Int. J. Electrochem. Sci., 8 **(2013)** 12509 - 12518

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Investigations and Kinetics Study for the Effet of Solution Flow Rate on the Performance of Electrocoagulation Unit Used for Nutrients Removal

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Received: 30 May 2013 / *Accepted:* 14 September 2013 / *Published:* 20 October 2013

This work investigates the performance of an electrocoagulation reactor for the removal of phosphate and nitrate ions from wastewater using monoplar iron vertical electrodes. Experimental results show that phosphate and nitrate removal efficiency was improved by increasing both solution flow rate and current density while it was decreasing by increasing ratio (N/P) and by increasing the initial ions 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 solution flow rate on the rate of mass transfer for both phosphate and nitrate ions in the form $K_P=0.005V^{0.537}$ and $K_N=0.0065V^{0.45}$ were deduced. This equation can be used for the preliminary design of an electrocoagulation unit used for phosphate and nitrate mixture removal from wastewater.

Keywords: Nutrient removal, electrocoagulation, kinetic study, wastewater, forced circulation,

1. INTRODUCTION

The presence of nutrients materials such as excess of nitrate and/or phosphates in wastewater causes the well known phenomenon 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 possibility of improving the performance of a electrocoagulation unit using a vertical monopolar iron electrodes for the treatment of wastewater containing a mixture of phosphates and nitrate ions simultaneously under forced circulation conditions and provides a thorough analysis and discussion of reaction kinetics under these conditions.

2. EXPERIMENTAL PART

The experimental setup and electrical circuit used is shown in figure (1), the setup consisted of 25 l storage tank made of plastic material, cylindrical Plexiglas column of 15 cm diameter and 60cm height, connected at the bottom to a perforated disc for solution flow, a 0.33 hp centrifugal pump connected to the bottom of the disc and a check valve for preventing solution from flowing downward. Two monopolar iron electrodes (cathode and anode) were placed vertically, with the anode (iron rod) at the center of the cell parallel to the cathode (iron cylinder) adherent to the wall of the column, the anode diameter was fixed at 3 cm. Before each run, iron electrodes were immersed in diluted carbon tetrachloride solution for few minutes for removing any greases or oxides, washed with distilled water, and finally connected to potentiostat/galvanostat (Autolab 263A). 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 15 l of synthetic solution of potassium nitrate (KNO_3) and potassium di-hydrogen phosphate (KH_2PO_4) with various initial concentrations was used, the initial concentrations of phosphate and nitrate ions were changed from 25 to 100 ppm, were placed at the electrolytic cell with 3.5wt% sodium chloride (constant concentration was used in all experiments), and then feed solution was forced into the electrocoagulation unit at different flow rates ranging from 2 to 4.5 liter/min that have been measured by means of a Rotameter.

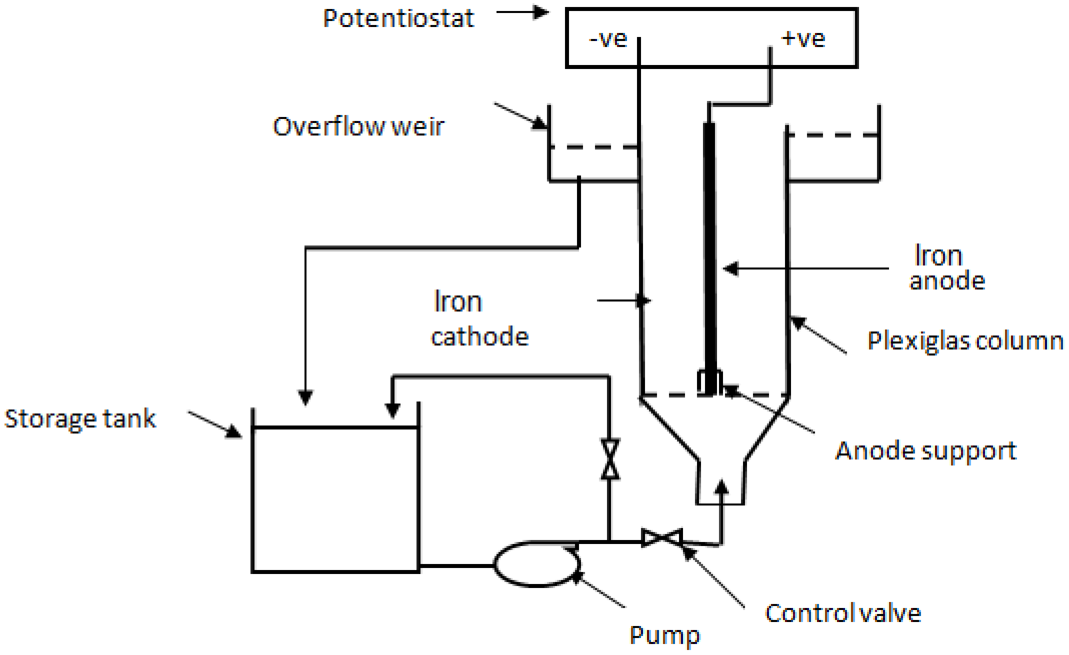

Figure 1. Experimental setup

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 200 to 1800 seconds, the ratio between nitrate and phosphate concentration (N/P) that ranged from 1 to 4, current density ranged from 0.312 to 2.34 mA/cm^2, solution pH was kept constant at 7. 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 any time of electrolysis process. In addition the kinetics of the process was investigated under different operating conditions.

3. RESULTS AND DISCUSSIONS

3.1. Effect of current density

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 10 to 75 mA (current density from 0.312 to 2.34 mA/cm^2) only values for 25 and 50 appear in figure 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 iron electrode with the formation $Fe^{+2}$and hence the formation of $Fe(OH)_2$ coagulant according to the following reactions[28]:

Cathode: $2H_2O + 2e = H_2+2OH^-$ (2)
Anode: $Fe = Fe^{+2}+2e$ (3)
in solution: $Fe^{+2}+2OH^- = Fe(OH)_2$ (4)

The overall reaction will be

$Fe + 2H_2O = Fe(OH)_2 + H_2$ (5)

with dissolved oxygen some of $Fe(OH)_2$ will be converted into $Fe(OH)_3$. Higher rate of freshly formed amorphous $Fe(OH)_2$ and/or $Fe(OH)_3$ that 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 $Fe(OH)_2$ and/or $Fe(OH)_3$ along with the adsorbed N and P compounds to the upper surface of the solution. Besides, the evolving H_2 bubbles and turbulences generated due to solution circulation will entrain solution in their wake and that 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 the removal of 89 to 96% of phosphate and that from 84 to 90% of nitrate can be achieved depending on current density for the same time interval.

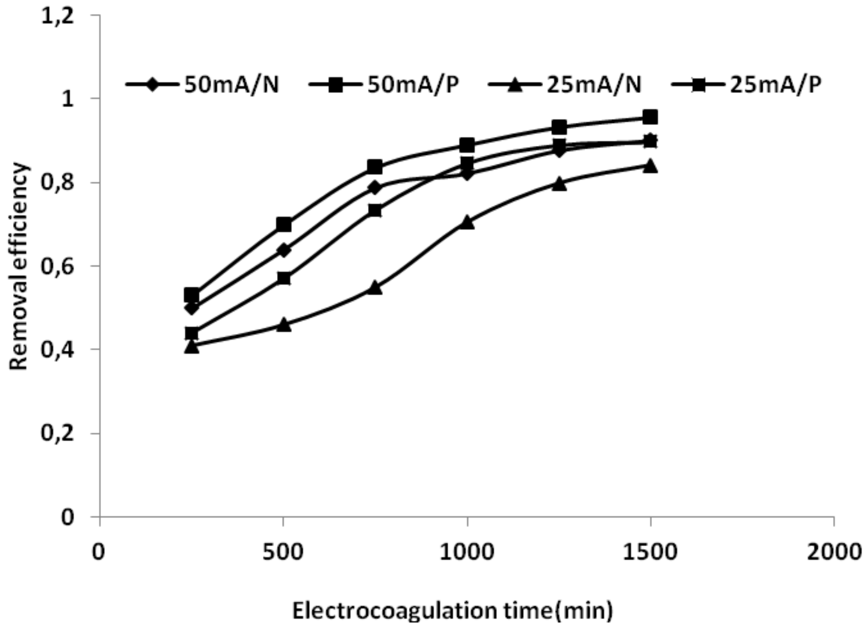

Figure 2. Removal efficiency vs electrocoagulation time for different current

3.2. Effect of solution flow rate and current density

Figure 3 shows that the removal efficiency of both Nitrate and phosphate ions have been increased by increasing the solution flow rate, which can be ascribed to the fact that increasing solution flow rate will improve mixing conditions in the unit.

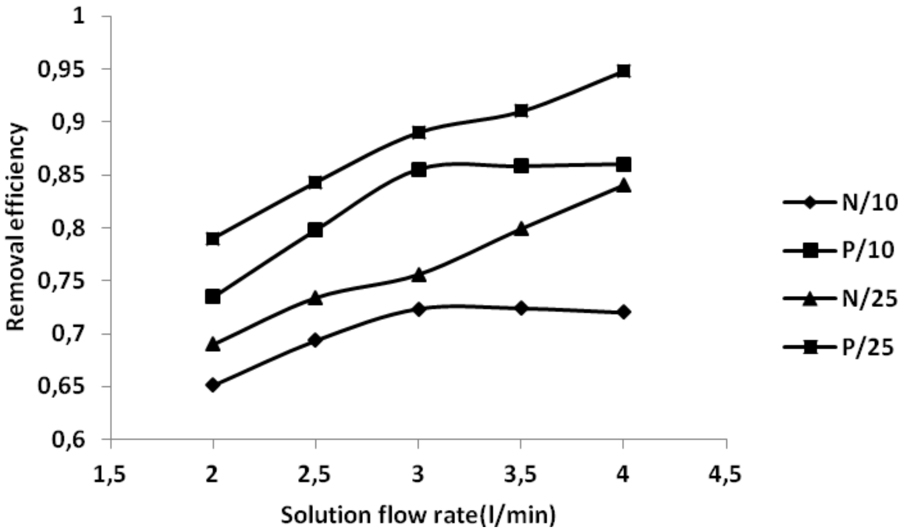

Figure 3. Effect of solution flow rate on removal efficiency for different ions at different current.

Improving mixing conditions will remove the freshly formed Fe^{+2} at the anode from the iron electrode to the solution bulk. Moving the Fe^{+2} away from the anode surface will prevent anodic polarization and improve dissolution of the anode. Also, turbulence generated by the rising gas bubbles 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. It has to be clarified also that increasing solution flow rate above certain limit especially at lower current densities will not affect the performance of the electrocoagulation unit, which can be ascribed to that at lower current densities the amount of freshly formed $Fe(OH)_2$ and/or $Fe(OH)_3$ will be of limited amount, thus increasing solution flow rate will hinder the formation of a coagulant network which plays a major rule in adsorption of suspended and/or dissolved ions.

3.3. Effect of initial concentration and nitrate to phosphate ratio

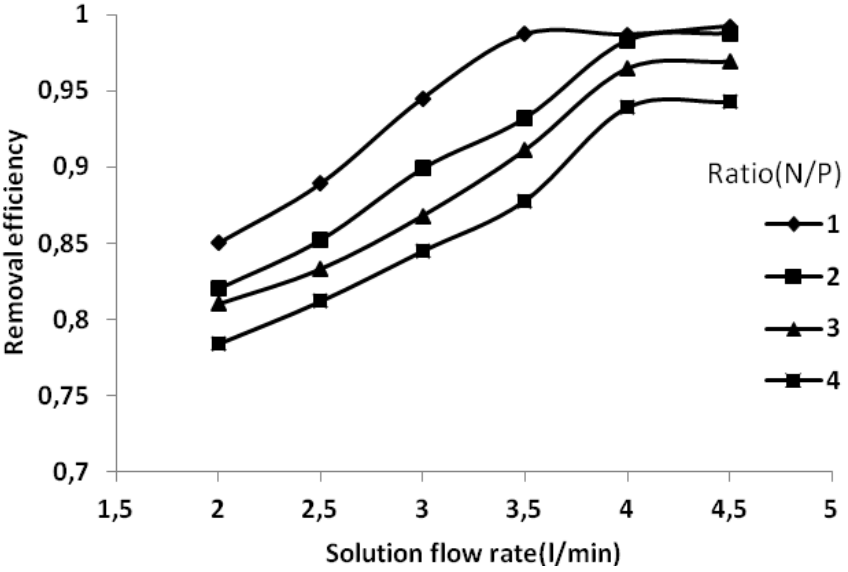

Figure 4. Removal efficiency vs solution flow rate for different (N/P) ratio.

As shown in figure 4 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 iron dissolution at the anode and hydrogen evolution at the cathode. In addition higher concentrations of these ions will block adsorption sites of $Fe(OH)_2$ and/or $Fe(OH)_3$ 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 with increasing solution flow rate, increasing solution flow rate above certain limit approximately has no effect on the process performance.

3.4. Kinetics analysis of phosphate and nitrate 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.

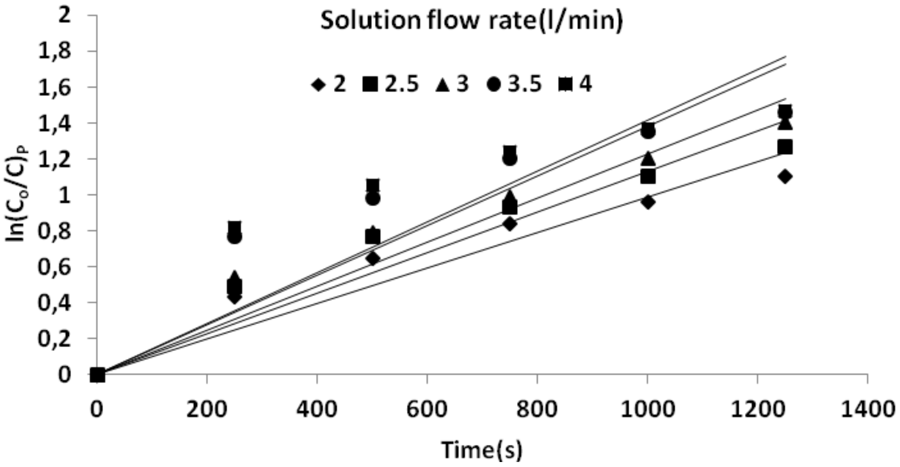

Figure 5. $\ln(C_o/C)_P$ vs time for different solution flow rate

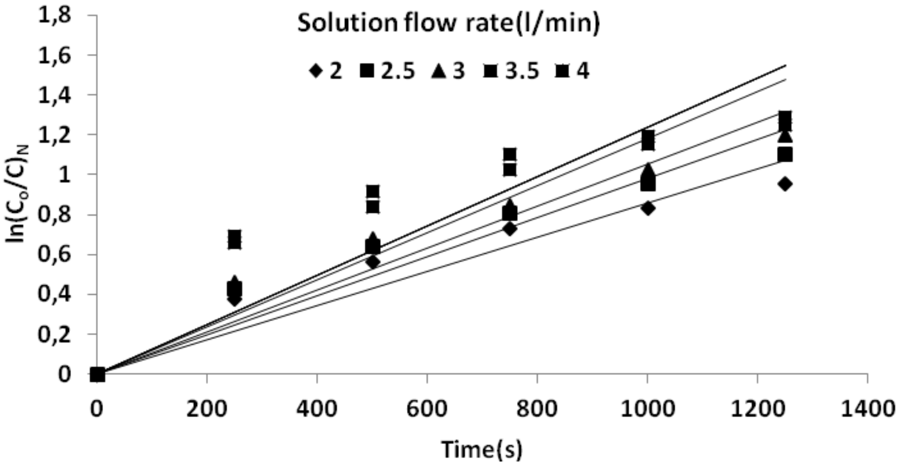

Figure 6. $\ln(C_o/C)_N$ vs time for different solution flow rate

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 increase by increasing solution flow rate.

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 lnV for finding out the values of α and γ for both nitrate and phosphate. The results show that a relations in the form that:

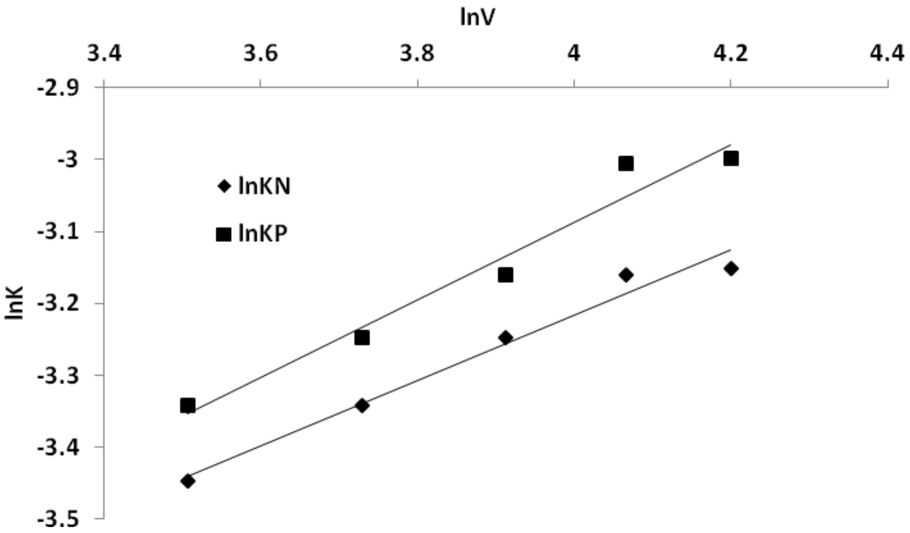

Figure 7. lnK vs lnV for both phosphate(K_P) and nitrate(K_N)

for phosphate removal the relation will be in the form

$K_P=0.005V^{0.537}$ (8)

and for nitrate removal it is in the form that:

$K_N=0.0065V^{0.45}$ (9)

the exponent obtained for the solutions flow rate in the above relations 8 and 9 are consistent with results obtained before for the relation between solution flow rate and mass transfer coefficient for diffusion controlled processes[30].

4. CONCLUSIONS

This work investigated the performance of an electrocoagulation reactor for the removal of phosphate and nitrate ions from wastewater using monoplar iron vertical electrodes. Experimental results show that phosphate and nitrate removal efficiency was improved by increasing both solution flow rate and current density while it was decreasing by increasing ratio (N/P) and by increasing the initial ions 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 solution flow rate on the rate of mass transfer for both nitrate and phosphate ions were deduced. This equation can be used for the preliminary design of an electrocoagulation unit used for phosphate and nitrate mixture removal from wastewater.

ACKNOWLEDGMENT
The authors would like to acknowledge the Deanship of Scientific Research (DSR), King Abdulaziz University, for funding and supporting the execution of this research under the grant number 351-135-1431(2nd stage).

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. H.A. Moreno-Casillas, D.L. Cocke, J.A.G. Gomes, P. Morkovsky, J.R. Parga, E. Peterson, *Sep. Purif. Tech.* 56 (2007) 204–211.
29. S. Irdemez, N. Demircioglu, and Y. Sevki Yildiz, *J. Hazard. Mater*. B137(2)(2006a)1231-1235.
30. J. M. Coulson, J. F. Richardson, J. R. Baand, and J. H. Harker, “Chemical Engineering”, Vol. 2, 3rd ed., Pergaman Press, London; (1985).