

Kinetics and Performance of Phosphate Removal from Hot Industrial Effluents Using a Continuous Flow Electrocoagulation Reactor

A.H. El-Shazly*, M.A. Daous

Chemical and Materials Engineering Department, Faculty of Engineering, King Abdulaziz University, Jeddah, Saudi Arabia

*E-mail: elshazly_a@yahoo.com

Received: 5 November 2012 / Accepted: 11 December 2012 / Published: 1 January 2013

This work investigates the reaction kinetics of phosphate removal from hot industrial effluent streams in a continuous-recirculating electrocoagulation reactor using monopolar aluminum electrodes. The effects of several variables on the unit performance were also investigated. Results show that the rate of phosphate removal follows a first order reaction kinetics and that the percent of phosphate removal increases by increasing the solution circulation flow rate, increasing current density, and the solution temperature while it was found to decrease by increasing the initial phosphate ions concentration. Data generated in this study allow for a thorough analysis of the electrocoagulation reaction kinetics, the reaction activation energy, and the reaction rate controlling mechanism as well as the effects of several important parameters on the reactor's performance and the phosphate removal process economic viability.

Keywords: Electrocoagulation, phosphate removal, flow systems, waste treatment

1. INTRODUCTION

The presence of excess phosphorus and/or nitrogen in wastewater causes a well known phenomenon called eutrophication, which is oxygen depletion in water as a result of growth of algae due to the presence of higher nutrient concentrations [1]. The usual forms of phosphorus found in solutions include orthophosphate, polyphosphate, and organic phosphate [2]. The principal phosphorus compounds in wastewater are generally orthophosphate forms together with smaller amounts of organic phosphate [3]. These phosphorus compounds, dissolved in surface or ground waters, are responsible for eutrophication in closed water systems, especially in lakes and enclosed bays where water is almost stagnant [4].

Current employed phosphorus removal techniques include chemical treatments such as adsorption, chemical precipitation, ion exchange, and electrodialysis, hybrid systems based on fly-ash adsorption and membrane filtration, and electrocoagulation [5-8]. Among these methods, adsorption, and chemical precipitation are the most widely used for phosphate removal [5–11]. Phosphate removal from aqueous streams is based on the conversion of soluble phosphate to an insoluble solid phase, which can be separated from water by means of sedimentation or filtration. In wastewater applications, the most common and successful methods to precipitate phosphate involve the use of dissolved cations, such as Al^{3+} , Ca^{2+} , Fe^{3+} and to a lesser extent Fe^{2+} . It was found that when iron and aluminum are present in water, FePO_4 and AlPO_4 form at a low pH range below 6.5, while at a higher pH range (above 6.5) iron and aluminum increasingly convert to oxides and hydroxides. However, precipitation of phosphate with calcium as apatites and hydroxyapatites at higher pH is more ideal for phosphate removal [3].

Wastewater treatment using electrochemical technologies have gained prominence during the past two decades. It has found industrial applications for water treatment and metal recovery from wastewaters resulting from various industries, such as tannery, electroplating, dairy, textile processing, oil, and oil refineries. In certain wastewater treatment applications, such as those involving refractory pollutants, electrochemical technologies may become the best wastewaters treatment choice [12-16].

Various types of reactors have found applications in electrochemical wastewater treatment processes. These include basic reactors, such as tank cells, plate and frame cells, and rotating cells, as well as, complicated three-dimensional reactor systems like fluidized bed, packed bed cell, or porous carbon packing cells [17, 18]. In order to enhance mass transfer from the bulk to the electrode surface and also to remove the deposited metal powders from the cathode, a rotating cathode cell was designed and employed [19, 20]. A pump cell is another variant of a rotating cathode cell, which uses a static anode and a rotating disk cathode with a narrow spacing between the electrodes that allow the entrance of the effluent stream. Dissolved metals are electrically collected and scraped as powders [21-23].

The present work provides a thorough analysis and discussion of reaction kinetics, reaction activation energy, and reaction rate controlling mechanism of phosphate removal from hot industrial effluent streams in a continuous-recirculation electrocoagulation reactor. The effect of several important parameters on reactor's performance and the phosphate-removal process is discussed as well.

2. MATERIALS AND METHODS

The experimental setup and electrical circuit used in this study is shown in figure (1). It consists of a cylindrical plexiglas column of 15-cm diameter and 60-cm height fitted at the bottom with a perforated disc for solution flow distribution. A 0.33 hp centrifugal pump was used to circulate test solution between a plastic recirculation tank and column through the perforated disc. Solution flow rates through the column was controlled by two parallel check valves and measured by a calibrated Rota-meter. Two monopolar aluminum electrodes (cathode and anode) were placed vertically inside

the Plexiglas column. These were consisting of a 3-cm diameter anode placed at the center of the column, and a hollow 0.1 cm thick cylinder lining the inner wall of the column as a cathode.

Before each run, the aluminum electrodes were immersed in dilute carbon tetrachloride solution for few minutes to remove any residual greases or surface oxides, washed with distilled water, and placed in their proper place in the column and connected to a potentiostat/galvanostat (Autolab 263A). A multirange ammeter was connected in series with the cell, while a D.C. voltmeter was connected in parallel to measure its voltage. In each run, 15 liter of potassium di-hydrogen phosphate (KH_2PO_4) with various initial concentrations ranging from 25 to 100 ppm were placed in the recirculation tank and mixed with 3.5 wt. % sodium chloride (constant concentration was used in all experiments). Test solution was then fed into the electrocoagulation unit and circulated at different flow rates ranging from 2 to 3.5 liter/min for different time interval ranging from 10 to 60 minutes. The phosphate concentration at any time was found by withdrawing 10 ml of phosphate solution from the circulating solution each 10 minutes and measured using U.V. Spectrophotometer (UV-1800 SHIMADZU), at a wave length (λ) of 885-nm. The percentage phosphate removal was then evaluated by the following equation:

$$\% \text{ phosphate removal} = 100(C_0 - C)/C_0 \quad (1)$$

Where C_0 is the initial phosphate concentration and C is its concentration at the end of electrolysis time.

The effects of various variables on phosphate removal from simulated wastewater solutions were investigated. These included solution flow rate, initial phosphate concentration, which ranged from 25 to 100 ppm, applied current density, and solution temperature. In addition the kinetics of the process was investigated under different operating conditions.

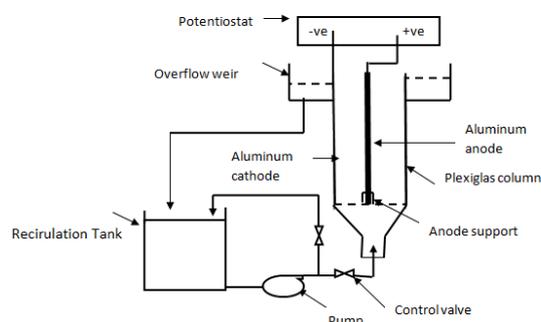


Figure 1. experimental setup

3. RESULTS AND DISCUSSIONS

3.1. Effect of applied current density

As shown in figure (2), the percentage of phosphate removal increases by increasing the applied current density within the range from 1 to 4 mA/cm^2 . These results can be explained by the

fact that, increasing current density would increase the dissolution rate of aluminum electrode according to Faraday's law [24] with the formation of Al^{+3} and hence the formation of $\text{Al}(\text{OH})_3$ coagulant according to the following reactions:



The overall reaction:



Higher rate of freshly formed amorphous $\text{Al}(\text{OH})_3$ have large surface area on which rapid adsorption of soluble phosphate and trapping of colloidal particles take place with a consequent removal of phosphates from wastewater. The upward liquid flow through the reactor continuously stirs the vicinities of the anode and cathode producing an improved mass transfer conditions inside the electrocoagulation reactor and a consequent decrease in the concentration polarization and in the anode tendency to passivate especially at higher applied currents.

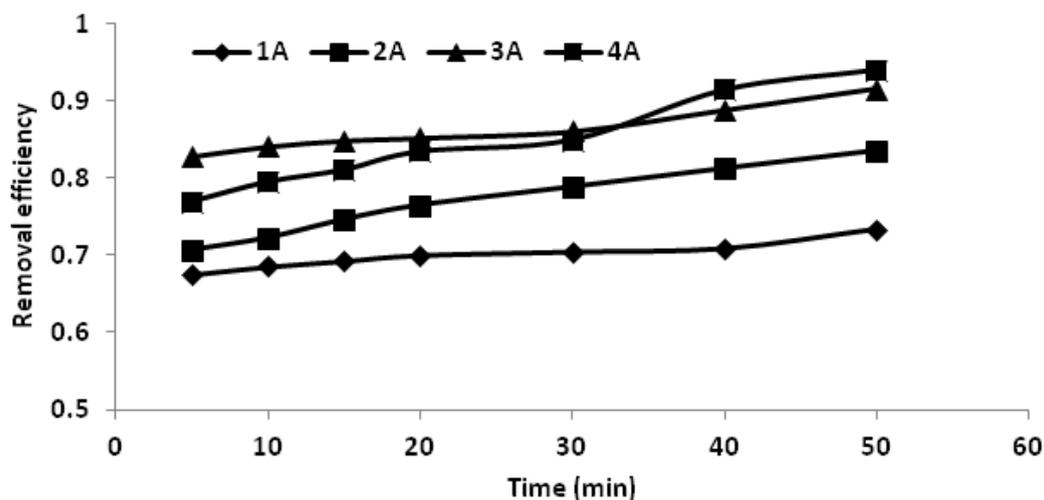


Figure 2. Removal efficiency vs time at different current density.

3.2. Effect of initial phosphate concentration.

As shown in figure (3), the removal efficiency of phosphate ions decreases by increasing initial phosphate concentration within the concentration range tested. this can be attributed to the fact that increasing phosphate concentration would increase concentration polarization via adsorption on the

anode and cathode with a consequent decrease in the rate of aluminum dissolution at the anode and hydrogen evolution at the cathode. Moreover, higher phosphates concentrations would rapidly block adsorption sites of $\text{Al}(\text{OH})_3$ and decrease its ability to adsorb more phosphate compounds[25].

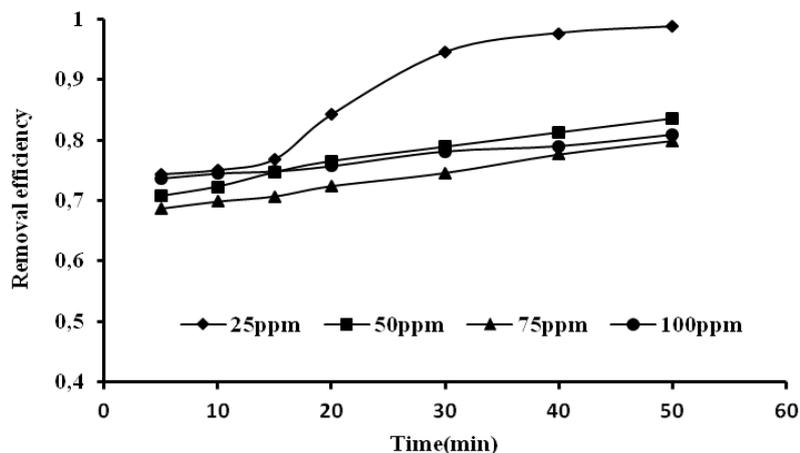


Figure 3. Removal efficiency vs. time at different initial phosphate concentration

3.3. Effect of solution flow rate

Figure (4) shows that the phosphate removal efficiency increases by increasing the solution flow rate, which can be attributed to the fact that increasing solution flow rate would improve mixing conditions in the reactor, which allows for a rapid mixing of freshly formed Al^{+3} at the aluminum electrode into the solution bulk. Moving Al^{+3} ions away from the anode surface prevents anodic polarization and improves dissolution of the anode. In addition, turbulence generated by the rising solution flow enhances the rate of mass transfer at the anode and cathode with a consequent decrease in concentration polarization which tends to slow down the rate of cathodic and anodic reactions and may lead to the anode passivation especially at high current densities.

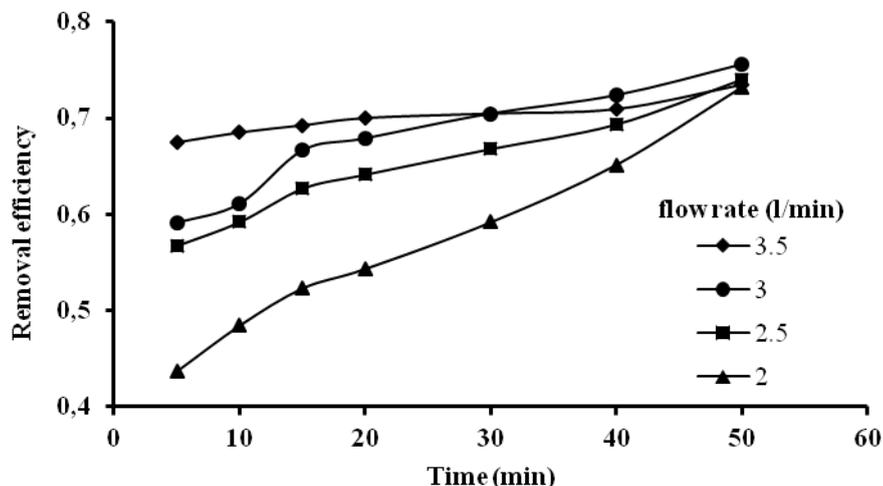
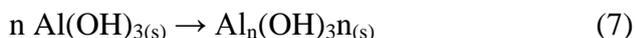


Figure 4. Removal efficiency vs. time at different solution flow rate

3.4. Effect of initial pH

It has to be mentioned that, depending on the pH of the aqueous medium other ionic species, such as dissolved $Al(OH)^{2+}$ and $Al_2(OH)_2^{4+}$ hydroxo complexes may also be present in the system. Anodic metal ions and hydroxide ions generated at the electrode surfaces react in the bulk wastewater to form various hydroxides and build up polymers [26]:



The suspended aluminum hydroxides can remove phosphates from the solution by sorption, co-precipitation or electrostatic attraction, followed by coagulation [27]. Figure (5) shows that the % removal efficiency increased by increasing initial solution pH up to 7, which can be ascribed to the fact that, increasing the solution pH can destroy the passive aluminum oxide layer that is formed at lower pH[28]. The above results are in agreement with the findings of Bektas et al [25] and Vasudevan et al[29] who reported that phosphate removal reached to its maximum values at initial pH 7 and pH 6 respectively

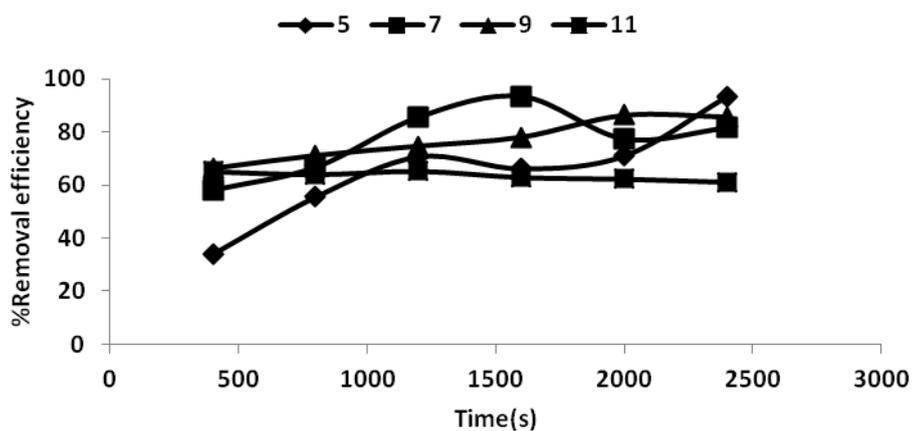


Figure 5. % Removal efficiency vs time at different solution pH

3.5. Effect of solution temperature

Figure 6 depicts the effect of solution temperature on the electrocoagulation reactor performance. Test results show that removal of phosphate ion increases by increasing solution temperature up to 60°C. A further increase in the solution temperature was found to decrease the removal efficiency of phosphate ions. These findings can be explained by the fact that increasing solution temperature can improve ions transfer from the anode and/or cathode surface to the solution bulk resulting from the decrease in solution viscosity and the consequent increase in the ions diffusivity according to Stocks equation $D\mu/T=\text{constant}$, where D , μ and T are ions diffusivity, solution

viscosity and solution temperature, respectively. The decrease in phosphate removal efficiency occurring at solution temperatures above 60°C is explained by the fact that higher solution temperatures also enhance the aluminum anode and cathode passivation by the formation of protective aluminum oxide layers, which decreases Al³⁺ ions dissolution and consequently the electrocoagulation reactor performance.

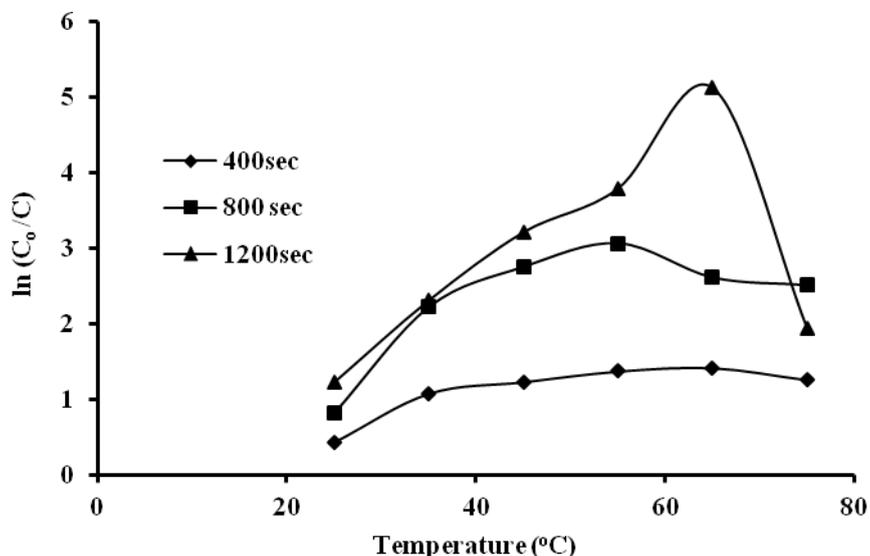


Figure 6. ln(C₀/C) vs. solution temperature at different electrocoagulation times

3.6. Kinetics analysis of phosphate removal by electrocoagulation

The kinetics of phosphate removal by electrocoagulation has been successfully described by the following first order rate equation [26]:

$$-V \left(\frac{dC}{dt} \right) = KAC \tag{8}$$

This upon integration yields:

$$V \ln \left(\frac{C_0}{C_t} \right) = KAt \tag{9}$$

Where V is the solution volume, C₀ and C_t are phosphate ions initial concentration and concentration at any time t, respectively, while K is the mass transfer coefficient and A is the anode surface area. Thus, the mass transfer coefficient K can be obtained from the slope of a plot of ln (C₀/C_t) versus t

Figure 7 shows that the electrocoagulation reaction kinetic data obtained in this study is well fitted by the first order rate equation given above and the calculated mass transfer coefficient increases with temperature within the reaction temperature range reported.

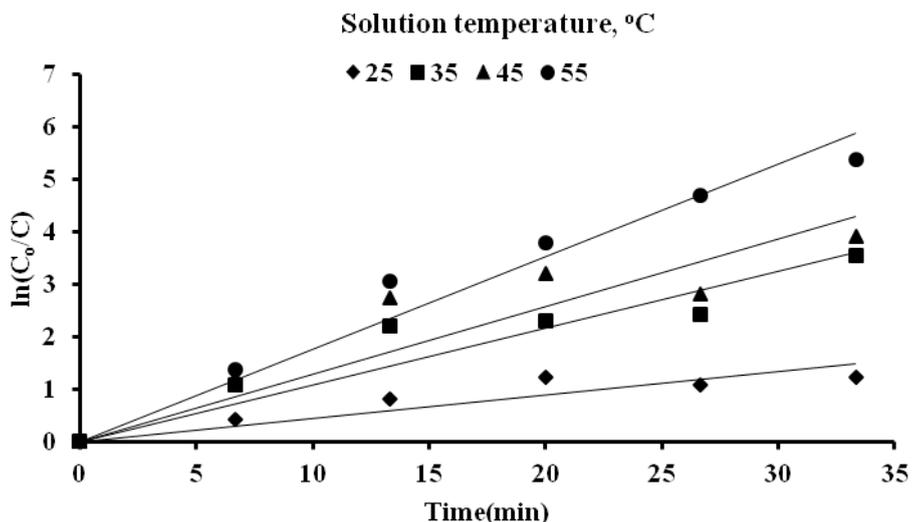


Figure 7. $\ln(C_0/C)$ vs. time at different solution temperature

The reaction activation energy was calculated using Arrhenius equation:

$$K = A_0 e^{-E/RT} \tag{10}$$

Where A_0 is Arrhenius constant, R is the universal gas constant, T is the reaction absolute temperature, and E is the reaction activation energy. Figure 7 shows that the temperature effect on the rate of electrocoagulation process is well described by Arrhenius equation. Moreover, data of figure 8 show that the activation energy of the process is about 20.95 kJ/mol, which confirms that the reaction is diffusion controlled and an increase in solution flow rate through the reactor would indeed improve the electrocoagulation reactor performance.

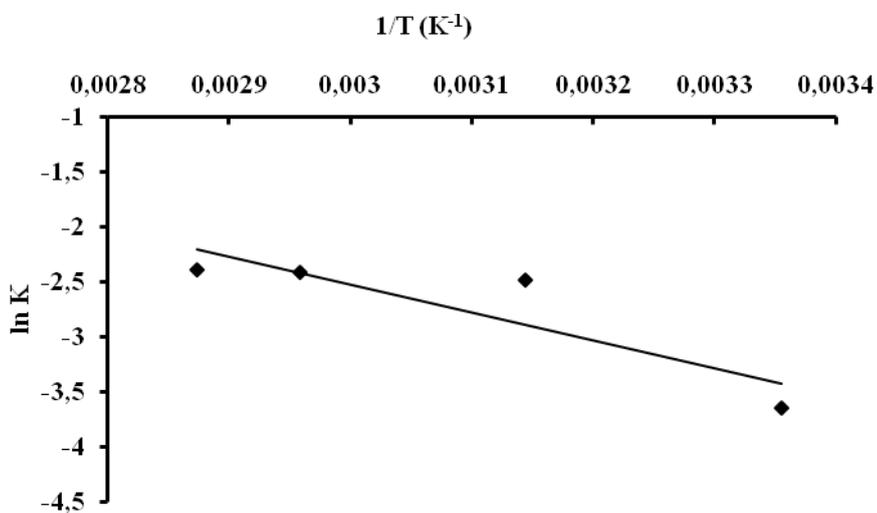


Figure 8. $\ln K$ vs $1/T$

3.7. Electric power consumption

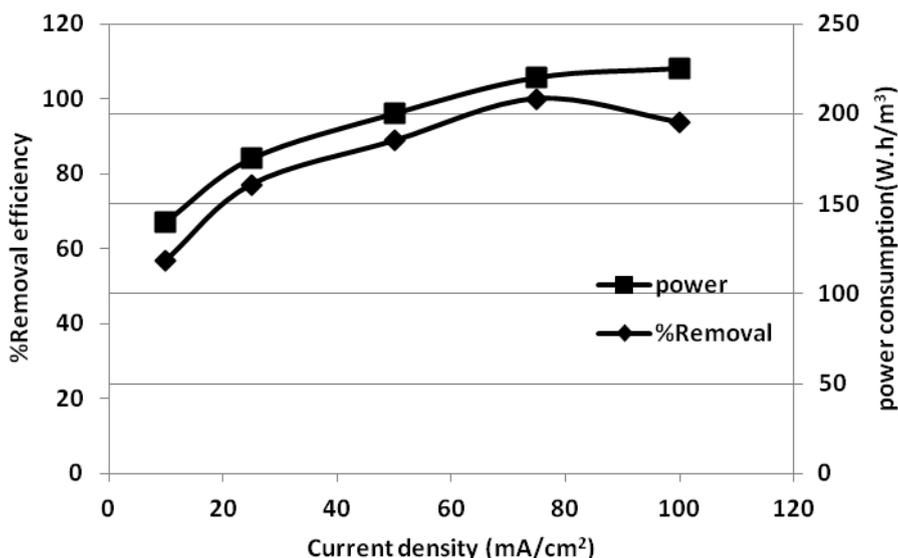


Figure 9. Effect of current density on both percentage removal efficiency and power consumption.

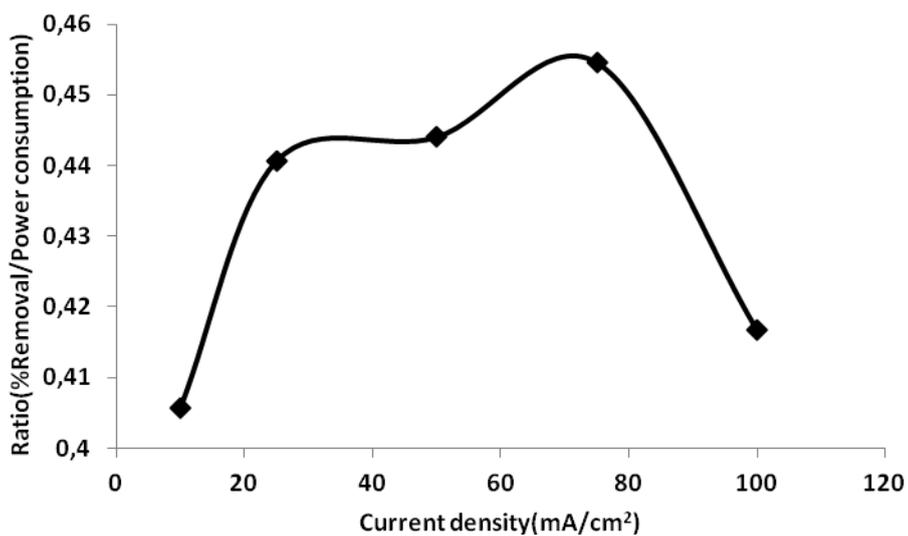


Figure 10. Effect of current density on the Ratio (% Removal efficiency/power consumption).

The electric power consumption of the process was calculated per m³ of the waste solution using the equation that [30,31]:

$$P = EIt/V$$

Where P is the specific power consumption (W.h/m³). E is the cell voltage in volt (V), I is the current in ampere (A), t is the time of electrocoagulation in hour (h) and V is the solution volume in

cubicmeter (m³). The time of operation was fixed at 60 min. As shown in figure (9), it is clear that increasing the current density will increase both power consumption and percentage removal efficiency. The increase in power consumption can be ascribed to the increased polarization on the two electrodes by increasing the current density [31].

To throw some light on the role of current density in the economy of the process the ratio (% removal efficiency/power consumption) was plotted versus current density as shown in figure (10), the results show that the ratio increased by increasing the current density from 10 to 90 mA/m² and then decreased dramatically by increasing the current density above this range, which suggests that the economy of the process is favored at certain range.

4. CONCLUSIONS

This work investigates the performance of an electrocoagulation reactor for the removal of phosphate ions from wastewater using forced circulation flow. Experimental results show that the electrocoagulation process can be described by a first order rate equation and further shows that the process activation energy is about 5.004 kCal/mol, which indicates that this reaction is diffusion controlled. This outcome is further confirmed by the observed improved reactor performance in phosphate ion removal through increased solution circulation flow rate. Experimental results further show that phosphate removal efficiency is enhanced by increasing current density and by decreasing initial phosphate concentration. An increase in reaction temperature up to a moderate value of 60°C was found to improve the reactor performance. However, a further increase in reaction temperature beyond this value results into a decrease in reactor performance.

ACKNOWLEDGEMENT

This work was funded by the Deanship of Scientific Research of King Abdulaziz University, Jeddah, Saudi Arabia under grant No. (351-135-1431).

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