Int. J. Electrochem. Sci., 8 **(2013)** 3176 - 3185

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Kinetics and Performance Analysis of Batch Electrocoagulation Unit Used for the Removal of a Mixture of Phosphate and Nitrate Ions from Industrial Effluents

A.H. El-Shazly[*] *, A.A. Al-Zahrani and Y.A. Alhamed*

Chemical and Materials Engineering Department, Faculty of Engineering, King Abdulaziz University, Jeddah, Saudi Arabia
[*]E-mail: elshazly_a@yahoo.com

Received: 12 December 2012 / *Accepted:* 19 January 2013 / *Published:* 1 March 2013

This work investigates the performance of batch electrocoagulation reactor for the removal of a mixture of phosphate and nitrate ions from wastewater. Experimental results show that phosphate and nitrate removal efficiency was improved by increasing both current density and initial solution pH while it was decreasing by increasing initial phosphate and/or nitrate concentrations. Experimental results further show that the electrocoagulation process can be described by a first order rate equation for the removal of both phosphate and nitrae. A correlations for the effect of initial phosphate concentration, nitrate concentration and current density were deduced and an overall correllation for the unit performance under different operating parameters in the form: $K = 0.033\ C_N^{-0.247}\ C_P^{-0.147}\ I^{0.206}$ was deduced. This equation can be used for the preliminary design of an electrocoagulation unit used for phosphate and nitrate mixture removal from wastewater.

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

1. INTRODUCTION

The presence of excess phosphates and/or nitrate 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]. Nitrate is a stable and highly soluble ion with low potential for co-precipitation or adsorption. These properties make it difficult to be removed from water. Therefore, treatment for nitrate is typically very complicated and expensive. Existing methods of removing nitrate from wastewater include ion exchange, biological decomposition, chemical treatment, reverse osmosis, electrodialysis and catalytic denitrification. Although Ion exchange is very efficient process, it is fairly high in capital and operating costs, with undesirable high residual constituents such as chlorides and bicarbonates in the treated water, which must be removed prior to consumption[2-4]. Another method, is biological decomposition, which is a stable and extremely effective process in reducing nitrate by nearly 100% without using any chemicals. Unfortunately, this process is generally time consuming, limited in temperature ranges, very costly and requires extensive maintenance. Therefore, it is utilized in most cases only for treating waste water for which the original nitrate concentration is sufficiently high [5].

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 [6-9]. Among these methods, adsorption, and chemical precipitation are the most widely used for phosphate removal [6-12]. 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 [13].

During the past two decades Wastewater treatment using electrochemical technologies have gained prominence. It has found industrial applications for water treatment and metal recovery from wastewaters resulting from various industries, such as tannery, electroplating, diary, 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 [14-18].
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 [19, 20]. 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 [21,22]. 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 [23-25]. Treatment of solutions containing both anions has received some attention by Mahvi etal.[26] to evaluate the performance of the continuous, combinative bipolar electrocoagulation-electrooxidation combined with electroflotation (ECEO–EF) reactor developed for the removal of phosphate and ammonia under different operational conditions of pH, voltage (V), and detention time.

The present work investigates the performance of a simple electrocoagulation unit using a vertical monopolar aluminum electrodes for the treatment of wastewater containing a mixture of phosphates and nitrate ions simultaneously under different conditions of operating parameters and provides a thorough analysis and discussion of reaction kinetics under these conditions.

2. EXPERIMENTAL

The experimental setup and electrical circuit used are shown in figure (1), the setup consisted of 1000 ml cylindrical glass container of 10 cm diameter and 15 cm height, two monopolar aluminum electrodes (cathode and anode) were placed vertically, with the anode at the center of the reactor parallel to the cathode to the wall of the cell. The cathode and anode diameters are 10 and 1.2 cm respectively. Before each run aluminum electrodes were immersed in diluted carbon tetrachloride solution for few minutes for removing greases, washed with distilled water, and finally connected to a D.C. power supply (15 volts, 10 A) fitted with a voltage regulator. A multirange ammeter was connected in series with the cell and a D.C. voltmeter was connected in parallel with the cell to measure its voltage. In each run 500 ml of synthetic solution of potassium nitrate (KNO_3) and potassium di-hydrogen phosphate (KH_2PO_4) with various initial concentrations was used, the initial concentration of phosphate was kept constant at 25 ppm while nitrate concentration was changed from 25 to 100 ppm, the solution also contains a constant concentration of 3.5% sodium chloride were placed at the electrolytic cell.

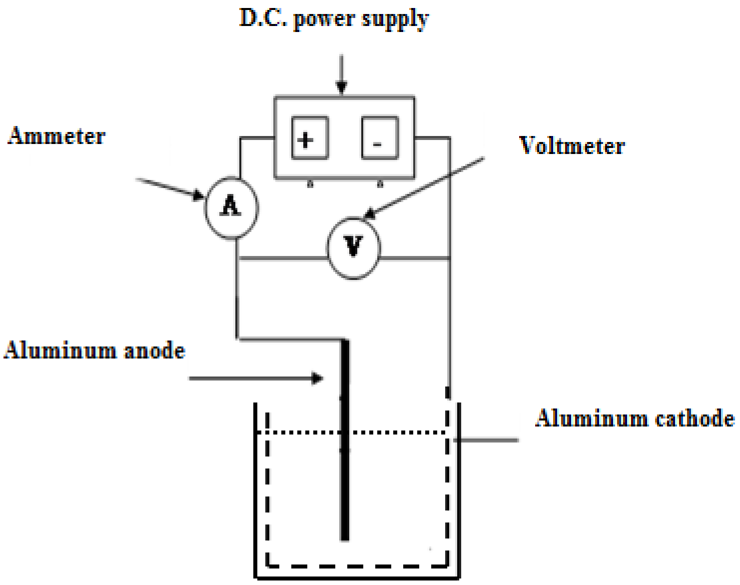

Figure 1. Experimental setup

Nitrate and phosphate concentrations for the fresh and treated solution were measured before and after each run by using a U.V. Spectrophotometer (UV-1800 SHIMADZU), 10 ml samples were drawn at different time intervals, diluted to 50 ml with distilled water, filtered to remove any possible interference from suspended particles, then acidified with 1 ml 1N HCl to prevent interference from hydroxides[27]. A calibration curve was prepared for the phosphate and nitrate within the concentration range used, a wave length (λ) of 885 and 220-nm were used for finding out the phosphates and nitrates concentrations respectively. Many variables were investigated for its effect on the removal efficiency of the both nitrate and phosphate such as, electrolysis time that ranged from 400 to 2400 seconds, the ratio between nitrate and phosphate concentration (N/P) that ranged from 1 to 4, current density ranged from 0.78 to 2.34 mA/cm^2, solution pH in the range from 3 to 9. The percentages phosphate or nitrate removals were then evaluated by the following equation:

$$\% \text{ removal} = 100(C_o - C)/C_o \qquad (1)$$

Where C_o is the initial phosphate or nitrate concentrations and C is its concentration at the end of electrolysis time.

3. RESULTS AND DISCUSSION

3.1. Effect of current density

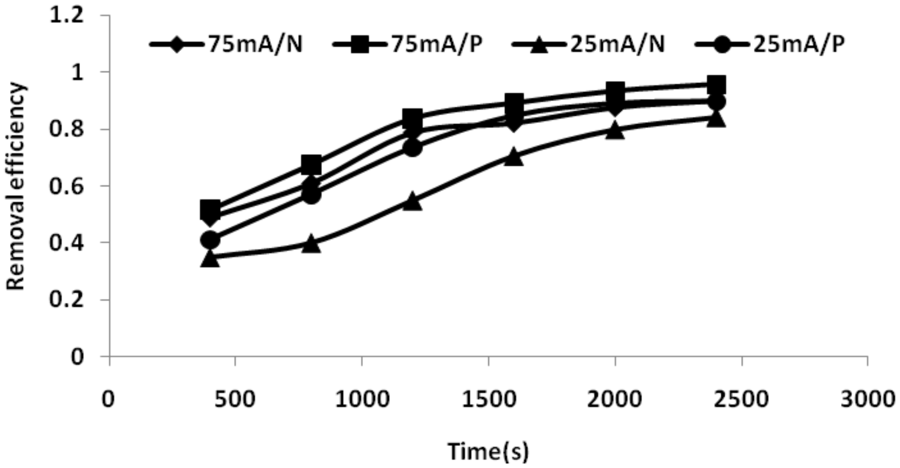

Figure 2. Removal efficiency vs time for different current density for both nitrate and phosphate ions.

As shown in figure (2), the removal efficiency of both nitrate (N) and phosphate (P) increased by increasing the applied current within the range from 25 to 75 mA (current density from 0.78 to 2.34 mA/cm^2). These results can be attributed to the fact that, according to Faraday's law, increasing the current density will increase the dissolution rate of aluminum electrode with the formation Al^{+3} and hence the formation of $Al(OH)_3$ coagulant according to the following reactions:

Anode: $2Al \rightarrow 2\,Al^{3+} + 6e$ (2)

Cathode: $6H_2O + 6e \rightarrow 3H_2 + 6OH^-$ (3)

$2\,Al^{3+} + 6OH^- \rightarrow 2Al(OH)_3$ (4)

The overall:

$AL + 3H_2O \rightarrow AL(OH)_3 + 3/2\,H_2$ (5)

Higher rate of freshly formed amorphous $Al(OH)_3$ have large surface area on which rapid adsorption of soluble nitrates and/or phosphates and trapping of colloidal particles take place with a consequent removal of nitrates and/or phosphates from wastewater. In addition the cathodically evolved H_2 bubbles float $Al(OH)_3$ along with the adsorbed N and P compounds to the upper surface of the solution. Besides, the evolving H_2 bubbles entrain solution in their wake decreases the anode concentration polarization and the anode tendency to passivate. The results as shown in figure 2 shows that for the same range of current density the removal of phosphate ions is predominant to nitrate ions and that removal of 90 to 95% of phosphate and that from 84 to 90% of nitrate can be removed depending on current density for the same time interval.

3.2. Effect of the ratio (N/P) in the feed solution

As shown in figure 3 the results show that the removal efficiency decreased by increasing the ratio (N/P) within the range from 1 to 4. This can be ascribed to the fact that, increasing N and P ions concentrations would probably increase activation 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. In addition higher concentrations of these ions will block adsorption sites of $Al(OH)_3$ rapidly and decrease its ability to adsorb more dissolved compound. It has to be clarified that the rate of N and/or P ions removal increased rapidly within the first 800s while decreased for longer time intervals which can be ascribed to the fact that at start time the freshly formed $Al(OH)_3$ will have large surface area that can remove higher amounts of N and P, increasing the time these adsorption sites will be blocked partially and the available adsorption sites will be limited and that will certainly reduce that removal rate of dissolved ions.

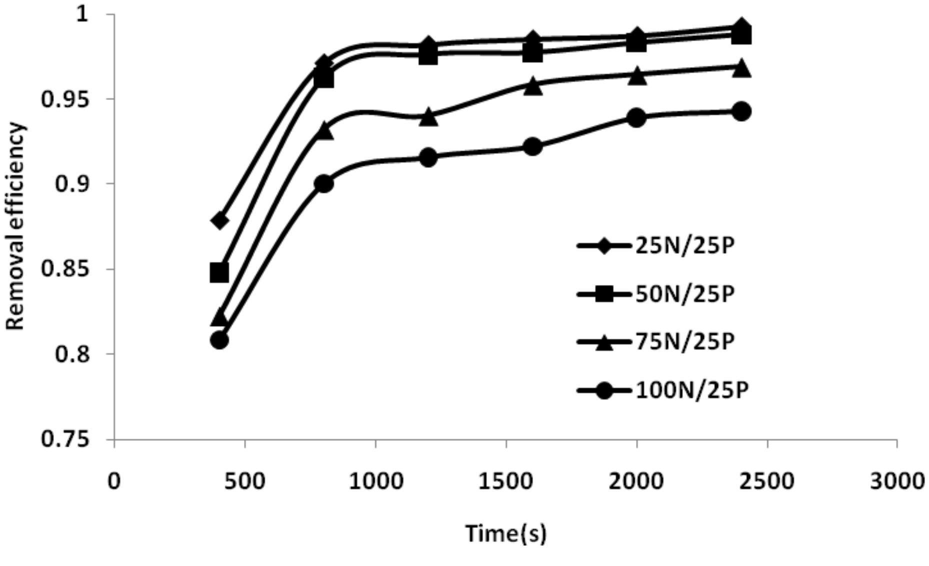

Figure 3. Removal efficiency vs time for different (N/P) ratio.

3.3. Effect of initial solution pH

Usually pH is considered as an effective factor on the performance of electrocoagulation process. As shown in figure 4 the phosphate and nitrate removal efficiency increased by increasing initial solution pH up to 7. This can be attributed to the reaction between dissolved aluminum ions and hydroxide ions to form the amorphous $Al(OH)_3$ the adsorbent of dissolved phosphate and nitrate ions. The results of this study have been confirmed by Koparal and Ogutveren [28] on the removal of nitrate from water by electroreduction and electrocoagulation. It has to be clarified that phosphate removal has been decreased by increasing initial solution pH above 7 which may be attributed to that at higher pH, the oxide surface will have a net negative charge and would tend to repulse the anionic phosphate and nitrate in the solution[29-31].

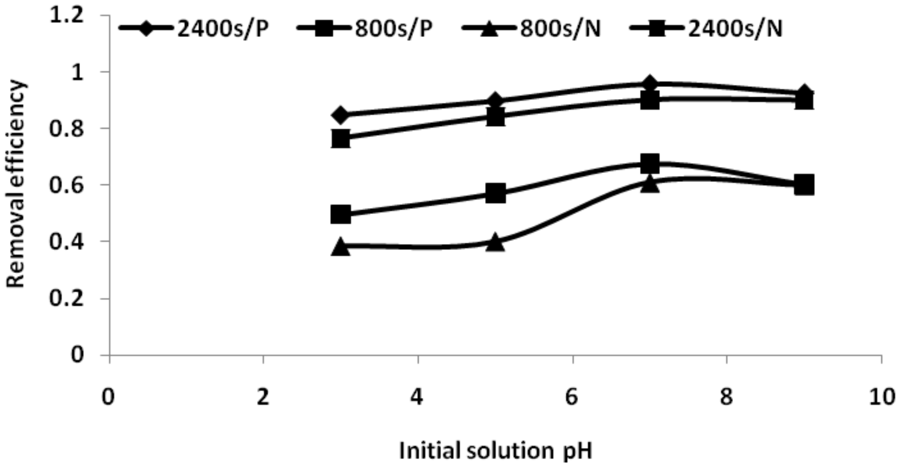

Figure 4. Removal efficiency of nitrate and phosphate vs initial solution pH at different time of electrocoagulation.

3.4. Kinetics analysis of phosphate removal by electrocoagulation

The kinetics of phosphate and nitrate removal by electrocoagulation has been successfully described by the following first order rate equation [30]:

$$-V\left(\frac{dC}{dt}\right) = KAC \qquad (6)$$

This upon integration yields:

$$V\ln\left(\frac{C_o}{C_t}\right) = KAt \qquad (7)$$

Where V is the solution volume, C_o and C_t are initial concentration of phosphate or nitrate ions and their concentrations 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 $\ln\left(\frac{C_o}{C_t}\right)$ versus t. Figures 5 and 6 show that the electrocoagulation reaction kinetics data obtained for both nitrate and phosphate ions removals are well fitted by the first order rate equation given above and the calculated mass transfer coefficients decrease by increasing the initial concentrations of both phosphates and nitrates.

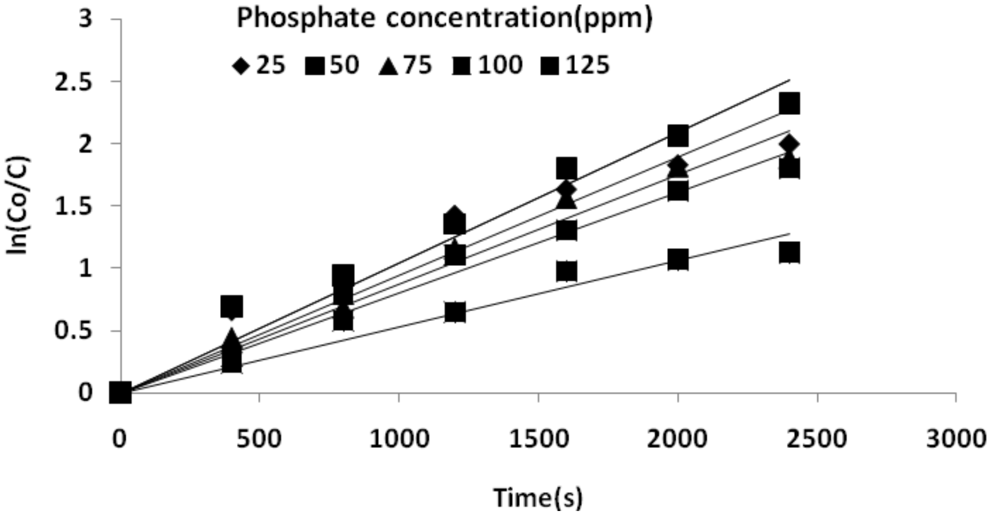

Figure 5. ln(Co/C) vs t at different initial phosphate concentration.

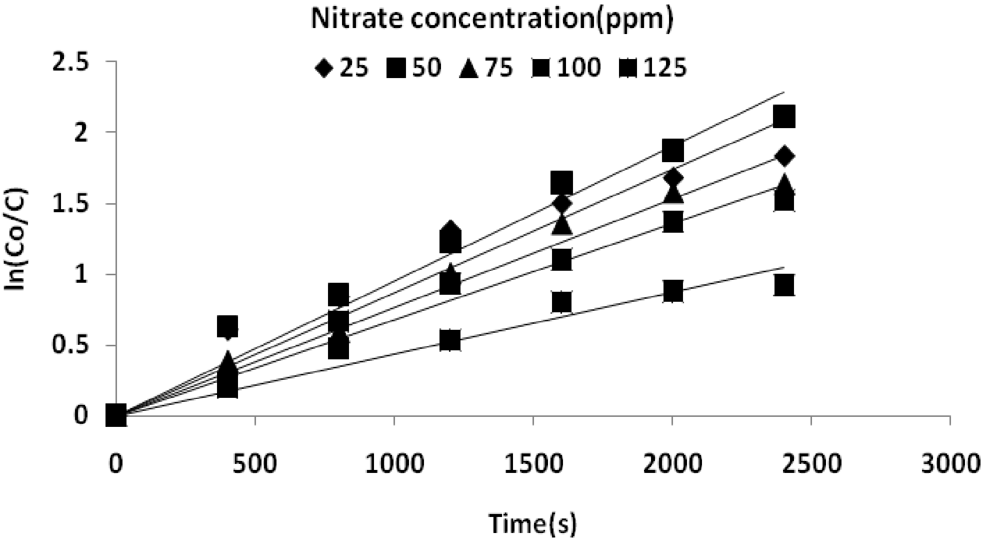

Figure 6. ln(Co/C) vs t at different initial nitrate concentration.

For modeling of the relation correlating the mass transfer coefficients with concentrations of both phosphate and nitrate a relation in the form $K=\alpha\ C^{\gamma}$ was considered. Figure 7 shows a relation between lnK versus lnC for finding out the values of α and γ for both nitrate and phosphate. The results show that a relations in the form that:

$$K= 0.044C_N^{-0.247} \tag{8}$$

$$K= 0.032C_P^{-0.147} \tag{9}$$

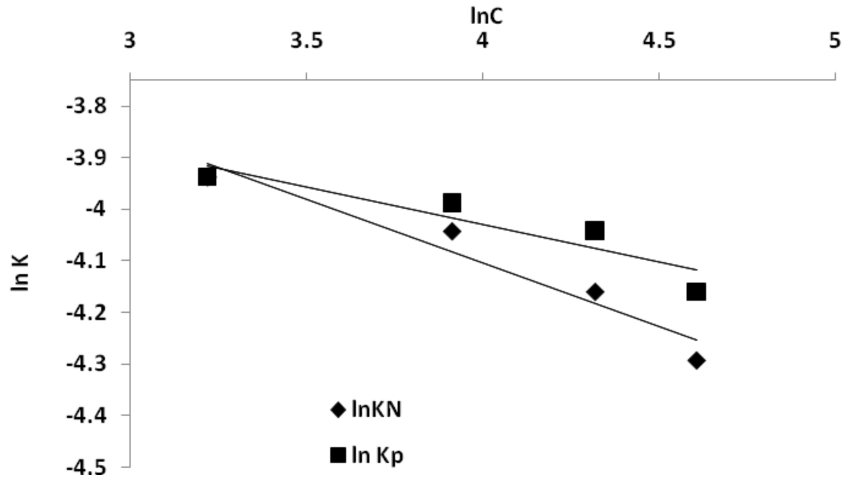

Figure 7. Relation between lnK versus lnC for nitrate and phosphate.

The above equations 8 and 9 show that the mass transfer coefficient for phosphate removal is higher than that for nitrates one.

Same equation can be deduced for effect of current on the mass transfer coefficient figure 8 shows that the relation between K and I can be in the form that:

$$K=0.109\ I^{0.206} \qquad (10)$$

An overall correlation for the effect of different parameters C_N, C_P and I on K was deduced by plotting K versus $C_N^{-0.247}\ C_P^{-0.147}\ I^{0.206}$. As shown in figure 9 the overall correlation is in the form that:

$$K=0.033\ C_N^{-0.247}\ C_P^{-0.147}\ I^{0.206} \qquad (11)$$

This equation is valid in the range from 25-125ppm for both C_N and C_P and I is in the range from 0.78 to 5.85 mA/cm^2.

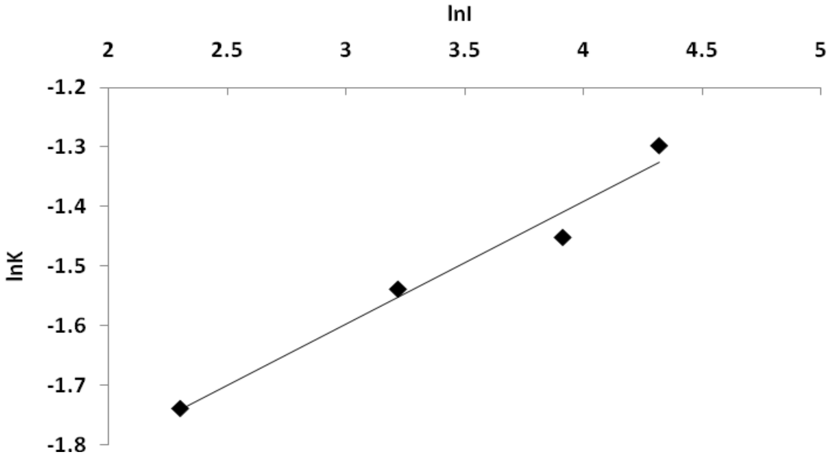

Figure 8. lnK vs ln I at constant nitrate and phosphate concentrations.

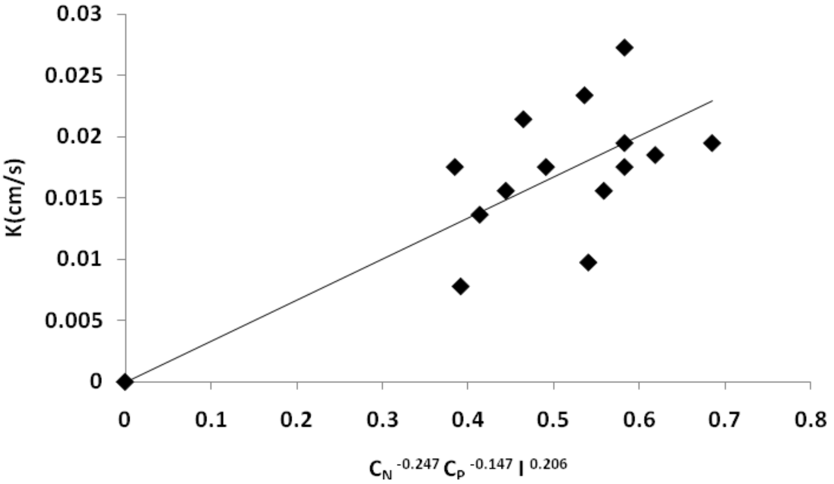

Figure 9. Overall correlation for the effect of different parameters on mass transfer coefficient for removal of a mixture of nitrate and phosphate by electrocoagulation.

The results show that R^2 of the data is low that is can be ascribed to the fact that other parameters such as anode diameter and the distance between electrodes have effects on the reactor performance. The above equation (11) can be used for preliminary design of an electrocoagulation unit used for phosphate and nitrate mixture removal from wastewater.

4. CONCLUSIONS

This work investigates the performance of an electrocoagulation reactor for the removal of phosphate and nitrate ions from wastewater using monoplar aluminum vertical electrodes. Experimental results show that phosphate and nitrate removal efficiency was improved by increasing both current density and initial solution pH while it was decreasing by increasing initial phosphate and/or nitrate concentrations. Experimental results further show that the electrocoagulation process can be described by a first order rate equation for the removal of phosphate and nitrae. A correlations for the effect of initial phosphate concentration, nitrate concentration and current density were deduced and an overall correllation for the unit performance under different operating parameters in the form: $K = 0.033\ C_N^{-0.247} C_P^{-0.147} I^{0.206}$ was deduced. This equation can be used for the preliminary design of an electrocoagulation unit used for phosphate and nitrate mixture removal from wastewater.

ACKNOWLEDGEMENTS
This project was funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under grant no. (339-135/431). The author, therefore, acknowledge with thanks DSR technical and financial support.

References

1. D.C. Bouchard, M.K. Williams, R.Y. Surampalli, *J. Am. Water Works Assoc.* 84 (9) (1992)85.

2. M.F. Dahab, *J. Environ. Systems* 17 (1)(1987)65.
3. S. Liang, M.A. Mann, G.A. Guter, P.H. Kim, D.L. Hardan. *J. Am. Water Works Assoc*. 91 (2)(1999) 79.
4. A.P. Murphy, C.D. Moody, *U.S. Patent* 5,616,252, April 1997.
5. L.W.Canter, *Nitrates in Groundwater*. Lewis Publishers, New York 1997.
6. L. Johansson, J.P. Gustafsson, *Water Res*. 34 (2000) 259.
7. N.M. Agyei, C.A. Strydom, J.H. Potgieter, *Cem. Concr. Res.*30 (2000) 823.
8. M. Rao, A.V. Parwate, A.G. Bhole, *Waste Manage*. 22 (2002) 821–830.
9. B. Bayat, *Water Air Soil Pollut.* 136 (2002) 69–92.
10. P.C. Kao, J.H. Tzeng, T.L. Huang, Removal of chlorophenols from aqueous solution by fly ash, *J. Hazard. Mater.* 76 (2000) 237–249.
11. S. Irdemez, Y.S. Yıldız, N. Demircioglu, *Proceedings of the International oil Congress*, Erzurum, Turkey, 2004, pp. 29–34.
12. E. Yıldız, *Sep. Purif. Technol*. 35 (2004) 241–252.
13. D.G. Grubb, M.S. Guimaraes, R. Valencia, *J. Hazard. Mater.* 76 (2000) 217–236.
14. G. Chen, *Sep. and Purif. Tech.* 38 (2004) 11–41.
15. A.H. El-Shazly, A.A. Al-Zahrani and S.S. Al-Shahrani, *Int. J. Electrochem. Sci.*, 6 (2011) 4141 - 4149
16. M.A. Daous, A.H. El-Shazly, *Int. J. Electrochem. Sci.* 7(2012)3513-3526
17. F.E. Elmore, *Br. Patent* 13,578 (1905).
18. M.S.M. Abdel-Aziz, A.H. El-Shazly, H.A. Farag, G.H. Sedahmed, *Energy Conv. Manag.* 52(2011)2870-2875.
19. A.H. El-Shazly, *Int. J. Chem. React. Eng.*, 9, A39 (2011)1-14
20. S. Ehdaie, M. Fleischmann, R.E.W. Jansson, A.E. Alghaoui, *J. Appl. Electrochem.* 12 (1982) 59–67.
21. D.R. Gabe, F.C. Walsh, J. Appl. Electrochem. 13 (1) (1983)3–22.
22. F.C. Walsh, D.R. Gabe, N.A. Gardner, *J. Appl. Electrochem* 12 (3)(1982) 299–309.
23. R.E.W. Jasson, N.R. Tomov, *Chem. Eng*. 316 (1977) 867.
24. R.E.W. Jasson, R.J. Marshall, J.E. Rizzo, J. *Appl. Electrochem*. 8(1978) 281–285.
25. R.E.W. Jasson, R.J. Marshall, J.E. Rizzo, J. Appl. Electrochem. 8 (1978)287–291.
26. A.H. Mahvi, S.J. Ebrahimi, A. Mesdaghinia, H. Gharibi, M. H. Sowlat, *J. Hazard Mater.* 192 (2011) 1267– 1274.
27. A.D. Eaton, L.S. Clesceri, A.E. Greenberg, M.A.H. Franson, Standard Methods for the Examination of Water and Wastewater, 19th ed., APHA, 1995.
28. A.S. Koparal, U.B. Ogutveren, *J.Hazard. Mater.* 89(2002) 83–94.
29. S.Irdemez, N. Demircioglu, and Y. Sevki Yildiz, *J. Hazard. Mater.* B137 (2) 2006a)1231-1235.
30. S. Irdemez, Y. Sevki Yildiz and V. Tosunoglu, *Sep. Purif. Tech*. 52 (2) (2006b)394-401.
31. S.Irdemez, N. Demircioglu, Y. Sevki Yildiz and Z. Bingul, *Sep. Purif. Tech*, 52 (2) (2006c)218-223.