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Removal of Cadmium by Electrocoagulation from Industrial Wastewater of Oil Refineries

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Mobile:

Abstract

This study's primary goal is to look into the possibility of removing cadmium from sewage of a North Refineries Company (Baiji), before discharging into open environments. The presence of environmental heavy metals like cadmium is harmful for living organisms. The chemical procedure used to remove heavy metals from wastewater is called Electrocoagulation Aluminum anode and stainless-steel cathode are used in (EC). The primary use of this method is with industrial effluent. where a sacrificial anode is electrolytically oxidized to create the coagulants in-situ. This method is becoming more popular in the water and wastewater treatment process due to its adaptability, environmental friendliness, and capacity to provide high process efficiency at minimal running costs. Several working parameters, to achieve a higher removal capacity. in voltage of 20. The optimum electrocoagulation time 70 min, initial pH 7.5, Electrical current 2,5 amp, and Mixing speed 300 rpm, NaCl concentration 1.5 g L^{-1}. Under the optimum conditions established, yields a very effective (98.7%). The method was found to be highly efficient and relatively fast compared to conventional.

Introduction:

Our most valuable resource is water, which is essential to human existence. However, many people throughout the world do not have access to hygienic facilities and clean water. More than 80% of the generated wastewater is not treated. [1]. The amount of water available from natural sources has been declining as a result of increased extraction for industrial, urban, and agricultural use. The expansion of activities that produce wastewater is also contributing to an increase in water contamination [2]. Concerns about the safe use of the limited water resources have arisen as a result of urbanization and the notable population growth. Large volumes of wastewater are produced everyday as a result of global population increase and industrial activity, underscoring the need for creative, effective, and financially viable approaches to treating the many wastewater streams [3]. Heavy metal-containing industrial effluent is either directly or indirectly released into the environment, particularly as companies grow. The majority of metals, including lead, cadmium, copper, nickel, and zinc, are inclined to accumulate in living organisms and are not biodegradable. It is well recognized that some of them are hazardous or carcinogenic. Therefore, it is dangerous to release them without providing proper care. Industrial wastewaters are highly regulate [4]. Therefore, they need to be treated before being released into sanitary sewers or surface water. [5].

Petroleum refineries require a lot of water for many purposes, including desalting, hydrotreating, distillation, and cooling systems. As a result, they produce a lot of effluent. There are significant amounts of aliphatic and aromatic petroleum hydrocarbons in the wastewater from petroleum refineries. Contaminants found in refinery effluents include ammonia, cyanide, oil, phenols, benzene, sulfide, and heavy metals[6]. Crude oil contains a variety of heavy metals, including nickel, vanadium, cadmium, lead, mercury, chromium, and others [7]. Cadmium is categorized as a hazardous element and is one of the heavy metals that pollute the environment [8]. Because cadmium ions may infiltrate the food chain and seriously endanger human health, they represent a concern to the environment. This includes possible harm to the kidneys and bones, and chronic exposure can lead to the emergence of diseases like hypertension [9]. Teratogenic and carcinogenic, cadmium is a hazardous heavy metal that is not necessary for the environment. Renal damage, pulmonary insufficiency, and adverse effects on the liver, blood, are all consequences of cadmium poisoning [10]. As an alternative to traditional coagulation, electrocoagulation uses electricity to remove colloids and suspended particles rather than chemical reagents [11]. One electrochemical method with several uses is electrocoagulation. An electric current is used in the electrochemical procedure known as (EC) to destabilize emulsified, dissolved, or suspended contaminants by producing by electrolyzing sacrificial anodes to dissolve coagulant species in situ, which are often formed of iron or aluminium. With regard to different forms of wastewater, it has the ability to eliminate both organic and inorganic impurities. Because it lowers the quantity of chemical dose, sludge production, and the high expenses associated with their disposal, EC is straightforward and cost-effective for wastewater treatment. A number of factors, including as pH, electrode, operating period, and current density, affect how successful the EC process is. Because of its adaptability and environmental friendliness, this procedure has lately garnered interest as a possible method for treating industrial wastewater. In addition to treating a range of wastewater types, such as landfill leachate, restaurant, car wash, slaughterhouse, textile, laundry, tannery, and petroleum refinery effluent, this technique has been utilized to remove bacteria, arsenic, fluoride, pesticides, and heavy metals from aquatic habitats. [12-14]. The aim investigates the study of cadmium ion removal from oil refinery wastewater using method electrocoagulation, and determining the optimal operating conditions that achieve the greatest removal of cadmium ions. and promises to be very useful for further applications of the EC process on the treatment of wastewater containing heavy metal ions.

Electrocoagulation principles

The fundamental idea of EC is derived from "electrolysis," which is the process of dissolving materials with electricity. When an electrolytic solution is exposed to an electric current during the electrolysis process, oxidation and reduction processes occur. In 1820, Michael Faraday introduced the electrolysis idea. The process is conducted in an electrolyte, water, or salt-melting solution that facilitates the movement of ions between two electrodes. The cathode receives positive ions, whereas the anode receives negative ions when an electrical current is supplied. The anions are oxidized and the cations are reduced at the electrodes [15].

Reactive anode material is dissolved in the solution using electricity in the water and wastewater treatment process. EC uses the leaching anode metal to produce coagulant species on-site. These metal ions can hydrolyze spontaneously in a water solution because they have two or three valence electrons. Although certain other metals can also be utilized, aluminum, iron, and stainless steel are the most often employed electrode materials. The metals listed above are widely available, reasonably priced, and useful. Pollutants are coagulated by dissolved metal ions in a water solution. Water is converted to hydrogen and hydroxide in the cathode. The hydrogen gas (H_2) produced during the cathode process can then be employed to help remove these fused materials using electrolytic flotation. Additionally, sedimentation occurs [16,17]. As seen in Image, 1. During the flotation process, the lightweight compounds will separate to the solution's top, while the heavier compounds will sediment towards the reactor's base. [18].

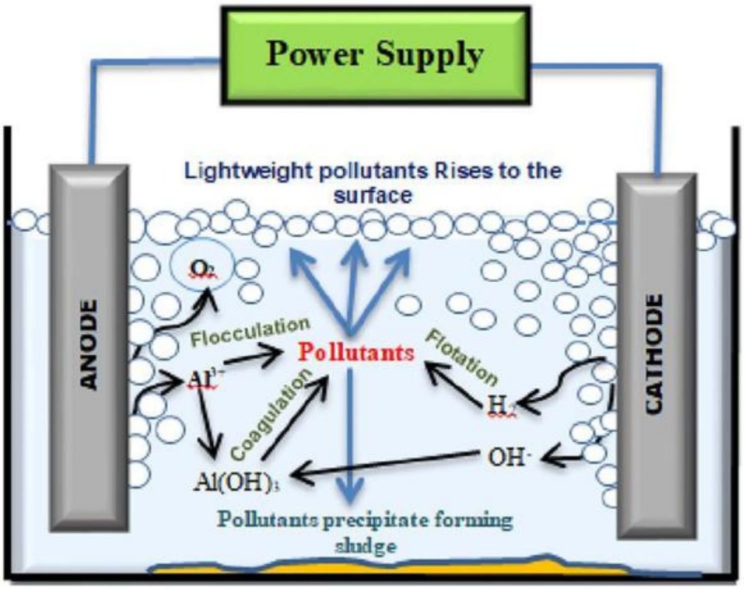

Image 1: Process diagram for electrocoagulation.

Because aluminium electrodes are reasonably stable and can produce highly adsorptive $Al(OH)_3$ coagulants, they were utilized as anodes. Equations (1), (2), (3), and (4) may be used to write The following reactions occur during the electrocoagulation process: [19]:

Anode $Al_{(S)} \longrightarrow Al^{3+}_{(aq)} + 3e^-$ (1)

Cathode $2H^+ + 2e^- \longrightarrow H_2$ (2)

$2H_2O \longrightarrow 2HO^- + H^+$ (3)

$Al^{3+}_{(aq)} + 3OH^- \longrightarrow Al(OH)_3$ (4)

Materials and Methods

All of the experiments were conducted in an EC reactor. A pH meter was used to test the pH after it had been changed using HCl purity 36% and NaOH solutions purity 99%. (inoLab pH 7110). To maintain the conductivity sodium chloride (NaCl purity 99.5%) was used. Mixing of the solution was done by using a magnetic stirrer (HPM-10), For supplying current, DC power supply (EXTECH 382213) was employed.

Sample Collection:

Samples of real wastewater were collected from the treatment plant of oil refineries (Baiji Refinery). This facility receives industrial wastewater from several refineries. All industrial wastes enter the wastewater treatment plant together. The wastewater samples were collected in plastic containers and cooled to 4 °C, then transported to the laboratory for analysis and electrochemical treatment to evaluate the electrocoagulation process, and were not subjected to any removal or pretreatment.

Electrodes:

The anode was made of aluminium (AA-4043) and cathode (SS 410). as depicted in Image, 2. three plates Aluminium, and three stainless steel plates with dimensions of 135 mm × 140 mm × 2 mm (Length, width and thickness respectively).

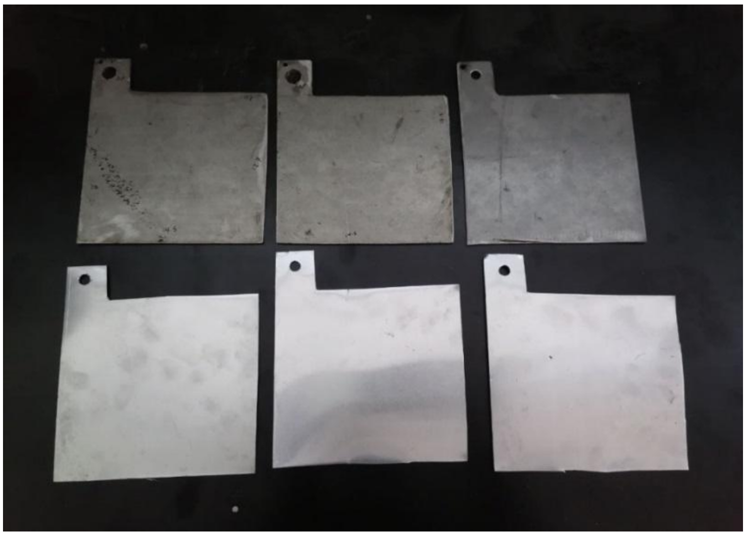

Image 2: The electrodes aluminium, stainless steel used for the electrocoagulation process.

Electrochemical cell:

The electrocoagulation reactor 2 Lit acrylic vessel with a working capacity of around 1.5 L and dimensions of 16 cm × 14 cm × 15 cm, the tests were carried out. A magnetic stirrer was employed for mixing, which produced extremely rapid mixing in the cell. A DC power source that could be adjusted (up to 30 V and 3 A) provided the electric current. Standard procedures for analyzing water and wastewater were followed, and a spectrophotometer (Hach DR3900 spectrophotometer) was used to measure the cadmium amounts. Cadmium levels in water and wastewater may be determined using the dithizone technique. Dithizone is available as a stable powder in the DithiVer Metals Reagent. A pink to red cadmium-dithizonate complex is created when cadmium ions and dithizone react in a basic solution, and this complex is then extracted. with chloroform. At 515 nm, test results are measured. [20].

Experimental Set-up

An EC setup schematic is shown in Image. 3. For every effort in this investigation, the EC reactor had a 2 Lit box with 1.5 Lit of model water inside. Three stainless steel (S.S) and three aluminum (Al) plates measuring 100 mm by 40 mm by 3 mm (length, breadth, and depth) were employed as electrodes in a mono-polar parallel mode. A DC power source was used to apply a current between 0.5 and 3 A. The solution was constantly agitated with a magnetic stirrer bar during the EC process, with the ideal rotational speed being between 50 and 350 rpm at room temperature. the electrodes were cleaned with water after each run and immersed in a 10% acetone solution for ten minutes to remove impurities and clean the aluminium electrode's surface. After removing the impurities, the respective electrode was dried before being used again in the subsequent experiments.

Image 3: Electrocoagulation's apparatus setup.

Evaluation of removal efficiency

cadmium removal efficiency (%) from artificial water that has been electrocoagulated has been computed as follows using Equation 5:

$$Removal\ rate\ (\%) = \frac{(C_{\circ} - Ct)}{C_{\circ}} \times 100 \qquad (5)$$

where the initial Cd^{2+} concentration is C_0 in wastewater before treatment, and the ultimate Cd^{2+} concentration after treatment is Ct. [21].

Operating parameters for efficient EC

How well the electrocoagulation process removes pollutants depends on a number of factors, including the conductivity of the solution, the type of power source, the pH of the solution, the distance between the electrodes, the length of the electrolysis, the current density, and other variables. To ensure that the EC process operates as efficiently as feasible.

Effect of pH

Starting pH is the most crucial of the several factors affecting EC effectiveness. Metal ions are known to dissolve as cations or as components of anions. It undergoes further hydrolysis based on the pH and the production of insoluble metal compounds by the electrolytic cell [22]. pH is a sig, according to experimental studies. Over the course of the electrocoagulation process, the pH of the solution varies. [23]. The pH of the waste increases when the initial pH is below 4, decreases when it is above 8, and remains relatively stable when it is between 6-8. This scenario demonstrates the presence of a pH buffer effect during electrocoagulation, which is different from the conventional chemical coagulation process. The ability of the pH to remain stable can be explained by the balance between the creation and use of hydroxyl ions in electrocoagulation, and the requirement for charge balancing before the conversion of soluble aluminum compounds to aluminum hydroxides [24] .The end pH of the electrolyte influences the solubility of the Al hydroxides, whereas the starting pH of the electrolyte influences process performance. Using HCl and NaOH solutions (0.1 M), the pH of the influent solution was brought to the appropriate values (2,5,7,11) in order to examine the effect of the initial pH. Cadmium removal from wastewater was studied, and the findings showed that a high removal rate occurred when the pH (7.5) at the beginning. As shown in the figure 1.

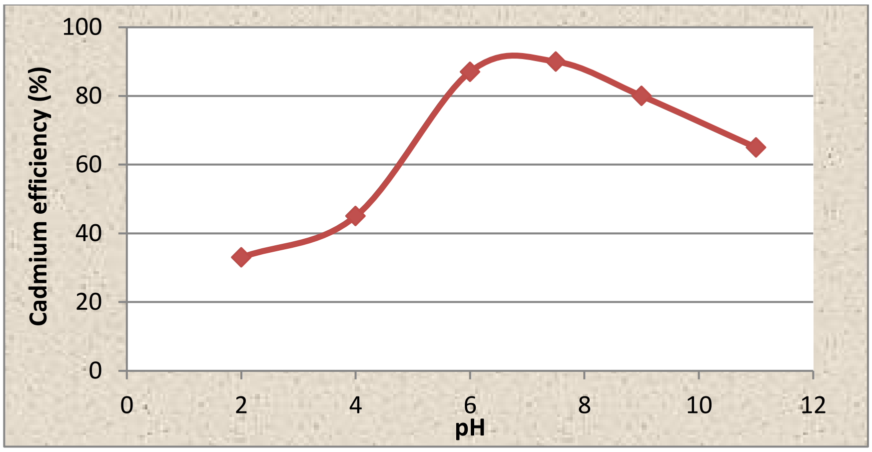

Fig. 1: pH's effect on electrocoagulation.

Effect of applied voltage

In electrocoagulation process's performance is greatly influenced by the applied voltage [25]. In the electrocoagulation process, the applied voltage is crucial. The rate of bubble formation, floc size and development, and coagulant dosing rate are all closely correlated with the applied voltage. These have to do with how quickly contaminants are eliminated. The effect of this parameter on how well the removal cadmium from wastewater is investigated across a variety of voltages. Using applied voltage levels (5- 30), the outcomes are displayed in Figure. 2. Increasing the applied voltage by 20 volts causes the rate of H_2 gas production to increase and the size of the bubbles to decrease, increasing the upward flow and accelerating the removal of contaminants and sludge flotation.

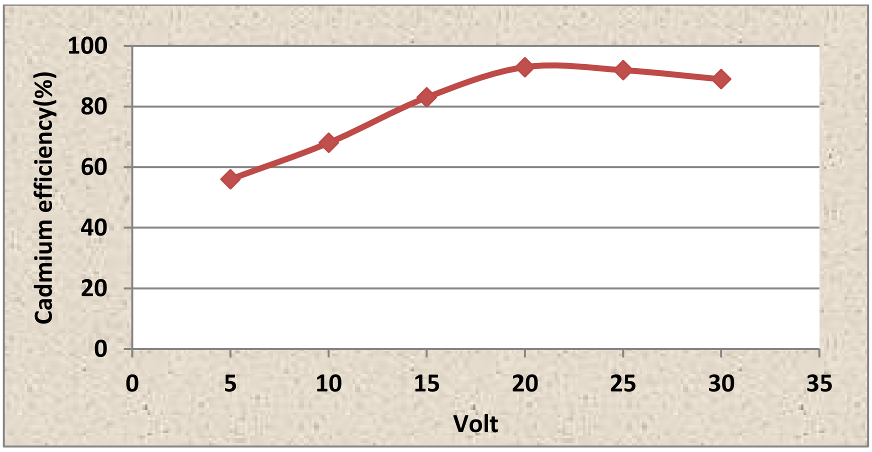

Fig. 2: Impact of the applied voltage.

Effect of applied current

This parameter controls the amount of metal added to the water through electrochemical processes as well as the amount of bubbles produced through electrolysis [26]. The amount of metal ions discharged at the anode is controlled by the applied current, which has a major impact on the (EC) process. The experiment was conducted at currents ranging from (0.5-3) Amp. Because the anode dissipated in accordance with Faraday's law:

$$W = \frac{(J \times t \times M)}{n \times F} \qquad (6)$$

J is the applied current density (mA/cm^2), *t* is the electrolysis time in; *M* is the relative molar mass of the electrode material under investigation; *n* is the number of electrons in the oxidation/reduction reaction; *F* is Faraday's constant (96,500 C/mol); and *W* is the amount of electrode material dissolved (g of M per cm^2). [27].

Cadmium removal efficiency rose to a certain amount upon raising the applied current in the aforementioned applicable range. plots, as shown in Figure 3, that at higher currents, more aluminum is oxidized, forming more coagulant for better removal, and achieving maximum removal efficiency along with high hydrogen bubble liberation at the cathode, which causes sludge to rise to the surface. In this sense, the cadmium removal process in question is still somewhat controlled by applied current. it was the current (2.5 Amp) the most efficient in remove.

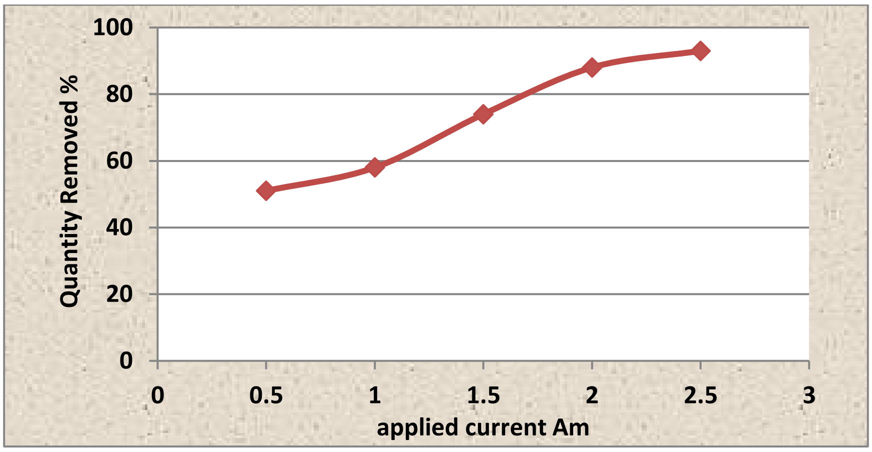

Fig. 3: Effect of applied current.

Effect of sodium chloride

Aluminum hydroxide is more readily available in the solution and the removal efficiency is improved when chloride ions are present because they eliminate the passive oxide layer that forms on the electrode surface. [28]. To reduce energy consumption, sodium chloride at a concentration between 0.5 and 2.5 g L^{-1} was added to the solution to boost its ionic conductivity. When the dose of NaCl was raised from 0.5 g to 1.5 gm, as shown in Figure 4, the percentage elimination increased. This is because the solution's conductivity increased.

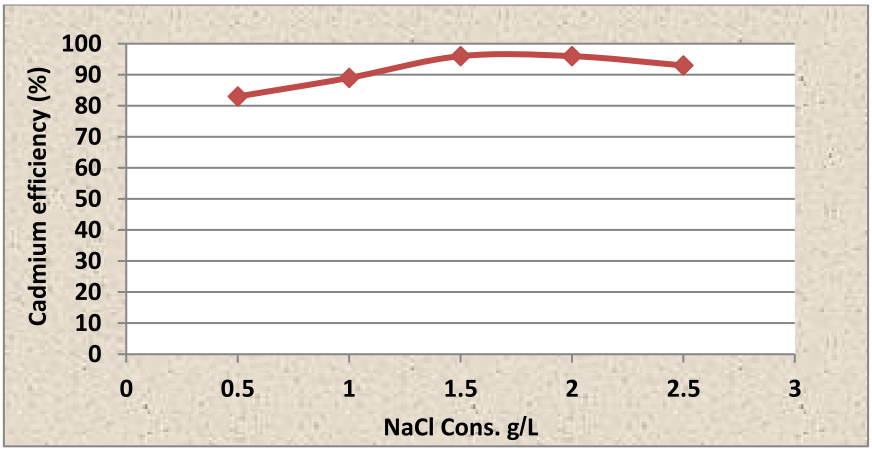

Fig. 4: Effect of sodium chloride, cons.

Effect of Electrode gap

Since the electric field relies depends how far apart the electrodes are, the inter-electrode gap is one of the most crucial factors in the electrocoagulation process. As soon as the
When the anode and cathode electrode gap (g) widen, the cell's resistance (R) rises and is controlled by the following relationship:

$$R = \frac{g}{KA} \qquad (7)$$

A (m^2) is the electrode surface area, and the conductance unique to a cell is K ($S\ m^{-1}$).. The g (m) value between the anode and cathode rises R (ohm) if A is greater. According to Faraday's law, when g increases, less oxidized metal is present, which lowers the effectiveness of pollution removal [29]. in Figure, 5. The results show that, removal efficiencies of cadmium increase when the distance 1.25 cm. The primary cause of this is a decrease in resistance between plates at constant voltage, which raises the current and raises the coagulant and bubble concentration.

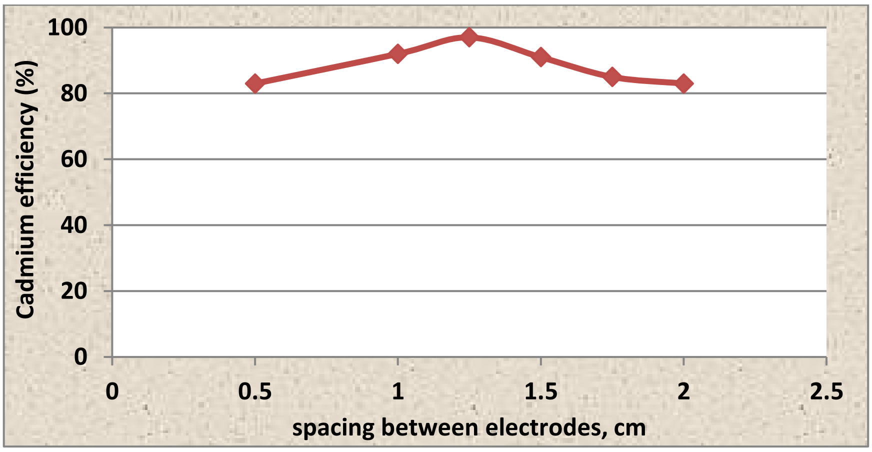

Fig. 5: Effect of Electrode gap.

Effect of Mixing speed

Mixing is frequently done manually by the EC process itself or with the aid of external equipment. Stirring speed is a critical parameter in EC procedures because it enhances the mass transfer kinetics processes by increasing the mobility of the ions in the solution. The faster the mixing speed, the faster the particles smash and the more metal ions and hydroxyl groups are released. The generation of metal hydroxides and flocs is influenced by the mixing speed [30]. To determine the ideal speed for removing cadmium using the EC method, the impact of stirring speed was examined while the reaction cell was being stirred at 50–350 rpm. The maximum removal efficiency was achieved at 300 rpm, as seen in Figure, 6. It is important to note that a bigger percentage of pollutants are removed when the stirring speed is increased. This is brought on by the quick hydrolysis of water, which produces Al $(OH)_3$, an adsorbent that may absorb cadmium ions.

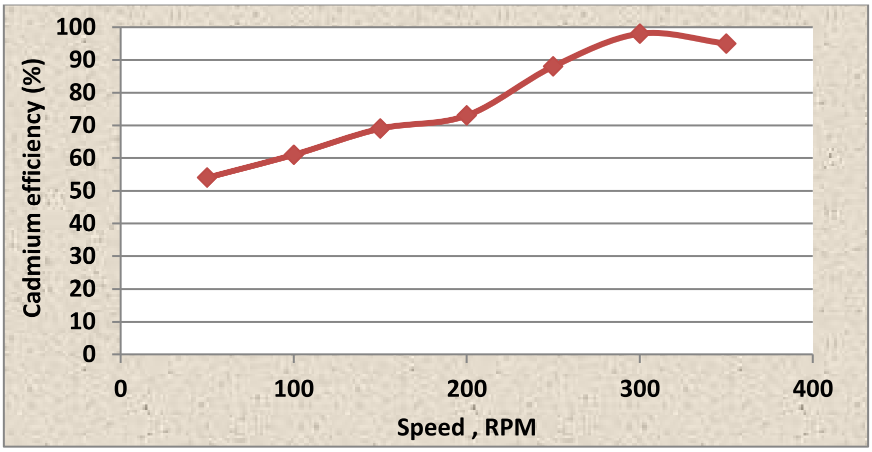

Fig. 6: Effect of stirring speed.

Effect of Electrolysis time

The electrolysis time also affects how well pollutants are removed. When the anode dissolves, metal hydroxides are produced, and the efficacy of pollutant removal also depends on the electrolysis time. The efficacy of pollutant removal increases as the electrolysis time increases, but once the ideal electrolysis time has been reached, the efficacy of pollutant removal stays constant and does not increase with the electrolysis time. The quantity of metal hydroxides produced increases with longer electrolysis times and steady current densities. A longer electrolysis time increases the development of flocs, which in turn increases the effectiveness of pollution removal. Since there are enough flocs available for pollutant removal, the efficacy of pollutant removal does not increase when the electrolysis time is longer than ideal [31]. It should be mentioned that longer electrolysis times result in higher energy and electrode material consumption, which raises process costs [32]. For effective treatment at the lowest feasible cost, a reaction time value must be selected. A 70-minute reaction time is a fair compromise for this study because higher values only result in energy consumption. The findings were displayed in Fig. 7. So, 70 minutes of treatment is vital to produce a reasonable amount of Al^{3+} ions. As demonstrated in Figure, 7. the maximum value of clearance rate of cadmium obtained at 70 minutes.

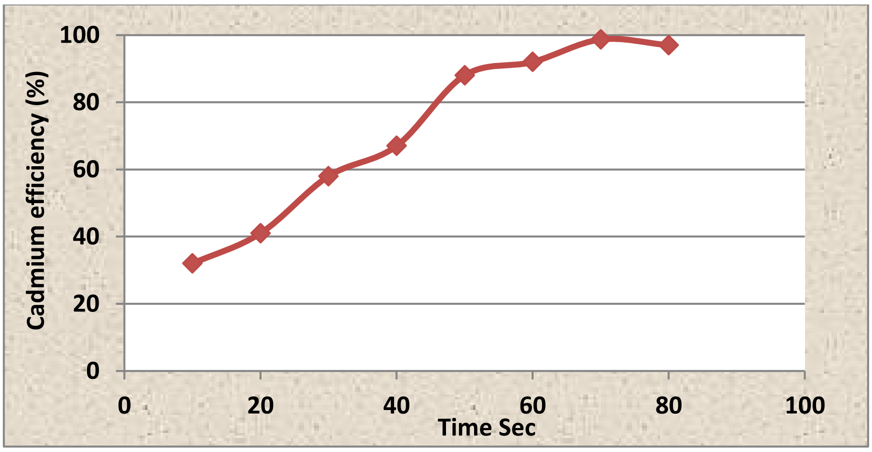

Fig. 7: Effect of reaction time:

Conclusions

The electrochemical method known as EC is highly effective in removing pollutants and has a broad variety of uses. It is frequently applied to the treatment of industrial effluent. In the current paper, cadmium removal from wastewater by electrocoagulation, Electrocoagulation was performed with the help of electrocoagulation reactor which is assembling of 6 electrodes (aluminum and stainless steel). The findings indicate that a rise in current, applied voltage, mixing speed, increasing the concentration of NaCl can improve the removal efficiency of cadmium. The optimum value of pH 7.5, allowing high removal rates of cadmium. The highest removal efficiency was achieved (98.7%). According to the study's findings, electrocoagulation appears to be a highly effective technique for decontaminating wastewater that contains cadmium.

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إزالة الكادميوم عن طريق التخثر الكهربائي من مياه الصرف الصناعي لمصافي النفط

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الخلاصة:

الهدف الأساسي لهذه الدراسة هو النظر في إمكانية إزالة الكادميوم من مياه الصرف الصحي لشركة مصافي الشمال (بيجي)، قبل تصريفها في البيئات المفتوحة. إن وجود المعادن الثقيلة البيئية مثل الكادميوم ضار بالكائنات الحية. الإجراء الكيميائي المستخدم لإزالة المعادن الثقيلة من مياه الصرف الصحي يسمى التخثر الكهربائي. يتم استخدام أنود الألومنيوم وكاثود الفولاذ المقاوم للصدأ في (EC). الاستخدام الأساسي لهذه الطريقة هو مع النفايات الصناعية. حيث يتم أكسدة الأنود المضحي كهربائيًا لإنشاء المواد المسببة للتخثر في الموقع. أصبحت هذه الطريقة أكثر شيوعًا في عملية معالجة المياه ومياه الصرف الصحي بسبب قدرتها على التكيف والود البيئي والقدرة على توفير كفاءة عالية للعملية بأقل تكاليف تشغيل. العديد من معلمات العمل، لتحقيق قدرة إزالة أعلى. بجهد 20. الوقت الأمثل للتخثر الكهربائي 70 دقيقة، درجة الحموضة الأولية 7.5، التيار الكهربائي 2.5 أمبير، وسرعة الخلط 300 دورة في الدقيقة، تركيز كلوريد الصوديوم 1.5 جم لتر$^{-1}$. في ظل الظروف المثلى المحددة، ينتج فعّالاً للغاية (98.7%) وجد أن الطريقة فعالة للغاية وسريعة نسبيًا مقارنة بالطرق التقليدية.