ELECTROCOAGULATION OF FERTILIZER INDUSTRY EFFLUENT USING STEEL 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 steel 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 79% for steel electrodes.

Keywords: Electrocoagulation, Fertitlizer industry effluent, Operating cost, Steel 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.

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 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 steel 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 using Mild steel (Commercial Grade, India) with a surface area of 7.8×10^{-3} m^2 (12 cm x 6.5 cm x0.1 cm) act as the anode. The cathode was a stainless steel (SS 304; SAIL, India) 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

Optimization of varying parameters was done by Taguchi's method in MINITAB software. For pH the range selected is from 1 to 10 for initial trials which are based on previous studies[3].The contact time is varied between 10 and 60 minutes and the range selected for current density is fixed based on initial trials. The Phosphate concentration of waste water after electrocoagulation was analysed using standard methods.

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):

$$\text{SVI}=\frac{\text{Settled sludge volume}\left(\frac{\text{mL}}{\text{L}}\right)\text{X}1000\left(\frac{\text{mg}}{\text{g}}\right)}{\text{Suspended Solids}\left(\frac{\text{mg}}{\text{L}}\right)} \qquad (1)$$

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 steel 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 the results are shown in Table2.

Table2 Design of experimental runs and their results

Run no	Current Density(A/m^2)	Electrode Gap(cm)	pH	Time (Minutes)	% phosphate removal
1	85	0.5	2.5	10	31.25
2	85	1	3	20	71.42
3	85	1.5	3.5	30	25
4	170	0.5	3	30	93.47
5	170	1	3.5	10	93.06
6	170	1.5	2.5	20	80.3
7	255	0.5	3.5	20	18.75
8	255	1	2.5	30	90.47
9	255	1.5	3	10	14.28

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 percentages were obtained for various combinations of parameters as in Table 2. The influence of parameters on the removal percentage has been evaluated using S/N ratio response analysis. The parameter with 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 percentage using the S/N ratios obtained for different parameter levels are listed in Table 3. It can be seen that for electrocoagulation process the most effective parameter on phosphate removal is the Current Density(the highest S/N ratio).The best optimum values for the parameters are pH-2.5,Contact time -20 minutes, electrode gap -1 cm,Current density 170 A/m^2.

Level	Current Density(A/m^2)	Electrode Gap (cm)	pH	Time (Minutes)
1	31.64	31.59	35.71	30.79
2	38.96	38.53	33.19	33.54
3	29.23	29.72	30.93	35.50
Delta	9.73	8.81	4.78	4.71
Rank	1	2	3	4

Table 3 Response table for Signal to Noise ratios

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 Fig 1. From Fig 1, it can be seen that as pH increases the phosphate removal rate increases and the rate decreases with further increase in pH. This is because the $Fe(OH)_3$ formed becomes unstable as the pH increases or decreases. The flocs of $Fe(OH)_3$ have large surface areas, which are useful for a rapid adsorption of soluble organic compounds and trapping of colloidal particles.

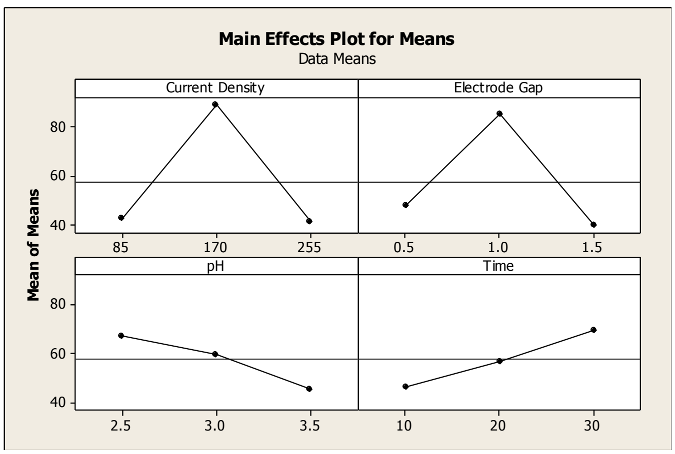


Fig 1The effects of experimental parameters on the S/N ratio for phosphate removal

The phosphate removal efficiency increases initially as the time increases then decreases. Ions concentration and their hydroxide flocs increase when the electrolysis time increases. The phosphate removal efficiency increases with current density and then decreases gradually. The increase in removal efficiencies as a result of an increase in current density can be explained by an increase in anode dissolution of metal electrodes and thus in floc formation at high current densities. According to Faraday's law, when current density increases, the amount of ion generated on the electrodes increases. Thus it causes an increase in floc formation and pollutants removal gets increased. In addition, it was established that the rate of bubble generation increases and the bubble size decreases with increasing current density. Both of these trends are beneficial in terms of high pollutant removal efficiency by H_2 floatation [4]. Increasing the spatial separation of electrodes reduces metal removal due to a decrease in current flow and coagulant generation. An optimal distance of 1 cm for removal of phosphate was identified. For later experiments, the electrode separation value of 1cm cm was used. This procedure promotes competition for the metallic cations between the generated coagulant agent and the cathode. Varying the intensity of the electric field causes opposite effects. If electric field intensity is increased, electrostatic attraction also increases and metal removal diminishes. Conversely, when field intensity is reduced, cathode attraction decays, thus increasing phosphate removal [5].

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 using the multiple linear regression models. The regression equations developed for phosphate removal is (2):

% phosphate Removal = 109 - 0.008 Current Density - 8.0 Electrode Gap - 21.7 pH + 1.17 Time (2)

The predicted values of the responses obtained using optimized parameters can be computed using the above equation. This equation considers only the significant parameters. The predicted and the actual values obtained as a result of the confirmation test is given in Table 4.

Table 4 Results of Confirmation experiment

Sample	pH	Time (min)	Electrode Gap (cm)	Current Density(A/m^2)	Phosphate Removal %	
					Actual	Predicted
Synthetic	2.5	30	1	170	80.45	80.49

For electrocoagulation process the actual values from the conformation test for phosphate removal is 80.45% for synthetic effluent. The predicted results for phosphate removal is 80.49%.Therefore the experimental results obtained under optimized conditions were close to the predicted results.

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 5.

Table 5 Characteristics of waste water before and after treatment using Steel electrodes

Parameter	Before Treatment	After Treatment
pH	9.85	9.66
Conductivity(mS/cm)	5.48	0.211
TDS(mg/L)	3106	108
COD(mg/L)	352	108
Nitrate(mg/L)	115	85.58
Phosphate(mg/L)	66	13.86
TSS(mg/l)	1528	600

The phosphate removal % obtained for original waste water was 79%, which is close to the predicted result. After the electrocoagulation process using steel electrodes only certain parameters like COD, phosphate and TDS 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 5.

Table 5 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 settled sludge is obtained as 80ml/l. Suspended solid concentration was obtained as 540mg/l. Thus a value of 148 is obtained for sludge volume index. Hence settling characteristics of the electrocoagulated sludge was good and results in low 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.

International Journal of Advanced Technology in Engineering and Science
Vol. No.5, Issue No. 05, May 2017
www.ijates.com
ijates
ISSN 2348 - 7550

So both energy and electrode consumption costs are taken into account as major cost items. Calculation of operating cost is expressed as (3) :

Operating cost= X $Energy_{consumption}$+Y $Electrode_{consumption.}$ (3)

Where $Energy_{consumption}$ and $Electrode_{consumption.}$ are consumption quantities per m^3 of treated waste water[4] . Unit prices, X and Y, given for the Indian market 2015, are electrical energy price Rs 5.95/kWh, electrode material price Rs 41/Kg for mild steel . The energy consumption (kWh) in the process was calculated according to the following equation (4):

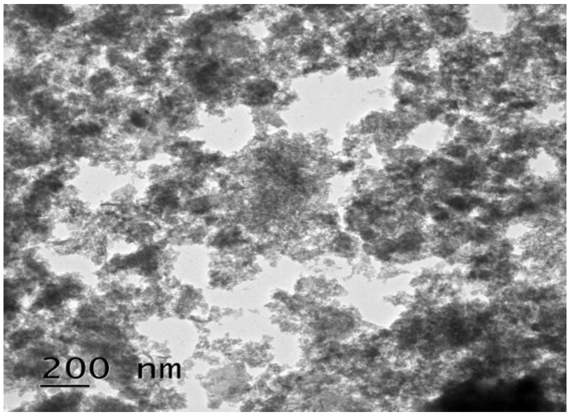
Energy= Current x Voltage x time (h) 10^{-3} (4)

Electrode consumption is the decrease in amount of the sacrified electrode before and after electrocoagulation.

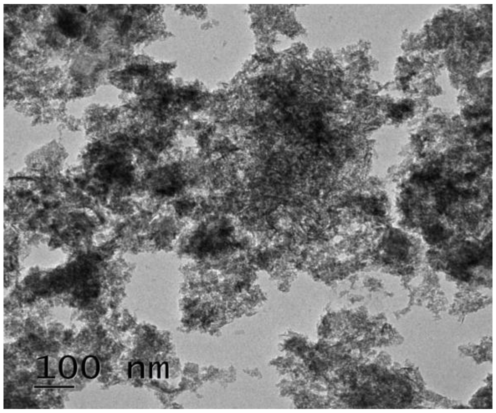
In this study the enegy consumption per m^3 for the optimum run of electrocoagulation (Current- 1A, Voltage 7V and time 30 min) was 4.375 kWh. The electrode consumption for 800 ml effluent was 0.862 g for the optimum run and thus electrode consumption per m^3 was 1.0775kg.The energy consumption costs and material costs are Rs.26.03 and Rs.44.17 respectively.

3.3. Characterization using TEM

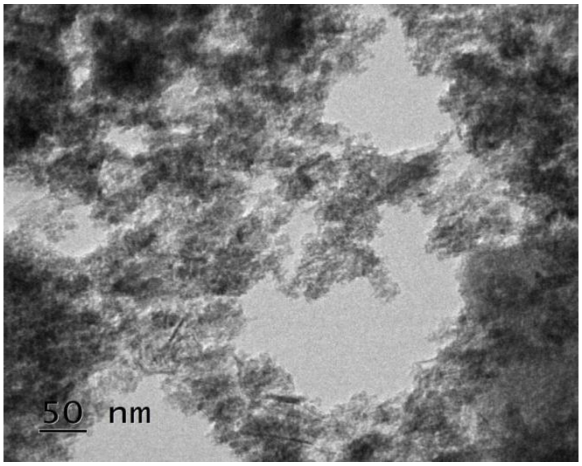
Fig. 2 shows TEM photographs as well as the corresponding size distributions of the biggest and the smallest particles obtained. The observed size decreases as the current density is increased. This is an expected result, previously found and explained for other metals [6].



Current density=63.75 A/m²



Current density=127.5 A/m^2



Current Density=191.25A/m^2

Fig 2 TEM images and size distribution of sediment by electrolytic process with steel electrode at various current densities.

The results clearly show that the particle size of the steel-phosphorous clusters can be controlled by variation of the current density, which directly influences the reduction potential at the cathode. The higher the current density, the higher the over potential, which is defined as the deviation of the reduction potential from the equilibrium potential. With increasing current density and therefore over potential, the particle size of the colloid decreases.

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 steel electrode was analyzed. The percentage removal obtained for TDS, COD, Nitrates, Phosphates were 96.52, 69.31, 25.86 and 93.24 respectively by steel electrodes. The parameters of the effluent COD and phosphate only met the relevant Indian dischargre standards for steel electrodes.

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.70.2 .The volume of sludge obtained for the process using steel electrodes was 80ml/l and the SVI was 148 ml/g, which showed that the settling characteristics of the sludge was good.

V ACKNOWLEDGEMENT

The authors wish to thank the Govt. Engineering College, Trichur, Thrissur, Kerala where the study was conducted.

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