Study of Electrocoagulation Process for Removal of Heavy Metals from Industrial Wastewater
A Review

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Abstract—The aim of this article is to review the relevant literature that published from 2008 to 2019 on topics related to electrocoagulation within the wastewater. The main objective is focusing on electrocoagulation process for the removal of heavy metals from industrial wastewater depending on the mechanism and several affected parameters such as pH current density, applied voltage, electrode material, time, applied voltage, inter electrode distance, initial concentration which have been published in journals.

Keywords—Electrocoagulation, industrial wastewater, heavy metal removal.

1. INTRODUCTION

Effluents from many industries are now one of the major sources of water pollution which represent important environmental problems. These pollutants in water causes considerable damage to the aquatic environment and significant source of environmental pollution. It contains several harmful chemicals that are toxic to biological life. The reuse of wastewater has become an absolute necessity and an urgent need to develop inexpensive techniques for treatment of wastewater. A number of conventional treatment techniques have been applied to overcome this problem such as catalytic oxidation, adsorption processes, ion exchange, biological processes, membrane separation processes, advanced oxidation processes, ultrafiltration, chemical precipitation, reverse osmosis, photo catalysis, chemical coagulation and electrocoagulation. Most of these methods are effective, although they are quite expensive and have many disadvantages and limitations.

Electrocoagulation (EC) is a promising technique for removal of pollutants from wastewater due to its simple, cheap to operate, easily available equipment and environmental friendly. But it has received little scientific attention (Siringi, et.al.,2012). This process has the potential to extensively eliminate the disadvantages of the classical treatment techniques. Moreover, the mechanisms of EC are yet to be clearly understood and there has been very little consideration of the factors that influence the effective removal of ionic species particularly heavy metal ions, oil wastes, foodstuff, suspended particles, polymeric wastes, phenolic wastes, arsenic, textile and dyes from wastewater by this technique (Chaturvedi, et.al.,2013).

2. ELECTROCOAGULATION PROCESS

Electrocoagulation is one of the most promising process gaining attention to researcher in the present era due to its high contamination removal efficiency. It is used for both the water and wastewater treatment. In electrocoagulation process, the oxidation occurs on sacrificial anode and reduction occurs at cathode in aqueous solution when current is applied. Aluminium and iron electrode material are most commonly used due to its various advantages such as availability, their low cost. The coagulant/precipitates, such as iron and aluminum hydroxides are formed in situ during the process, are non-toxic in nature, and have high contaminants removal efficiency (Hakizimania,et.al.,2017). In electrocoagulation process, electrode material and their area, solution pH, current density and treatment time plays a significant role, whereas, presence of electrolytes and distance between electrode also can affects the process (Thakur, et.al., 2016).

MECHANISM OF ELECTROCOAGULATION

Mechanism of electrocoagulation is not fully known because of its complex reaction. The solution which to be treated by electrocoagulation is filled in the reactor. Electrodes of similar or dissimilar material are dipped into the solution and classified as anode and cathode. These electrodes are connected to the power source, through which the current is passed into the solution. When current is passed through aluminium and iron anodes Al^{3+} and Fe^{2+} ions, respectively, are formed. At cathode hydrogen gas and hydroxide ions are
released at the same instant of time. These hydroxide ions combine with the Al\(^{3+}\) and Fe\(^{2+}\) ions in solution and formed aluminium and iron hydroxides, respectively, which act as a coagulant (pulkka, et. al.,2014). Aluminium and iron are commonly used electrode in electrocoagulation process. In the iron electrode, two mechanisms have been proposed.

Mechanism 1:
Anode: 4Fe(s) → 4Fe\(^{2+}\)(aq) + 8e\(^-\)(aq)
4Fe\(^{2+}\)(aq) + 10H\(_2\)O(l) + O\(_2\)(g) → 4Fe(OH)\(_3\)(s) + 8H\(^+\) (aq)
Cathode: 8H\(^+\)(aq) + 8e\(^-\) → 4H\(_2\)(g)
Overall: 4Fe\(^{2+}\) + 10 H\(_2\)O(l) + O\(_2\)(g) → 4Fe(OH)\(_3\)(s) + 4H\(_2\)(g)

Mechanism 2:
Anode: Fe(s) → Fe\(^{2+}\)(aq) + 2e\(^-\) Fe\(^{2+}\)(aq) + 2OH\(^-\)(aq) → Fe(OH)\(_2\) (s)
Cathode: 2H\(_2\)O(l) + 2e\(^-\) → H\(_2\)(g) + 2OH\(^-\)(aq)
Overall: Fe(s) + 2H\(_2\)O(l) → Fe(OH)\(_2\)(s) + H\(_2\)(g)

In case of iron electrodes various form of monomeric ions such as Fe(OH)\(_3\) and polymeric hydroxyl complex such as Fe(H\(_2\)O)\(_6\)\(^{3+}\), Fe(H\(_2\)O)\(_5\)\(^{2+}\), Fe(H\(_2\)O)\(_4\)(OH)\(^{3+}\), Fe(H\(_2\)O)\(_6\)(OH)\(^{2+}\)and Fe\(_2\)(H\(_2\)O)\(_6\)(OH)\(_4\)\(^{4+}\) are generate in an electrolyte system.

In the case of aluminium electrode reactions are as follows:

Anode: Al(s) → Al\(^{3+}\)(aq) + 3e\(^-\)
Cathode: 3H\(_2\)O(l) + 3e\(^-\) → 3/2 H\(_2\)(g) + 3OH\(^-\)
Al\(^{3+}\)ions further react to hydroxyl ion and formed aluminium hydroxides and polyhydroxides such as Al(H\(_2\)O)\(_6\)\(^{3+}\), Al(H\(_2\)O)\(_5\)\(^{2+}\), Al(H\(_2\)O)(OH)\(^{3+}\)etc.(Chouhan, et.al.,2018).
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(umarat,et.al.,2015).

To determine theoretical dissolved mass of iron from anode, Faraday’s law can be used.

\[ m = \frac{I \times t \times M}{z \times F} \]
where \( m \) is the amount of anode material dissolved (g), \( I \) is the current (A), \( t \) is the electrolysis time (sec), \( M \) is the molecular weight (g/mol), \( z \) is the number of electrons involved in the reaction, and \( F \) is the Faraday’s constant.

Edris Bazrafshan, et. al. (2012) studied the operating parameters and their effects such as applied voltage, number of electrodes, and reaction time on a real dairy wastewater in the batch EC process. Aluminum electrodes were used and in the potassium chloride used as electrolytes. It has been observed that the removal efficiency of COD, BOD\(_5\), and TSS increased with increasing the applied voltage and the reaction time. The result showed that EC process is efficient and it achieved 98.84% COD removal, 97.95% BOD\(_5\) removal, 97.75% TSS removal, and >99.9% bacterial indicators in 60min at 60 V. It has been observed that the treatment rate was increased upon increasing the applied voltage and reaction time. It has been observed that the results demonstrated the technical feasibility of EC process using aluminium electrodes as a reliable technique for removal of pollutants from dairy wastewaters.

Edris Bazrafshan, et. al. (2014) investigated the efficiency of EC process using aluminum electrodes in basic red 18 dye
removal from aqueous solutions. This study was performed in a bipolar batch reactor with six number of aluminium electrodes which connected in parallel. An attempt to achieved higher removal efficiency several important parameters, like initial pH of solution, initial dye concentration, applied voltage; conductivity and reaction time were studied. The electrochemical technique showed satisfactory dye removal efficiency and reliable performance in treating of basic red 18. At initial concentration 50 mg/L, in voltage of 50 V, reaction time of 60 minutes, conductivity 3000 μS/cm and pH 7, the maximum dye removal efficiency was equal to 97.7%. The efficiency of dye removal was increased with increase of applied voltage and in contrast electrode and energy consumption was increased simultaneously. In this study it was observed that the method was found to be highly efficient and relatively fast compared to different conventional existing techniques for dye removal from aqueous solutions.

Mohamed Hasnain Isa, et. al. (2015) investigated that the EC process and hydrothermal mineralization methods for the removal of boron from wastewater and its recovery using Box-Behnken Model as experimental setup was developed. An initial study was performed on four preselected variables (pH, current density, concentration and time) using synthetic wastewater. In this Response surface methodology (RSM) was used to evaluate the effect of process variables and their interaction on boron removal. The optimum conditions as pH 6.3, current density 17.4 mA/cm², and time 89 min were obtained and at an initial concentration of 10.4 mg/L, 99.7% boron removal was achieved. The process was effective on using RSM with a desirability value of 1.0. It has been observed that boron removal efficiency enhanced with increase in current density and treatment time and it also increased when pH was increased from 4 to 7 and then decreased at pH 10. Adsorption kinetics study showed that the reaction followed pseudo second order kinetic model; evidenced by high correlation and goodness of fit. Thermodynamics study showed that mechanism of boron adsorption was chemisorption and the reaction was endothermic in nature. Furthermore, the adsorption process was spontaneous as indicated by negative values of the adsorption free energy. Treatment of real produced water using EC resulted in 98% boron removal. The hydrothermal mineralization study indicate that borate minerals recovered as recyclable precipitate from EC flocs of produced water.

Umran Tezcan Un and Sadettin Eren Ocal (2015) investigated that EC process for the removal of cadmium (Cd), copper (Cu) and nickel (Ni) from a simulated wastewater by using batch cylindrical iron reactor. The various influential operational parameters like initial pH (3, 5, 7), current density (30, 40, 50 mA/cm²) and initial heavy metal concentration (10, 20, 30 ppm) on removal efficiency were examined in cylindrical electrochemical reactor. It was observed from the result that removal efficiencies were significantly affected by the applied current density and pH. The experimental results indicated that the highest Cd, Ni, Cu removal of 99.78%, 99.98%, 98.90% were achieved after 90min EC at the current density of 30 mA/cm² and at pH 7 using supporting electrolyte (0.05 M Na₂SO₄). The experimental results revealed that the removal of heavy metal ions by this design electrochemical cell was successfully achieved.

Mohammad Al-Shannag, et. al. (2015) studied that EC process for the removal of heavy metal ions, namely Cu²⁺, Cr³⁺, Ni²⁺ and Zn²⁺, from metal plating wastewater. In this study an electro-reactor was used with six number of carbon steel electrodes having monopolar configurations. Three of the electrodes were designated as cathodes and other three as anodes. The results showed that the removal efficiency of heavy metal ions increases with increasing both EC residence time and direct current density. Over 97% of heavy metal ions were removed efficiently by conducting the EC treatment at current density (CD) of 4 mA/cm², pH of 9.56 and EC time of 45 min. These operating conditions led to specific energy consumption and certain amount of dissolved electrodes of around 6.25 kWh/m² and 1.31 kg/m³, respectively. In the process of metal plating removal using EC consumes low amount of energy, making the process economically feasible and possible to scale up. The kinetic study demonstrated that the removal of such heavy metal ions followed pseudo first-order model with current-dependent parameters.

Amira Doggaz et, al. (2019) investigated that EC process for the removal of divalent iron and zinc cations from water with aluminium electrodes in a discontinuous system: the effect of hydrocarbonate HCO₃⁻ ion frequently present in liquid waste and in groundwater on the EC process. For this two ions, the presence of hydrocarbonate strongly limits the pH variations by its buffering properties and reduces the rates of Al dissolution by corrosion. Removal of this two cations was then shown to need longer treatment times and larger amounts of dissolved aluminum. The local pH gradients near the electrode surface with hydrocarbonate free water was previously shown to permit local formation of stable Zn and Fe hydroxides, which actively contribute to their elimination, the presence of hydrocarbonate nearly suppresses this positive phenomenon, leading to far less efficient EC treatment. Whereas removal of zinc cations from carbonated water can be considered as their simple adsorption on the Aluminum flocs, Fe²⁺ ions are oxidized to Fe(OH)₃ by air oxidation after their adsorption. Use of an overall adsorption model allowed quantitative comparison of the EC treatments, with very different adsorption parameters for the two metal studied.

Results observed were
- Hydrogen carbonate in water affects Zn²⁺ and Fe²⁺ removal by EC.
- Hydrogen carbonate suppresses formation of metal hydroxides near the cathode.
- Higher energy and more aluminum were required in the presence of the anion.
- Data of treatment runs can be efficiently discussed by using an adsorption model.

Warren. Reátegui- Romero, et. al. (2018) analyzed the benefits of EC through three case studies. The effluents were from different industrial sectors. The effluent from the San Rafael-Minsur S.A Mine was the final tailings of the tin
concentration process. Using iron anode, a current density of 22.35 A/m² and 45 minutes of process, it was possible to remove Fe (99.17%), Mn (99.97%), TSS (99.35%) and other metals like Cu, Zn and Cd were removed more than 99%, while the removal of Pb was varied, the pH remained in a range of 6.6 to 8. The effluent from the Conchán Oil Refinery was immediately taken out of the API separator without any previous treatment, the result observed that in 30 minutes at 50 A/m² using Al anodes, 98% NTU, 60% of oils and fats and 32.27% phenol, were removed with an energy consumption of 3.04 $/m³, while the pH remained in a range between 8 to 9. The effluent from the treatment ponds of the waste disposal plant (Befesa-Perú) was processed using iron anodes with a time of 30 min and 110 A/m², reaching a removal of 95.6% NTU and 45.14% COD, with an energy consumption of 3.30 kWh/m³ at a cost of 0.29 $/m³, while the pH remained in a range of 8 to 8.3.

Deepak Sharma, et. al. (2019) studied EC process for the treatment of electroplating effluent (EPE) by using iron as a sacrificial electrode. The initial concentration of chromium (VI) and lead (Pb) was found to be 55.3 and 3.5 mg/dm³ in electroplating effluent (EPE). With four-plate configurations, a current density (CD) = 73.5 A/m² and pH = 3.5 was found to be best. At this operating condition, maximum 91.7% Cr (VI) (i.e., 4.92 mg/dm³) and 91.3% Pb (i.e., 0.304 mg/dm³) removal obtained in 90minutes EC. Anode consumption was increased with a decrease in pH. It was observed that the energy consumption increased with a rise in pH. The settling characteristics of EC treated sludge were also analyze at different pH and settling at pH 9.5 was found to be best. Study showed that EC treatment is successfully applicable to treat heavy-metal-oriented waste water and this technique was very effective to treat real waste water (electroplating effluent) with minimum cost.

P. Krystynik, et. al. (2019) studied that the application of the method for removal of hexavalent chromium from an industrial effluent. The experimental approach followed the trail from a laboratory towards a pilot-scale unit. Initially, the laboratory unit was used for optimization of the most important process parameters and using the technology it was demonstrated that hexavalent chromium(Cr(VI)) was efficiently removed from the treated effluent. Optimization experiments revealed high efficacy within the removal of Cr(VI) together alongside its reduction towards Cr(III), and total removal efficacy exceeded 95%. Experiments performed with industrial effluent revealed a reduction in Cr(VI) below detection limit. Pilot-scale unit was used for long-term trials focused on the treatment of the industrial effluent. On contaminated industrial site a continuous pilot-scale unit (0.5 m³/h) was operated and revealed removal efficiencies of all contaminants below detection limit. Power consumption was observed during the process was only 0.24 kWh/m³; all the contaminants were reduced below their detection limit. Fatih Ilhan, et.al.(2019) studied EC process using iron and aluminum electrodes as an alternative method to precipitation of these metals mostly achieved by pH adjustment. The effects of the pH adjustment on removal before and after the EC process were investigated, and cost analyses were also compared. It was observed that a high proportion of removal was obtained during the first minutes of the EC process; thus, the current density did not have a great effect. In addition, the pH adjustment after the EC process using iron electrodes, which were 10% more effective than aluminum electrodes, was found to be much more efficient than before the EC process. In the process where kinetic modelling was applied, it was observed that the heavy metal removal mechanism was not solely due to the collapse of heavy metals at high pH values, and with this modelling, it was seen that this mechanism involved adsorption by iron and aluminum hydroxides formed during the EC process. When comparing the ability of heavy metals to be adsorbed, the sequence was observed to be Cr>Cu>Ni>Zn, respectively.

**TABLE I. APPLICATIONS OF ELECTROCOAGULATION IN THE TREATMENT OF INDUSTRIAL WASTEWATER**

<table>
<thead>
<tr>
<th>Research group</th>
<th>Operating conditions</th>
<th>Optimum Removal Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anbari et al. (2008)</td>
<td>Electrode: Fe T.T.: 20 min CD: 15 mA/cm²</td>
<td>Cyanide: 91.8%</td>
</tr>
<tr>
<td>Akbal et al. (2011)</td>
<td>Electrode: Fe &amp; Al T.T.: 20 min CD: 10 mA/cm²</td>
<td>Cu: 100% Cr: 100% Ni: 100%</td>
</tr>
<tr>
<td>Dermentzis et al. (2011)</td>
<td>Electrode: Fe &amp; Al T.T: 20 min CD: 15 mA/cm²</td>
<td>Cr: 91.8% Cd: 99.78% Ni: 99.89%</td>
</tr>
<tr>
<td>Bazzafshon et al. (2012)</td>
<td>Electrode: Al T.T.: 20 min</td>
<td>COD: 98.84% BOD: 97.95% TSS: 97.75%</td>
</tr>
<tr>
<td>Isa et al. (2015)</td>
<td>T.T: 89 min CD: 17.4 mA/cm² pH: 6.3</td>
<td>B: 99.7%</td>
</tr>
<tr>
<td>UnTezcan and Ocal (2014)</td>
<td>Electrode: Fe CD: 30 mA/cm² pH: 7</td>
<td>Cu: 98.99% Cd: 99.78% Ni: 99.89%</td>
</tr>
<tr>
<td>Sharma et al. (2019)</td>
<td>Electrode: Fe T.T: 90 min CD: 73.5 mA/cm² pH: 3.5</td>
<td>Cr(VI): 91.7% Pb: 91.3%</td>
</tr>
</tbody>
</table>
3. PARAMETER AFFECTED ON ELECTROCOAGULATION

Following are the effect of different operational parameters on removal efficiency of heavy metals from wastewater sample obtained from different industries was investigated inorder to determine the operating optimum conditions which have been published in journals.

Effect of pH:
The initial pH of solution is one of the important factors affecting the performance of electrochemical processes as pointed by several authors. pH is a critical operating parameter influencing the performance of EC process. pH of the medium changes throughout the process, depending on the type of electrode material and initial pH. The EC process exhibits only some buffering capacity, mainly in alkaline medium, that prevents large changes in pH and a decrease of the pollutant removal efficiency. In acidic media, higher removal efficiencies are obtained. Efficiency of removal increased when initial pH of the wastewater increased (Koby, et.al.,2003).

Effect of Current Density:
The effect of current density is an important parameter for pollutant removal within the electrocoagulation(EC) process that effects the metal hydroxide concentration formed during the method. High current density especially results in decomposition of the electrode material. With the increase of the current density higher values of removal efficiencies were obtained. The higher efficiency of removal of contaminants with increased current density was because of the higher amount of ions produced on the electrodes that promote destabilization of the pollutant molecules and the aggregation of the induced flocs, while increasing hydrogen evolution. However, the increase of the current density causes higher consumption of the anode material. Current density influences coagulant dosage as well as bubble formation rate, their size and the flocs growth(Bani,et.al.,2010). Current density is an important factor influence the electrocoagulation (EC) process. It is found that, the removal efficiency of TS, COD and FC are increased quickly up to current density of 20 mA/cm². This is explained the fact that, the coagulant production on the anode and cathode increases at the same time as increase the current density. But, at higher current density (25–30 mA/cm²), the removal of TS, COD and FC are nearly constant(Mahesh,et.al.,2006).

Effect of Electrode Material:
The most commonly used electrode materials for EC are aluminum and iron. They are cheap, readily, available and effective(Chen,et.al.,2000). Electrode material defines which electrochemical reactions happen within the EC system. Optimal material selection depends on the pollutants to be removed and the chemical properties of the electrolyte. In general, aluminum seems to be superior compared to iron in most cases when only the efficiency of the treatment is considered. Aluminium electrodes were most effective in removing color of the wastewater, whereas iron electrodes removed COD and phenol from the wastewater more effectively than aluminium electrodes. A joint arrangement of aluminium and iron electrodes removed color, COD and phenol with high efficiency. Iron electrodes and a combination of iron and aluminium electrodes gave the highest arsenic removal efficiencies. From metal plating wastewater similar results were obtained for copper, chromium and nickel removal.

Effect of EC Time:
Reaction time is one of the most significant operational parameters for all electrochemical treatment processes as with the increase of reaction time, corrosion of electrodes releases higher amounts of coagulant ions in the solution, an increase in reaction time improved the efficiency of phosphate removal (Behbahani,et.al.,2013). Increase in electrolysis time leads to an increase in coagulant concentrations that has been reported to reduce the floc density, then lead to reduce their settling velocity(Zodi,et.al.,2009). The EC time is an important parameter that is influential on the electrocoagulation(EC) process. Electrolysis time is of vital importance in the performance EC process. It is found that, removal efficiency of TS, COD and FC increases with increasing electrolysis time up to 15 min, thereafter removal efficiency observed almost constant. The removal efficiency increased with settling time.

Effect of Electrolyte (NaCl) Concentration:
It is important to investigate the effect of electrolyte concentration since actual wastewater usually contains certain amount of salts as the electrolyte concentration increased, the removal efficiency increased due to the increment of the electrical conductivity reaching the maximum value. However, with the increase in NaCl concentration, the removal efficiency decreased (Prasanna,et.al.,2005). Sodium chloride is usually employed to increase the conductivity of the water or wastewater to be treated. The effect of electrolyte type on the removal efficiency using Fe and Al electrodes respectively in the presence of different supporting electrolytes including NaCl, KCl, CaCl₂, NaF, Na₂CO₃, Na₃PO₄ were studied. Experiments were done using NaCl as it is cheap and the solution contains high conductivity so it need low voltage for electrocoagulation and hence it is economical in industrial scale. Usually, NaCl was used as supporting electrolyte in electrochemical process and KCl is used to obtain the conductivity in EC process(Panizza,et.al.,2000;Yang,et.al.,2000).

Electrical Energy and Electrode Consumption:
Electrical energy consumption is a significant economical parameter in the electrocoagulation process. It can be seen that the longer contact time of the system applied, the weight of the electrode consumed in the simple EC process has been increased. The variation of electrical energy consumption increased proportionally with contact time.

Effect of Applied Voltage:
In all electrochemical processes applied voltage is the most significant parameter for controlling the reaction rate within the electrochemical reactor(Mollah,et.al.,2001). It is well
known that this variable determines the production rate coagulant, adjusts also bubble production, and hence affects the growth of formed flocs.

The Effect of Inter Electrode Distance:
The distance between the electrode is an important variable to optimize operating costs. According to the characteristics of the effluent, the process efficiency is often improved by varying the distance between the electrodes.

Effect of Operating Temperature:
Temperature is another important operating condition which will affect pollutant removal efficiency in wastewater treatment. The turbidity removal efficiency from abattoir wastewater in the EC process increased by increasing solution. The results show that increasing temperature has a negative effect on removal. However, it should be noted that the operation of electrocoagulation(EC) process at higher temperature significantly reduced electrical energy consumption and fluid conductivity increases. Therefore, the production of hydroxide species increases rapidly then enhances pH value (Yilmaz,et.al.,2008; Katal,et.al.,2011; Vasudevan,et.al.,2009).

4. CONCLUSION
This review was focused on the electrocoagulation method to treat the industrial wastewater by studying the mechanism, chemical reaction on the electrodes used and the affected parameters such as pH, current density, electrode material, time, electrical energy and electrode consumption, applied voltage etc. It was found that electrocoagulation technique is an effective treatment for the removal of heavy metals from industrial wastewater as it is economically and having higher removal efficiency via other conventional treatment methods. This process required simple equipment and easy operation.

5. REFERENCES


