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ELECTROCOAGULATION OF FERTILIZER INDUSTRY EFFLUENT USING COPPER ELECTRODES

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ABSTRACT

Fertilizer industry is the largest agro-based industry and also one of the most polluting sectors in India. The effluent generated from the fertilizer industry is about 500 liters / tons of urea produced. The effluent discharged from fertilizer industry does not contain toxic compounds or pathogenic bacteria but it contains considerable amount of Nitrate & Phosphate. The continuous discharge of the effluent into soil or surrounding water bodies can cause adverse environmental effects. The limitations in the physico-chemical methods and biological methods make it necessary to develop a process which effectively removes phosphate from the fertilizer industry effluent while reducing sludge production rate and chemical consumption. The use of electrocoagulation process, overcomes many of the limitations of conventional systems. Electrocoagulation using copper electrodes has been evaluated in this study. Synthetic effluent having the characteristics of fertilizer industry effluent was prepared and electrocoagulated by varying process variables such as pH, time, electrode gap, and current density. . The variables were optimized by Taguchi's method using minitab software, version 16 for phosphate removal. The maximum phosphate removal for the optimized run was 96.65% for copper electrodes.

Keywords—Electrocoagulation, Fertitlizer industry effluent, Operating cost, Copper electrodes,Taguchi's method

I. INTRODUCTION

Water is an essential and basic human need for urban, industrial and agricultural use and has to be considered as a limiting resource. In this sense, only 1 % of the total water can be used for human needs. Inadequate water supply and water quality deterioration represents serious contemporary concerns for municipalities, industries, agriculture and the environment in many parts of the world. Factors contributing to these problems include continued population growth in urban areas, contamination of surface water and ground water, uneven distribution of water resources and frequent droughts caused by extreme global weather patterns. Our present environmental problems are originated from unplanned utilization of natural sources depending on the especially industrialization. Increase in variation of products, more benefit wishes of industrialists, incorrect applications and deficiencies of regulations are the major reasons of the industrial waste water pollution. Discharging wastewater without treatment in to surface water resources can affect the water quality and aquatic life negatively. Especially the amount and concentration of wastewater determine how they harm the intake habitation.

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Among various kinds of industries, fertilizer industry is considered as one of the most polluting sectors in India in terms of effluent composition as well as volume of discharge. Modern synthetic fertilizers are composed mainly of nitrogen, phosphorous, and potassium compounds with secondary nutrients added. The use of synthetic fertilizers has significantly improved the quality and quantity of the food available today, although their long-term use is debated by environmentalists. Due to industrialization and global competitive market trends, it has emerged as a major industrial activity in small and medium sector to cater the needs of agriculture. There are huge numbers of fertilizer industries engaged in producing fertilizer and are spread over in all state across the country due to increasing trends.

Phosphorus is critically needed to improve soil fertility for crop production in a large area of Asia. In recent years, some non conventional P fertilizers such as phosphate rock and partially acidulated phosphate rock have been tested as potential alternatives to conventional water soluble P fertilizers like single superphosphate and triple superphosphate.

A study was conducted on evaluation of an integrated precipitation and Enhanced Biological Phosphorus Removal (EBPR) process for the treatment of fertilizer plant wastewater and effluent detoxification, assessed by microtoxicity and seed germination tests[1].Effluent samples were collected from a local P fertilizer industry and were characterized by their high fluoride and P content. First, the samples were pre-treated by precipitation of P and fluoride ions using hydrated lime.Another study was conductedon the removal efficiency of reverse osmosis (RO) and nanofiltration (NF) membranes to reduce fluoride and phosphate load to less than 8 mg L^{-1} and 2 mg L^{-1} , respectively[2].

The main focus of the present study was to to optimize the electrocoagulation process with the process variables pH, time, temperature and current density using Taguchi's method. And the performance of electrocoagulation process for the removal of phosphate in fertilizer industry effluent using copper electrodes was also analysed.

II. MATERIALS AND METHODS

2.1. Materials

A 1000 ml glass beaker was used as the reactor for phosphate removal. Electrocoagulation copper (Commercial Grade, India) with a surface area of $7.8x10^{-3}$ m^2 (12 cm x 6.5 cm x0.1 cm) act as the anode. The cathode was also a copper sheet of the same size as the anode. From previous studies the electrode spacing was varied as 0.5, 1, 1.5 cm [3].DC power supply is the source of power. Both electrodes are then connected to a DC power supply. Mica is given as the material for various spacing so that current does not pass into it.

2.2. Preparation of synthetic waste waster

Synthetic wastewater was prepared based on the characteristics obtained from the analysis of original wastewater sample. Synthetic wastewater was prepared due to the need of an influent source with constant feed concentration. The chemicals used for the preparing synthetic waste water are glucose, ammonium nitrate, monopotassium phosphate, dipotassium phosphate.The composition of synthetic waste water is given in Table 1.

Table1Composition of synthetic waste water

Component	Concentration
Glucose (mg/L)	200
Ammonium Nitrate(mg/L)	40
Monopotassium Phosphate(mg/L)	28
Dipotassium phosphate (mg/L)	20
Nutrient Solution(ml)	10

2.3. Batch study

Batch study was conducted to determine the effect of various operating parameters such as pH, contact time, electrode gap and current density in the removal of phosphate from the synthesized fertilizer wastewater. It was carried out in 1000 ml beaker using electrodes of 12 cm x 6.5 cm x 0.1 cm and 800 ml volume of wastewater with known concentrations of phosphate. Constant voltage of 24 V is fixed. Experiment was done in two phases. Waste water samples of initial phosphate concentration 76 mg/l were taken in the reactor. Each batch was separately kept, for varying time each without adding external coagulant. After the flocs settle down the phosphate concentration is measured by using spectrophotometer.

2.4. Optimization of parameters

In order to study the effect of process variables on electrocoagulation using copper electrodes, initial trials were conducted to fix the ranges. Some of the initial trials conducted is given in the Table 2 and Table 3.

Table 2 Variation of phosphate removal percentage with time at constant electrode gap ,current density and pH.

Trials	Time(Minutes)	Phosphate Removal %
1	10	97.89
2	15	98.1
3	20	98.42
4	25	94.73
5	30	92.5
6	45	83.15
7	60	64.47

Table 3 Variation of phosphate removal percentage with pH at constant electrode gap, Current density and time

Trials	pH	Phosphate Removal (%)
1	5	82.5
2	7	96
3	8	93.5
4	8.56	98
5	9	98
6	9.31	91.1
7	10	63.4

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2.5. Calculation of sludge volume index

The sludge volume index (SVI) is the volume in milliliters occupied by 1 g of a suspension after 30 min settling. SVI typically is used to monitor settling characteristics of activated sludge and other biological suspensions. Although SVI is not supported theoretically experience has shown it to be useful in routine process control.SVI can be determined by using (1):

$$SVI = \frac{\text{Settled sludge volume}\left(\frac{mL}{L}\right) X1000 \left(\frac{mg}{g}\right)}{\text{Suspended Solids}\left(\frac{mg}{L}\right)} \quad (1)$$

2.6. Sediment analysis by TEM

Microstructure of the byproduct particle obtained by electrocoagulation using steel and copper electrodes was analyzed by TEM.

III. RESULTS AND DISCUSSION

3.1. Electrocoagulation using copper electrodes

3.1.1. Results of electrocoagulation process

The total number of experiments with four process variables and three levels in Taguchi's design are 9 experimental runs. The complete 9 runs of experimental data and their results are given in Table 4.

Table4 Design of experimental runs and their results

Run no	Electrode Gap(cm)	Current Density(A/m^2)	Time (minute)	pH	Phosphate Removal
1	0.5	85	10	8.5	95
2	0.5	127.5	15	9	83.11
3	0.5	170	20	9.5	59.09
4	1	85	15	9.5	92.3
5	1	127.5	20	8.5	90.27
6	1	170	10	9	81.81
7	1.5	85	20	9	75
8	1.5	127.5	10	9.5	95.65
9	1.5	170	15	8.5	92.59

The experimental data obtained according to Taguchi experimental design were analyzed by using Minitab 16 software package to determine the effects of each parameter on phosphate removal.

3.1.2. Determination of optimum parametric levels for phosphate removal

The experiments were conducted as per the orthogonal array and the phosphate removal % were obtained for various combinations of parameters as in Table 4.The influence of parameters on the removal percentage has been evaluated using S/N ratio response analysis. The parameter with the greatest influence was determined by the difference between the maximum and minimum value of the mean of S/N ratios. The response table for S/N ratios and ranking of predominant parameters influencing the phosphate removal % using the S/N ratio obtained for different parameter levels are listed in Table 5.

Table 5 Response table for Signal to Noise ratios

Level	Electrode Gap(cm)	Current Density(A/m^2)	Time (Minutes)	Ph
1	37.79	38.79	39.14	39.33
2	38.89	39.04	39.01	38.05
3	38.82	37.67	37.35	38.12
Delta	1.10	1.37	1.79	1.28
Rank	4	2	1	3

It can be seen that for electrocoagulation process the most effective parameter on phosphate removal is the Time (highest S/N ratio). The best optimum values for the parameters are pH-8.5, contact time- 10 minutes, Electrode gap -1 cm and current density 127.5 A/m^2.

3.2. Analysis of electrocoagulation process

3.2.1. Effect of Each Parameter on Phosphate Removal

The effect of experimental parameters on the S/N ratio for phosphate removal is shown in Fig1.

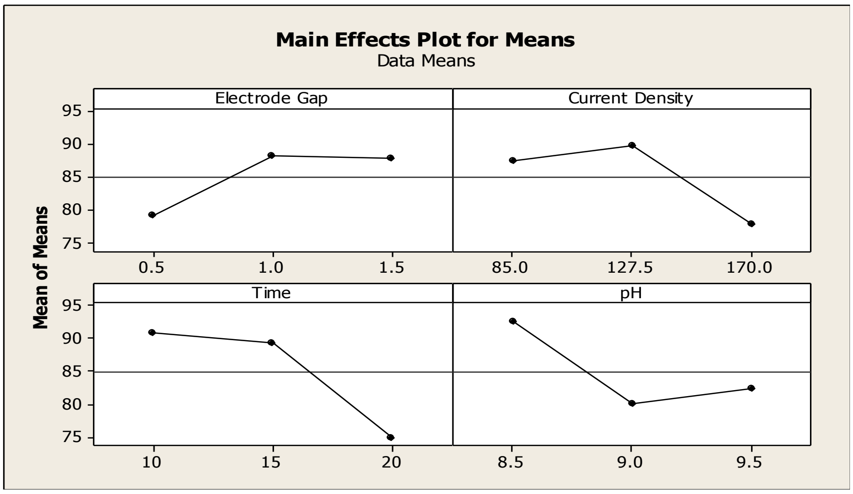

Fig 1The effects of experimental parameters on the S/N ratio for phosphate removal

The first parameter was the inter electrode distance which was chosen in the range 0.5 to 1.5 cm. With a small inter electrode distance; the gas which was blown in the cathode compartment induces a great floating phenomenon of the phosphorus-copper complexes formed on the anode electrode. This latter operation permitted further dissolution of the Copper anode and increased the complex formation at the metal-solution interface. However for short inter electrode distance the current density becomes too high and cause short circuit. Therefore the experiment has been done with inter electrode distance of 1 cm, although the ohmic resistance will be higher, This distance is usually used by industrial electrochemical processes [4].

In all electrochemical processes, current density is the most important parameter for controlling the reaction rate within the electrochemical reactor. It is well known that the current density determines the production rate of coagulant (amount of Cu^{2+} ions released by the anode), adjusts also bubble production, its size and distribution, and hence affects the growth of flocs in the EC reactor with different electrode configurations.

Fig.1 shows the effect of current densities on the removal rate of phosphate, and indicates that the removal rates of phosphate increases, as expected, with increasing current density. Current density studies were accomplished at the original pH values (8.5-9.5) and the final pH values varied between 7 and 8. EC system was more

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successful in less time periods at high current density. It can be explained by additional partial removal of phosphate by direct electroreduction at the cathode or by electroless deposition [5].

The studied range of pH was 8.5 to 9.5. The results, reported in Fig. 1, show that the phosphate removal process is more efficient for a pH of 8.5. These results may be explained mainly by the strong presence of the hydroxycopper in this pH range which maximized the phosphorus hydroxide copper complex formation. For all experiments whatever initial pH, the final pH of the solution converged to the value of 7.6. This value represents the pH where the phosphorus-copper complexes are strongly present inducing an efficient copper complexation by phosphate. Working at a pH below 8 led to a negligible complexation by phosphate rather than the hydroxide complexation of the copper. This result means that it was possible to use directly the fertilizer waste water which have an initial pH between 7.5-9.5 and a strong mineralization. According to the chemical characteristics of fertilizer industry water there is no a need to increase the price of the treatment by the addition of chemical products (acid or base) in the electrocoagulation process, contrary to the processes based on the precipitation or the adsorption [4] .

3.2.2. Confirmation test

The experimental confirmation test is the final step in verifying the results drawn based on Taguchi's design approach. The confirmation experiments were conducted with the optimum parameters obtained and the results were compared with the predicted results obtained using the multiple linear regression models. The regression equations developed for phosphate removal is (2)

Phosphate removal % = 207 + 8.68 Electrode Gap - 0.113 Current Density - 1.60 Time - 10.3 pH (2)

The predicted values of the responses obtained using optimized parameters can be computed using the above equation. The equation considers only the significant parameters.The predicted and the actual values obtained as a result of the confirmation test is given in Table 6.

Table 6 Results of Confirmation experiment

Sample	pH	Time (min)	Electrode Gap(cm)	Current Density(A/m^2)	Phosphate removal %	
					Actual	Predicted
Synthetic	8.5	10	1	127.5	96.65	97.72

3.2.3. Application of Optimized Results to Real Waste Water

Waste water was collected from a fertilizer industry,and its characteristics were analyzed again as per standard methods. The characteristics of the waste water before and after treatment is are given in Table 7.

Table 7 Characteristics of waste water before and after treatment using Steel electrodes

Parameter	Before Treatment	After Treatment
pH	9.85	10.24
Conductivity(mS/cm)	5.48	5.18
TDS(mg/L)	3106	2931
COD(mg/L)	352	36

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Nitrate(mg/L)	115	33.39
Phosphate(mg/L)	66	2.82
TSS(mg/l)	1528	546

The phosphate removal percentage obtained for original waste water was 95.72 %, which is close to the predicted results.After the electrocoagulation process using copper electrodes only certain parameters like COD, Nitrate, Phosphate have met the general discharge standards.

3.2.4. Calculation of sludge volume index

Spellman's Standard Handbook for Wastewater Operators gives an in depth analysis of what typical SVI values should be and what they mean. This should be used to judge what further actions need to be taken for most favorable operation of the waste water treatment plant. Interpretation of SVI results is given in Table 8.

Table 8 Interpretation of SVI Results

SVI Range	Expected Condition
< 100mL/g	Old sludge; possible pin floc; increasing effluent turbidity
100mL/g to 250mL/g	Normal operation; good settling; low effluent turbidity
> 250mL/g	Bulking sludge; poor settling; high effluent turbidity

Volume of sludge was obtained as 90 ml/l. And the suspended solid concentration obtained was 346 mg/l. Thus the calculated value for sludge volume index was 260 ml/g.Hence settling characteristics of the electrocoagulated sludge was poor and results in high effluent turbidity.

3.2.5. Operating cost

Operating cost is one of the most important parameters in the electrocoagulation process because it affects the application of any method of waste water treatment. The operating cost includes material (Mainly electrodes) cost, electrical energy cost, labor, maintenance and other costs. The latter cost items are largely independent of the electrode material. Thus, in this study the operating cost was calculated with electrodes and electrical energy costs. So both energy and electrode consumption costs are taken into account as major cost items. Calculation of operating cost is expressed as (3) :

$$\text{Operating cost} = X\ \text{Energy}_{consumption} + Y\ \text{Electrode}_{consumption.} \quad (3)$$

Where $\text{Energy}_{consumption}$ and $\text{Electrode}_{consumption.}$ are consumption quantities per m^3 of treated waste water[6] . Unit prices, X and Y, given for the Indian market 2015, are electrical energy price Rs 5.95/kWh, electrode material price Rs 379.8/Kg for copper . The energy consumption (kWh) in the process was calculated according to the following equation (4):

Energy= Current x Voltage x time (h) 10^{-3} (4)

Electrode consumption is the decrease in amount of the sacrified electrode before and after electrocoagulation. In this study the enegy consumption per m^3 for the optimum run of electrocoagulation (Current- 0.75, Voltage 5.4 V and time 10 min) was 0.84375 kWh. The electrode consumption for 800 ml effluent was 0.291 g for the optimum run and thus electrode consumption per m^3 was 0.36375kg.The energy consumption costs and material costs are Rs.5.02 and Rs.137.78respectively.

3.3. Characterization using TEM

Fig 2 is the photograph of the by-product from the electrolysis experiment using the copper electrode. Apparently, it consists of copper compounds including copper phosphate, copper phosphorus oxide, or copper hydroxide. The by-products were thoroughly dried in an oven and subsequently looked like ceramic powder. Mainly, phosphorus oxides were observed and various copper phosphates and copper phosphorus oxides were included in the by-product. It should be noted that the phosphate ions could be removed by oxidation at the cathode as well as by reaction with copper.

Fig2 Sediment by electrolytic process with copper electrode in Fertilizer Industry Effluent

Fig 3 shows the microstructure of the by-product particle observed through transmission electron microscopy. The aggregated particle size was very large and non-uniform. However, the primary particle in the aggregated particle was very homogeneous and its size was around 10 nm. The particles were massively aggregated. The by-product primary particles might spontaneously aggregate in the solution with each other and grow to be a sufficiently large size for precipitation. Such inorganic particles can agglomerate very well in a base condition, so that the by-product particles can easily coagulate and precipitate as well.

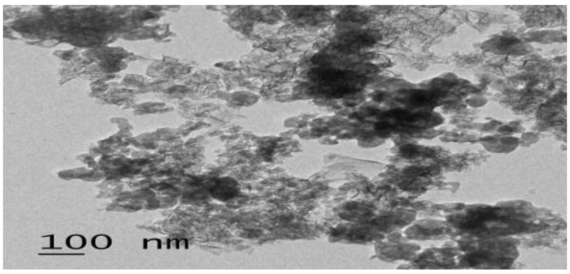

Fig 3 Micrograph of sediment by electrolytic process with copper electrode in fertilizer industry effluent by transmission electron microscope

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IV. CONCLUSIONS

Various studies have reported that electrocoagulation process is better than other conventional methods. The present study evaluated the performance of such a electrocoagulation process for the treatment of the Fertilizer industry effluent. In this study, fertilizer industry effluent was subjected to electrocoagulation so as to meet the effluent discharge standards. Optimum conditions were found out by Taguchi in Minitab software. The removal of phosphate by copper electrode was analyzed. The percentage removal for TDS, COD, Nitrates, Phosphates were 4.8,89.77, 71.07 and 95.70 respectively by copper electrodes . The parameters of the effluent COD, phosphate and nitrate met the relevant Indian discharge standards for copper electrodes .The percentage removal for TDS by copper electrodes was very less.

The operating cost, which included the electrode cost and energy cost, for the process and volume of the sludge obtained and SVI of the sludge from the process were also evaluated. The operating costs per m^3 for the process using steel electrodes was Rs.142.8 .The volume of sludge obtained for the process using steel electrodes was 90ml/l and the SVI was 260 ml/g, which showed that the settling characteristics of the sludge was poor.

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