0.2 A/dm^2 by using iron electrodes at pH 7.0[33]. Dermentzis et al., 2011 studied the effect of current density on the removal of Cr and it was observed that 100% removal was achieved for the current 40 mA/cm^2 by electrocoagulation wastewater treatment process [48]. Tezcan et al., 2015 studied the effect of various current densities on the removal of cadmium by electrocoagulation process, and it was observed that 99.78% removal of Cd was obtained 30mA/cm^2 in 90 min [49].

3.1.3. Effect of treatment time

The Faraday Act state that the generation of metal ions are directly proportional to the treatment time and owing to these studies were done to determine the optimum treatment time [41]. Mahvi et al., 2006 reported that the complete removal of chromium can be achieved in 20-60 min for electrode Al or Fe [38]. Shakir et al., 2009 studied the effect of treatment time on the % removal of Pb by electrocoagulation process and according to the author 100% removal was achieved in 120 min by using aluminum as an electrode. Shakir et al., 2009 also reported the same % removal in same treatment time by using stainless steel electrodes as-well [39]. Bazrafshan et al., 2006 reported 99% removal of cadmium in 20 min by using iron electrode [40]. Kobya et al., 2010 observed 99.4 % removal of cadmium in 30 min process time with 30 A/m^2 of current density [45]. Hamdanet et al., 2014 reported that in 10 min treatment time 99.9% removal of chromium ion can be achieved by electrocoagulation process [46].

4. CONCLUSIONS

Pollution created due to the discharge of heavy metals into the water bodies is a serious problem around this blue planet due to their harmful and dangerous on man and environment. In this review, the electrocoagulation process is studied and presented as a practical user-efficient and promising technology for the removal of heavy metal ions such as $Pb^{+2/+4}$, Cd^{+2} and $Cr^{+2/+3/+6}$ from wastewater. The review imparts light on the important process variables such as current density, initial pH, and treatment time and discusses their effect on the removal of heavy metals from wastewater. Researchers are working extensively in the area of wastewater treatment by electrocoagulation technique but generally in either lab scale or batch mode. Hence future scope can be potentially pointed out in using electrocoagulation wastewater treatment technology for great measure wastewater management plant or continuous electrocoagulation reactors.

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