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ISOTHERM STUDIES ON SONO-ELECTROCOAGULATION FOR REMOVING Ni IN AQUEOUS SOLUTION

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ABSTRACT – *This study involves the electrocoagulation (EC) and sono- electrocoagulation (SEC) for the removal of Ni2+ from aqueous solution. The influence of operating parameters such as type of electrode, current density, electrolyte concentration, pH on the removal of Ni2+ ions was studied. The sacrificial electrodes used are Iron (Fe) as cathode and aluminium (Al), titanium (Ti), Stainless steel (Fe) as anode. The removal efficiency obtained was 86% for EC and 95% for SEC. The experimental adsorption data was modeled with Langmuir, Freundlich, Temkin isotherms and data were found to fitted well with (R2=0.975) Freundlich isotherm model with an adsorption capacity of qe=15.10 (mg/g), The result reveals that SEC shows an increase in removal percentage compared to EC. Industrial effluent containing Ni2+ can be treated using optimum conditions obtained for both EC and SEC process from aqueous solution.*

Keywords—Electrocoagulation, Sono- Electrocoagulation, Heavy Metal

1. INTRODUCITON:

Heavy metal discharges from various industries like electroplating, textile, pulp, leather, automobiles, etc., are the source of water and environmental pollution. Statistics indicates that about 1,00,000 tons of wastewater discharges from every industries worldwide [1]. most of the heavy metals such as, nickel [1], copper, zinc [1,2], arsenic [3], boron [4], cobalt [5], lead [6], chromium [7] are not biodegradable that trends to harmful to the groundwater and environment, due to direct discharge of without careful treatment.

Various techniques are available for the treatment of heavy metals such as, chemical precipitation [8], adsorption [9,10,25,28], ion exchange [11], reverse osmosis12], electro-dialysis 13,26,27], electrocoagulation [14], constructed wetlands [29], bioremediation [30] etc. These methods have some disadvantages like more addition of chemicals and excessive amount of sludge, which leads to secondary treatment.

Meanwhile, different hybrid treatment is carried out like electrocoagulation / flotation [15], electro-oxidation [16] electrocoagulation / ozonation [17], electrocoagulation / photo-fenton [18], electrocoagulation / sonication [19-23] in both dye and heavy metal.

Recently, electrocoagulation is one of the attractive significant methods for heavy metal treatment. In this method, no addition of chemicals, less amount of sludge production, no need for the secondary treatment is required. In electrocoagulation metals like iron (Fe) acts as cathode and aluminium (Al) as anode are generally utilized to generate the electric current that results dissolution at anode surface.

Anode: Al $\rightarrow$ Al3-+3e-

Cathode: 3H2O + 3e- $\rightarrow$ 3OH-+ 3/2H2

Sonication is the process of applying the sound energy and it will form free radicals that aids to better efficiency. In liquid, the rapid vibration of the tip causes cavitation bubbles [23]. The collapse of thousands of bubbles releases the tremendous energy to the cavitation field and leads to decolourization and demineralization of the pollutant [23]. It has been coupled with electrocoagulation for betterment of removal efficiency [24].

In this present study, our aim is to combine the electrocoagulation and ultrasound irradiation to enhance the better removal efficiency in an aqueous solution. Although electrocoagulation method was widely used for the heavy metal removal, by our knowledge, no previous work has been carried out by the combination of both technologies.

2. METHODS AND MATERIALS:

2.1. Model Wastewater Synthesis

Raw nickel solution was prepared for 1000 mg/l by dissolving (NiSO4.6H2O) in distilled water. In this experiment pH was adjusted by using (NaOH/HCl).

2.2. EC Apparatus

In lab-scale batch experimental setup was carried out. The electrocoagulation experiment was carried out by 200ml cylindrical reactor made up of glass. In this process stainless steel act as cathode and aluminum act as anode. Plates thickness of 2mm were used as electrode of dimension of 12cm x 3.5cm. The one-half of the electrode was immersed in the wastewater and effective surface area of the electrode is 7cm x 3.5cm. The inter electrode distance was maintained as 1.5cm. Agitation of 400rpm was provided by means of magnetic stirrer. The DC power supply [0-30V and 0-8A] was used to provide electric current density to the electrolytic cell.

Sonochemical (SCh) studies were performed using a heischlerSonicator model UP-2020 S Programmable Ultrasonic Liquid Processor equipped with an 11 mm titanium-alloy probe. The Sonicator was operated at 24 kHz and the ultrasonic power was set 20 to 100%.

Electrocoagulation

Sonication

2.3.Measurements

Samples were taken after the reaction reached the steady state in one experiment, and then separated by centrifugation. The supernatant was used to measure the removal efficiency of nickel ion. The pH was monitored with a pH meter (Roy instrument) and the conductivity was measured with a conductivity meter (LIDA DDS-11A, China). The amount of Ni^{2+} in solution was analyzed using dimethylglyoxime by spectrophotometric.

Sample from EC and SEC

3. RESULT AND DISCUSSION:

3.1. Effect of pH

In the Fig 1, shows that the effect of pH carried out for 4, 5.5, 6.5, 7.5 at the concentration of 10ppm. It has been established that the initial pH is an important parameter which has a considerable influence on the performance of EC process. It could be seen from the Fig. 1 that the Ni^{2+} removal efficiency increases with the increment of pH and the maximum removal efficiency occurs at pH value from 6 to 8. Apparently the increment of removal efficiency is slight at pH 6–8, while the increment is significant at pH 3–6. At low initial pH condition, the hydrolysis products of Al^{3+} are soluble aluminum hydroxides, which are not capable of absorbing the pollutants. The removal efficiency increases slightly at pH from 7 to 8. This can be explained by the fact that besides the adsorption effect of flocs, there exists precipitation reaction of Ni^{2+} at alkali pH condition. Based on the above condition at initial neutral pH, the Ni^{2+} removal is dominated by both adsorption and precipitation. At basic pH condition, the removal approach of precipitation dominates. At the pH (6-7) condition the value is high. Because, the utilization rate of electro-generated Al ions is larger in neutral condition.

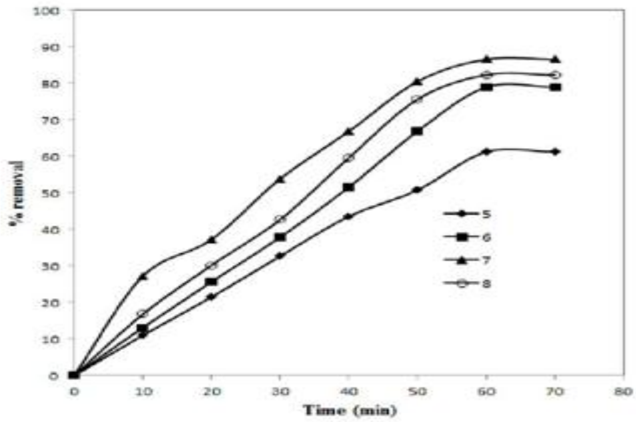


Fig 1: Effect of pH on EC: anode:Fe, cathode: Al, electrode distance: 2cm, conc:10ppm current density: $4.5 mA/cm^2$

3.2. Effect on Concentration

The effect of concentration on Ni^{2+} ion was carried out at optimum pH of 7 by varying other parameter (10, 20, 30, 40, 50ppm). It can be observed from Fig. 2 that the removal rate of Ni^{2+} ions is increases with decrease in initial Ni^{2+} concentration. This can be related to the fact that the amounts of dissolved Al ions are constant for applied current density and time. Even though, the removal efficiency of EC process had decreased, due to the amount of Ni^{2+} ions removed by increasing the initial concentration. Because, the amount of Al dissolution in different initial Ni^{2+} concentrations is constant but at higher initial Ni^{2+} loading, these ions have more chances of being removed from the solution by EC process.[V. Khandegar et al.,]

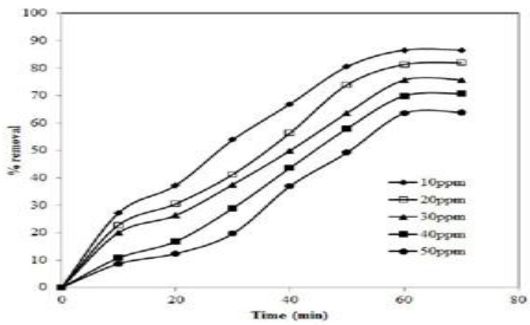


Fig. 2: Effect of concentration on EC: anode:Fe, cathode: Al, electrode distance: 2cm, current density: 4.5mA/cm², pH: 7

3.3. Effect on Current Density

Current density is the most important parameter which determines the reaction rate of anode and cathode. The amount and concentration of produced Al^{3+} and OH^- are controlled by current density. The effect of current density on removal efficiency is shown in the Fig.

It can be ascertain that the removal efficiency of Ni^{2+} increases with the increase in current density (2.5 4.5mA/cm²) this increase may be due to, more Al^{3+} and OH^- which could form monomeric and polymeric aluminum hydroxides by hydrolysis reactions are produced on the surface of anode and cathode respectively.

By increasing the current density to 6.5mA/cm², there a decrease in percentage removal this may due to the fact that, not all the electro-generated Al ions takes part in the adsorption process. The Ni/Al ratio of flocs could be considered as the amount of Ni element adsorbed by per Al element. Ni/Al decreases with the increase of current density [Yan Li, Mengxuan Yin]. As the current density increases, the whole amount of metal hydroxide increases and the surface hydroxyl groups will increase. However, the amount of residual Ni^{2+} decreases with the increment of current density. This leads to the competitive adsorption effect among Al hydroxide flocs (or the surface hydroxyl groups). [HosseinJafariMansoorian et al.,]

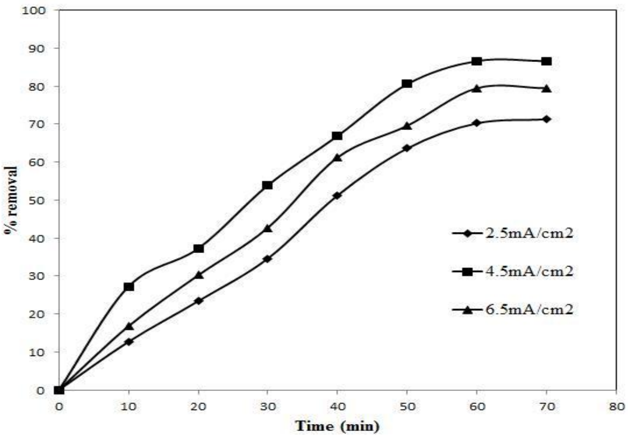


Fig. 3: Effect of current density on EC: anode:Fe, cathode:Al, electrode distance:2 cm, pH:7, conc:10ppm.

3.4. Effect on Electrocoagulation and Sono-Electrocoagulation

Fig. 4 shows the results of combined batch experiment carried out, (electrocoagulation, ultra sonication, sono-electrocoagulation). It can be observed from the fig that the sonication alone does not shows significant removal efficiency. This may be due to formation of free radicals which will not enhance the oxidation process in heavy metal. In electrocoagulation the removal efficiency is increased by increasing the time and current density due to the generation of aluminum hydroxide by hydrolysis reactions are produced on the surface of anode and cathode respectively. Sono-electrochemical method provides afaster and dynamic mean to reduce the requisite retention time for separation of coagulants. This studyshows that the combined process promotes flocculation through vigorous mixing and oxidation through formation of radicals which contribute to the enhancement and oxidation of soluble pollutant. It can also be observed from the Fig. 4 that sono-electrocoagulation removal efficiency is higher compare to other process at lower current density (1mA/cm²), this may be due to coupling of OH° with Al^{2+} to form Al^{3+} and OH^- generated by electrodes react to form various monomeric and polymeric aluminum hydroxide species, such as Al $(OH)^{2+}$, Al $(OH)^{3+}$. These species undergo complex polymerization and partly transform into insoluble amorphous aluminum hydroxides, which have abundant surface hydroxyl groups for adsorbing heavy metal ions and penetration of hydroxyl (OH°) and hydrogen (H°) radicals into water resulting in hydrogen peroxide formation which in turn oxidizes the dissolved inorganic compounds.[P. Maha Lakshmi et al.]

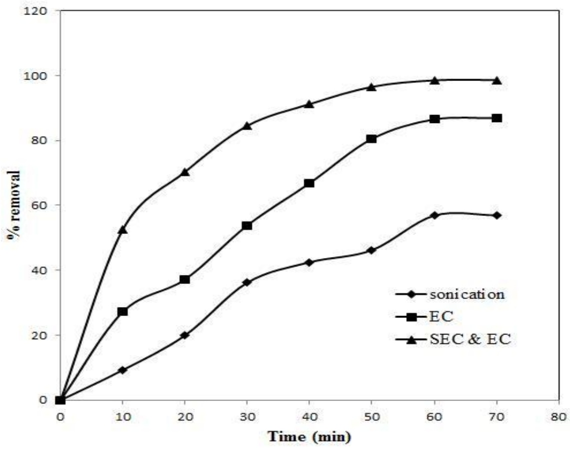


Fig: 4 Effect of EC and SEC: anode:Fe, cathode:Al, electrode distance:2cm, pH:7, conc:10ppm, frequency:24KHZ, amplitude:80%

4. EQULIBRIUM STUDIES

The concentration of Ni^{2+} in solution before and after adsorption was determined by using an UV spectrophotometer. Prior UV spectrophotometer measurement, the heavy metal solutions were properly diluted to ensure that the metal concentration in the sample was linearly dependent on the detected absorbance. The analyses were detected at 470 nm.pH meter for measurement of pH of solution. Samples were taken at definite intervals (0–70 min) for the residual metal ion concentrations in the solution. Isotherm studies were recorded by varying the concentration (10– 50 mgL^{-1}) of Ni^{2+}.

The adsorption capacity qe ($mg\,g^{-1}$) after equilibrium was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where m is the difference in electrode weight (g), V is the volume of the solution (L), $C0$ is the initial concentration of metal (mg L^{-1}), Ce is the equilibrium metal concentration (mg L^{-1}) and qe is the metal quantity adsorbed at equilibrium (mg/g). The initial pH of the solution was adjusted with either HCl or NaOH. The percent removal of metals from the solution was calculated by the following equation:

$$\%removal = \frac{(C_0 - C_i)}{C_0} X100$$

where Co (mg/L) is the initial metal ion concentration and Ci (mg/L) is the final metal ion concentration in the solution.

5. ADSORPTION ISOTHERMS

5.1. Langmuir Isotherm

The Langmuir isotherm assumes monolayer deposition of adsorbate on homogenous adsorbent surface. It is well known that the Langmuir equation is intended for a homogeneous surface. The mathematical expression of Langmuir isotherm is given as

$$q_e = \frac{Q_{max} bC_e}{1 + bC_e}$$

The linearization of the equation is given as

$$\frac{C_e}{q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}}$$

where 'b' is the binding constant and Qmax refers the maximum adsorption capacity, evaluated by plotting Ce/qe against Ce.

5.2. Freundlich Isotherm

The Freundlich isotherm is an empirical model relating the adsorption intensity of the sorbent towards adsorbent. The isotherm is adopted to describe reversible adsorption and not restricted to monolayer formation. The mathematical expression of the Freundlich model is

$$q_e = K_F C_e^{1/n}$$

where KF and n are the constants which give adsorption capacity and adsorption intensity respectively. A linear form of the Freundlich model can be written as follows.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

A plot of lnqe versus lnCe gives a straight line with slope KF and intercepts 1/n. The values of KF and n along with the linear regression co-efficient R^2 for the present experimental conditions have been obtained for Nickel heavy metal. It can be noticed that the estimated regression coefficients of Freundlich isotherm model (> 0.9) indicates that the Freundlich isotherm model satisfactorily matches with the experimental observation.

5.3. Temkin Isotherm

Temkin and Pyzhev (1940) considered the effect of adsorbate/adsorbate interactions on adsorption isotherm and suggested the following

$$q_e = B\ln A + B\ln C_e$$

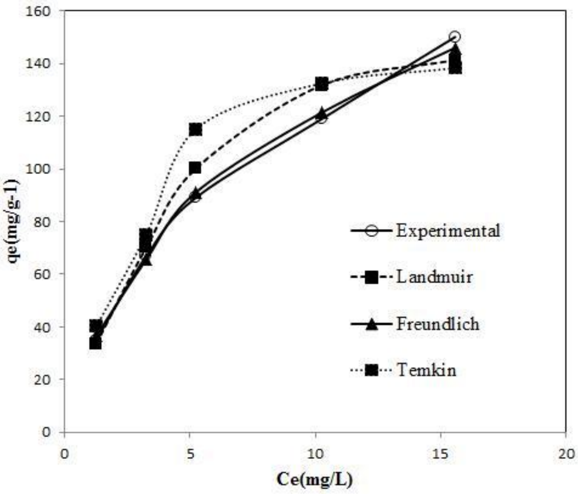
where $B = \frac{RT}{b}$, A and B are the Temkin constants. A plot ofqe versus lnCe enables to determine the constants A and B. The estimated A and B along with the linear regression co-efficient R^2 for zinc heavy metal.Temkin isotherm model does not satisfactorily match with the experimental observations.

The values of qm and K were determined by plotting lnqe versus ε^2. The estimated K and qm along with the linear regression co-efficient R^2 for Nickel heavy metal.

The values of sorption energy (Es) (kJ mol−1) can be calculated from the equation,

$$E_s = \frac{1}{\sqrt{2K}}$$

If the magnitude of Es is between 8 and 16 kJ mol^{-1}, the adsorption process proceeds by ion-exchange or chemisorptions, while for values of Es< 8 $kJmol^{-1}$, the adsorption process is of a physical nature.



4.1 Comparison of isotherm model prediction with the experimental observations for Nickel ions pH:7 , time : 80 min

6. CONCLUSION:

In this work, the removal of (Ni^{2+}) by batch EC and SEC process was carried out in aqueous solution. The effect of pH, initial concentration and current density were studied to optimum the process. Further result indicates that the equilibrium time obtains at 70 mins and the removal percentage was 86 at initial concentration of 10ppm, pH 7 and current density 4.5mA/cm^2 for electrocoagulation process whereas for SEC 98 removal was achieve at an optimum time of 30 mins. The data was fitted with Langmuir, Freundlich, Temkin isotherms and identified best fit to an experimental data is Freundlich isotherm model with a maximum adsorption capacity of qe=14.10 (mg/g). Finally, this study suggest that industrial effluent containing Ni^{2+} can be treated using optimum conditions obtained for both EC and SEC process of aqueous solution.

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