Removal of Phosphorous Compounds by Electrochemical Technique.

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Abstract – **The possibility of using electrocoagulation technique to remove phosphorus compounds from waste effluent using an electrochemical reactor has been investigated. To increase the surface area of the anode, a new anode design consisting of raschig rings connected together with a thin wire of aluminum and placed in a perforated plastic basket located above the horizontal cathode was used. Removal of phosphorus compounds was found to be due to combined effect of sweep coagulation and adsorption. The removal of phosphorus compounds was investigated in terms of various parameters namely: pH, operating time, current density, initial phosphorus concentration and addition of NaCl. The study revealed that the optimum conditions for the removal of phosphorus compound were achieved at current density = 8.59 "mA/cm²", pH = 7, NaCl concentration = 1 "g/L" and temperature of 25°C remarkable removal of 100% of phosphorus compound after 30 min can be achieved for most of concentrations.**

Keywords-electrocoagulatio; phosphorus removal; Al electrode; rashing rings.

I. INTRODUCTION

Increasing input of nitrogen and phosphorus compounds to receiving surface waters, especially to lakes and artificial reservoirs lead to increase of primary production of water born organisms and finally its consequence is disappearance of oxygen in waters [1]. The phosphorus is present in water environment in smaller quantities than nitrogen and it is necessary for all kind of living phytoplankton organisms so its concentration is of crucial importance in water quality protection. Beginning from 1970s phosphorus removal from wastewater has been recognized as one of basic processes necessary to be done in all wastewater treatment plants. Continuous development of knowledge concerning phosphorus occurrence, mechanism of its removal and evolution of process technologies led to modern technical solutions which allow to efficient removal of this wastewater constituent. The load of phosphorus discharged to receiving waters comes from various groups of sources of which the main sources are agricultural use of fertilizers, domestic and industrial wastewater, and atmospheric deposition [2], [3]. Phosphorus removal techniques are chemical treatments like adsorption [4-6], chemical precipitation [7], ion exchange, electro dialysis hybrid systems containing fly-ash adsorption and membrane filtration[8] and electrocoaculation [9-11]. Electrocoagulation is the process utilizing "sacrificed" anodes to form active coagulant which is used to remove pollutant by precipitation and flotation in situ. Compared with traditional chemical coagulation, electrocoagulation has, in theory, the advantage of removing the smallest colloidal particles; the smallest charged particles have a greater probability of being coagulated because of the electric field that sets them in motion. It has also the advantage of producing a relatively low amount of sludge [12]. Electrocoagulation is an ideal technology to upgrade water quality. A diversity of opinions exists in the literature for explaining both the key mechanisms and the best reactor configurations [13, 14]. These empirical studies invariably prove the viability of the technology, but singularly fail to fully capitalize on its potential. This is due to a lack of fundamental understanding of the system and hence the inability to accurately predict performance. In addition to this gap we believe that there is a room for improvement of the process of electrocoagulation via the development of more efficient electrochemical reactors. The aim of the present work is to study the performance of a fixed bed reactor with horizontal cathode made of an aluminum sheet insulated with epoxy from its back placed below a fixed bed anode. The anode consists of a single layer of raschig rings connected together with a thin wire of aluminum. Several parameters such as initial pH, conductivity, current density, phosphate concentration, NaCl concentration and electrolysis time, were investigated for their effects on the removal efficiency of phosphorous compounds.

II. EC. THEORY

All electrocoagulation reactors "Fig. 1." are electrochemical cells that consist of an electrode arrangement in contact with the polluted water, with coagulant production *in situ* being their distinguishing feature. To release the coagulant, an applied potential difference across the electrodes is required. Potential requirements for the electrodes can be deduced from the electrochemical half-cell reactions occurring at each electrode, which will vary according to the operational pH and the species present in the system. Aluminium, the most commonly used anode material; go through anodic dissolution as shown in equation (1)
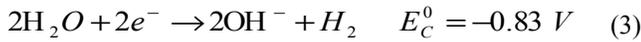
$$Al^{3+} + 3e^- \leftrightarrow Al \qquad E_A^0 = 1.66\,V \qquad (1)$$

Oxygen evolution is also possible at the anode (Equation.2).

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad E_A^0 = -0.40\,V \qquad (2)$$
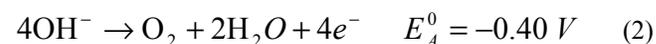
Simultaneously, an associated cathodic reaction, usually the evolution of hydrogen, occurs. The reaction occurring at the
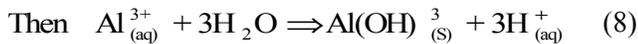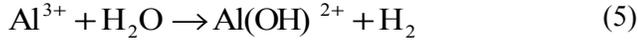
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cathode is dependent on pH. At neutral or alkaline pH, hydrogen is produced via Equation (3),

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad E_C^0 = -0.83 \ V \quad (3)$$

While under acidic conditions, Equation (4) best describes hydrogen evolution at the cathode.

$$2H^+ + 2e^- \rightarrow H_2 \quad E_C^0 = 0 \ V \quad (4)$$
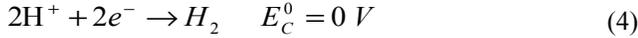
Al3+and OH− ions generated by electrode reactions react to form different monomeric and polymeric species, which transform finally into Al(OH)$_3$(S) depend upon total metal concentration and pH.

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H_2 \quad (5)$$

$$AlOH^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \quad (6)$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+ \quad (7)$$

$$\text{Then} \quad Al_{(aq)}^{3+} + 3H_2O \Rightarrow Al(OH)_{3(S)} + 3H_{(aq)}^+ \quad (8)$$

both Al cathode and anode may be chemically attacked by OH$^-$ ions in view of the amphoteric nature of Al [15].

$$2Al_{(S)}^0 + 6H_2O + 2OH_{(aq)}^- \Rightarrow 2Al(OH)_{4(aq)}^- + 3H_{2(g)}$$
(9)
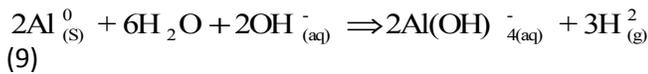
Accordingly, two major interaction mechanisms are being proposed namely: precipitation and adsorption, each one being suggested for a separate pH range. Flocculation in the low pH range is explained as precipitation while the higher pH range (>6.5) as adsorption [16].
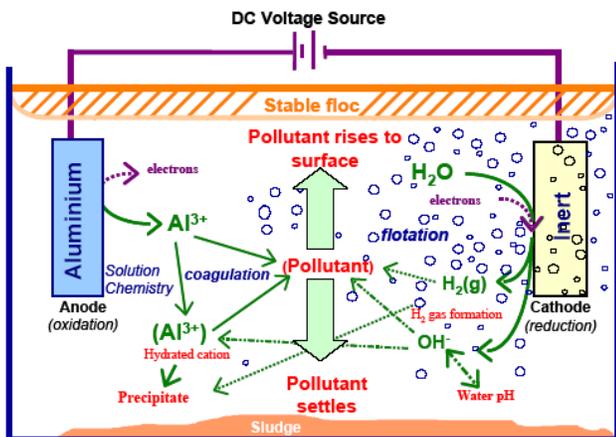

Figure1. Interactions occurring within an electrocoagulation reactor

III. EXPERIMENTAL PART

A. Material and methods

A stock solution of each phosphorous compound was prepared by using an analytical grade of chemicals and dissolving them in distilled water. Experimental solutions of the desired concentrations were obtained by successive dilution with distilled water. The pH of the solution was adjusted by means of HCl and/or NaOH solution. A digitally calibrated pH-meter ((HaNNa, Model pH 211) and a conductivity – meter were used to measure the pH and the conductivity of waste solutions. The analytical determination of phosphorous compounds was carried out with the standard spectrophotometric procedure [17] using U.V spectrophotometer (UNICO, Model U.V 2100).

B. Experimental Set-up

The experimental set-up used in the present work is schematically shown in "Fig. 2". The EC cell consists mainly of a rectangular vessel made of plexi-glass with the dimensions 10 cm × 10 cm square base and a height of 20 cm. An aluminum 10 cm × 10 cm sheet was insulated with epoxy from its back and then placed on the bottom of the cell as the cathode. The anode consists of a single layer of raschig rings connected together with a thin wire of aluminum to make sure that all rings were fed with electrical current "Figure. 2.b". The rings were placed in a perforated plastic basket. The rings were arranged at random within the bed. The anode-cathode distance was kept at 0.5 cm. The electrical circuit consists of power supply (40V, 20A) with a voltage regulator and multi-range ammeter, all connected in series with the cell, a voltmeter was connected in parallel with the cell to measure its voltage.
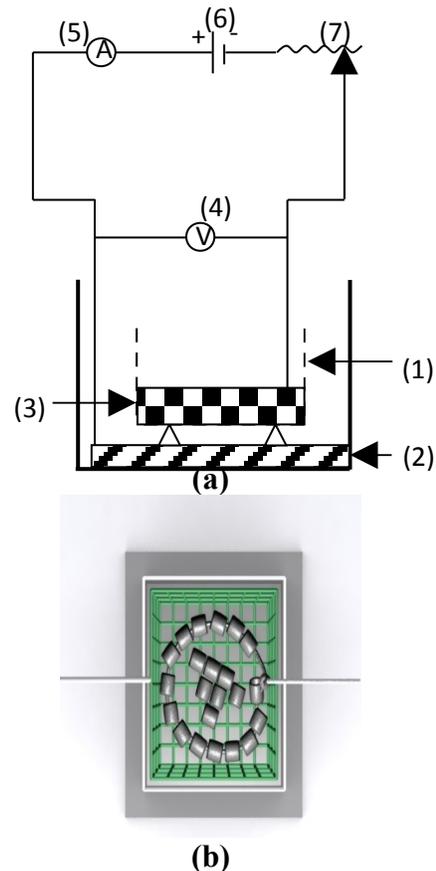

(a)

(b)

Figure. 2. (a) Schematic view of the experimental system. (1) perforated basket, (2) Al cathode,(3) Fixed bed of Al raschig anode, (4) voltammeter,

(5) ammeter, (6) power supply and (7) resistance. (b) Schematic view of the fixed bed of Al raschig anode.

C. Electrocoagulation Procedures

For each run a 1.5 L of the synthetic waste solution was mixed with the appropriate amount of sodium chloride which was employed as a conductor. The solutions were placed into the electrolytic rectangular cell. The pH was adjusted by the addition of NaOH and/or HCL solutions. Direct current from the D.C power supply was passed through the solution via the two electrodes during the 180 minutes of electrolysis run. 10 mL of the solution was drawn at every 5 minutes interval for the first half hour and 30 minutes interval for the remaining time of the run. The location of the drawn samples was kept constant for each run. Samples were filtered, and then taken for absorbance measurements at an appropriate wave length of the maximum absorption for each of the phosphorous compounds. The measured absorbance was then converted to the residual concentration of the compound using a calibration curve obtained from a plot between the absorbance versus the known concentration for each compound.

The electrodes were washed with HCl solution (15% w/v) before each run in order to remove any adhering scales or oxides. Following each run, the electrodes were washed with distilled water, dried until they are used again. The efficiency of phosphorus compounds removal, % Removal, was calculated as

$$\% \ removal = \frac{Ci - Cf}{Ci} * 100 \qquad (10)$$

Where; C_i is the initial phosphorus compounds concentration "mg/ L" and C_f is the final phosphorus compounds concentration "mg /L".

IV. RESULTS AND DISCUSSION

A. Effect of current density (C.D.) and time of electrolysis

Batch electrocoagulation experiments were conducted for 2.5 h for different current densities. "Fig. 3" Shows the effect of changing the time of electrolysis on the % removal of phosphorous. It was found that the % removal of phosphorous increases with increasing the time of electrolysis until reaches equilibrium at 1h. "Fig. 3" also shows that an increase in current density from 2.45 to 9.82 "mA/cm²" increases the percentage removal of phosphorus from 80 to 100 .This is ascribed to the fact that at higher current densities the dissolution of anode to Al^{3+} ions increases according to Faraday's law. Al^{3+} ions undergo hydrolysis and the resulting aluminum hydroxides produce more sludge with a consequent significant removal of phosphorus due to phosphorus adsorption on $Al(OH)_3$ and its polymeric compounds [18]. Furthermore, more hydrogen bubbles are generated at the cathode; these bubbles improve the degree of mixing of aluminum hydroxides and phosphorus and enhance the flotation ability of the cell with a consequent increase in the percentage removal [19]. Also, it was demonstrated that bubbles density increases and their

size decreases with increasing current density, resulting in a greater upwards flux and a faster removal of phosphorus and sludge flotation [20].
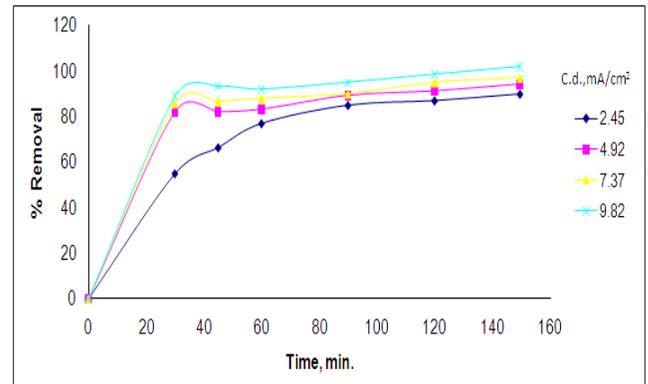

Figure.3. Effect of electrolysis time on the Percentage Removal of (phosphrous $C0$: 40"mg/L", C.D.:4.92 "mA/cm²," pH: 5.2, and temp 25◦C).

B. Effect of sodium chloride concentration

Sodium chloride is usually employed to increase the conductivity of the solution to be treated. Solution conductivity affects the cell voltage and consumption of electrical energy in electrolytic cells. "Fig. 4". shows the effect of sodium chloride concentration on the percentage removal of phosphorus. It was found that, as sodium chloride concentration increases from 0.5 to 5 "g/L", the percentage removal of phosphorus increases from 80 to 95 This may be explained by the fact that the higher chloride ion concentration, the higher the ability of chloride ions to destroy any passive oxide film which tends to form on the anode and limit anode dissolution, hence it increases the availability of aluminum hydroxide in the solution and improve the efficiency of phosphorus removal [21]. Also, as the concentration of sodium chloride increase, the activity of the dissolved Al^{3+} in the anode vicinity decreases by virtue of interionic attraction [22] between sodium chloride and the dissolved Al^{3+}, accordingly the potential required to dissolve the aluminum anode (e) decreases according to Nernest equation:

$$e = e_o - \frac{RT}{ZF} \ln a_{Al^{+3}} \qquad (11)$$

where e is the electrode potential, e_o is the standard electrode potential, F is Faraday's constant [$F = 96500$ coulomb], Z is the number of electron involved in the reaction and R is the gas constant ($R = 8.13$ J/mol.K), $a_{Al^{3+}}$ is the activity of Al^{3+} The decrease in the potential required to dissolve the anode reduce the tendency of aluminum to passivate and reduce the tendency of chlorine and oxygen evolution at the expense of aluminum dissolution.
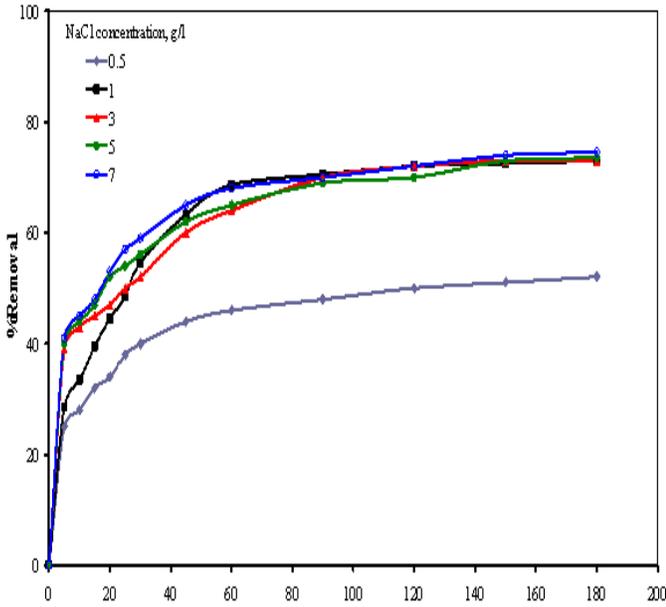
Figure. 4. Effect of NaCl concentration on phosphorus removal efficiency (*C*0: 40"mg/"L, C.D.:4.92 "mA/cm²", pH: 5.2, and temp: 25∘C).

C. Effect of the initial pH value

It has been established that the pH value of the solution is an important parameter which influences the performance of the electrocoagulation process. To examine its effect, the sample was adjusted to the desired pH using sodium hydroxide or hydrochloric acid solutions. "Fig. 5" shows the effect of pH on percentage removal of phenol. The data showed that the percentage removal of phosphorus increased from 65 to 100. This is attributed to the amphoteric character of aluminum hydroxide which does not precipitate at very low pH [23], while high pH leads to the formation of $Al(OH)_4^-$ which is soluble and useless for adsorption of phenol [24]. The results show that the optimal pH is 8 at which higher percentage removal of phosphorus could be reached but the difference between the percentage removal at pH7 is small .Then the optimal value of pH can be considered 7 and these results are accordance with published works [25].
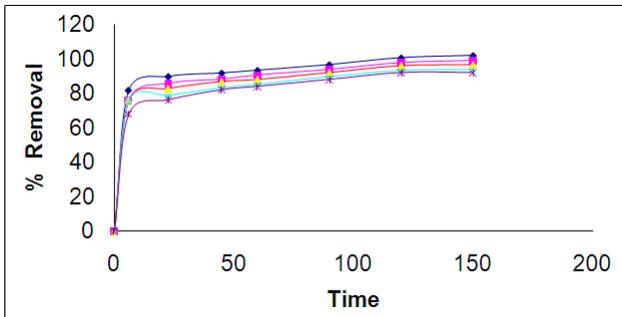

Figure. 5. Effect of pH value on phosphorus removal efficiency (*C*0: 40"mg/L", C.D.:4.92 "mA/cm²", and temp: 25∘C).

D. Effect of initial phosphorus compound concentration

"Fig. 6". shows that the percentage removal gradually decreases from 100 to 75 as the phosphorus concentration increased from 5 to 50 mg/L. This is ascribed to the fact that at a constant current density, the same amount of aluminum ions passes to the solution at different phosphorus concentration. Consequently, the formed amount of complex aluminum hydroxides was insufficient to coagulate the greater number of phosphorus molecules at higher phosphorus concentrations.
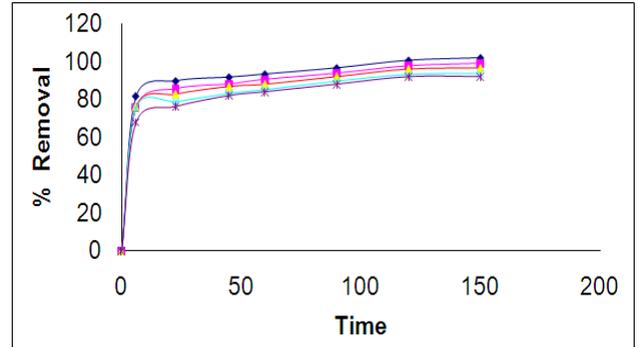

Figure 6. Effect of initial phosphorus compound concentration on phosphorus removal efficiency (*C*0: 40"mg/L", C.D.:4.92 "mA/cm²", and temp: 25∘C).

E. Effect of temperature

The effect of temperature on the percentage removal of phosphorus is shown in "Fig.7". The percentage removal increases from 90 to 100 as the temperature increases from 25 to 45°C, beyond this temperature, there is a little effect on removal efficiency.

Temperature influences the rate of phenol removal via the following effects:

(i)   Increase of temperature increases the rate of Al^{3+} hydrolysis to $Al(OH)_3$ [26].

(ii)   Increase the temperature increases the diffusivity of Al^{3+} according to the Stokes-Einstein's equation with a consequent increase in the rate of mass transfer of Al^{3+} from the anode surface to the solution bulk. Beyond 40°C, the solubility of $Al(OH)_3$ in the solution increases with a consequent loss of the coagulant [27].
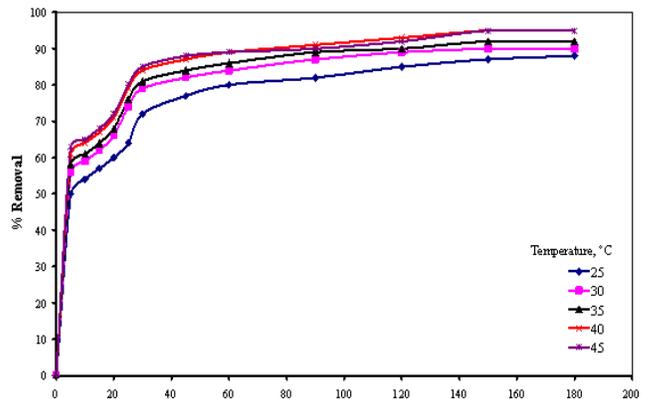
Figure 7. Effect of Temperature on the Percentage Removal of phosphorus(C0: 40"mg/L", C.D.:4.92 "mA/cm^{2}", and pH=5.2).

V. CONCLUSION

EC of phosphorus compounds using Al raschig rings connected together as a scarified anode seems to be a very efficient method for wastewater treatment as revealed by the present study. Experimental parameters such as pH, time, current density, electrolyte concentration, initial phosphorus compound concentration and temperature were investigated for phosphorus compounds removal. The experimental results revealed that the phosphorus compounds percentage removal is enhanced by sweep coagulation and adsorption. Maximum removal of phenolic compounds was attained at pH = 7, NaCl concentration = 1 "g/L", current density = 8.59 "mA/cm^{2}", temperature = 25°C. Increase in the current density and NaCl concentration resulted in an increase in the phosphorus compound removal. Meanwhile, removal efficiency of phosphorus compounds decreases with the increase in initial phosphorus compound concentration. Comparison of the presented data with the data obtained using other cell designs for phosphorus removal by EC shows that the present cell design is superior to other designs in every respect especially in the higher separation efficiency.

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