INTRODUCTION

The Peruvian anchovy (*Engraulis ringens*) is mainly used as a raw material in the production of fish flour. This industry utilizes significant volumes of water and generates abundant quantity of wastewater [Putra et al., 2020; Omil et al., 1996]. Dispatching fish from ships to flour factories involves using sea water as the transportation fluid. This water is known as “pump water,” and it is an effluent containing around 3.5% of organic matter, either as dissolved solids, suspended solids, or oils and fats [Espinoza, 2016]. Before being discharged into the sea, pump water is usually treated to decrease its organic matter content and consequently, prevent environmental pollution. In this regard, the Peruvian Ministry of Environment has issued guidelines for the management of these sewage waters, fixing the maximum allowed content for suspended solids at 700 ppm and for oils and fats at 350 ppm [Ministry of Environment, 2018].

Presently, pump water is treated with coagulants and flocculants to reduce the concentration of organic matter to comply with the environmental regulations [Loza Pacheco, 2014]. This treatment reports a removal efficiency of 85.8% and 99.2% for TSS and fats, respectively [Cristóvão et al., 2014]; however, this treatment process increases the concentration of inorganic salts in
the treated water and favors the buildup of salts in solids [Espinoza Villegas, 2016], thereby restricting the possibility of using it as animal feed or fertilizer.

As part of the search for more affordable technologies for treating the effluents of fishing industries, there have been reports on treatment processes in continuous flow aerobic bioreactors that attain chemical oxygen demand (COD) of 86% and TSS removal efficiency of 37% [Ching and Redzwan, 2017] as well as in anaerobic reactors with COD removal efficiencies of up to 94% [Putra et al., 2020]. The technologies using aerobic or anaerobic bioreactors are both affordable and ecofriendly, but they require long treatment times to reach maximum pollutant removal efficiency; hence, they are hardly scalable for pump water flows of approximately 200 m$^3$/hour from fish flour factories [Espinoza Villegas, 2016].

Electrocoagulation is one of the alternative technologies applied to different types of wastewater and offers advantages, such as low-cost installation and operation, a lower production of sludge volumes, [Elkacmi et al., 2020], high removal efficiency, no requirement of additional chemicals, and shorter treatment times. [Castañeda et al., 2020]. This technology is an electrochemical process, whereby two electrodes, called anode and cathode, receive electrical current supply [AlJaberi, 2019]. It is from the anode or sacrificial electrode (usually made of aluminum or iron), where metallic cations are generated and hydrolyzed in situ to form coagulants [Rodriguez et al., 2010], which agglomerate colloidal particles. This process separates pollutants through flotation and precipitation due to the small hydrogen bubbles generated by the cathode [Akansha et al., 2020].

The electrolytic process with aluminum (Al) electrodes as the anode and cathode thereby produce controlled quantities of coagulants through the following reactions:

Anode \[ \text{Al} (s) \rightarrow \text{Al}^{3+} + 3e^- \] (1)

Cathode \[ 3\text{H}_2\text{O} + 3e^- \rightarrow \frac{3}{2}\text{H}_2(g) + 3\text{OH}^- \] (2)

The resulting $\text{Al}^{3+}$ and $\text{OH}^-$ ions react to form many monomeric species, which eventually form aluminum hydroxide [$\text{Al(OH)}_3$]. [Nawarkar and Salkar, 2019] in concentrations that are dependent on the current intensity and treatment time.

\[ \text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ \] (3)

The formed $\text{Al(OH)}_3$ absorbs and agglomerates the colloidal particles for subsequent flotation and precipitation [Nidheesh, 2020; Mollah et al., 2004]. The retrieved solids contain aluminum originating from the sacrificial electrode, although in lower concentrations, given the control of current and treatment times of the electrocoagulation process.

There have been several reports on utilization of electrocoagulation for the treatment of wastewater with high organic content [Azarian et al., 2018; Mores et al., 2018]; however, this technology has not been tested in sea wastewater such as pump water, which has higher ionic content due to dissolved salts (3.5%) and high content of organic matter. Moreover, using chemicals in the treatment of pump water from fishing industries results in negative impact on treatment costs and retrieval of low-quality solids (sludge) with high metal content and low value, which limits its application. In view of these issues, this study aims at assessing the efficiency of electrocoagulation for the removal of TSS from pump water resulting from fish flour industries and optimizing the abovementioned process using Response Surface Methodology (RSM).

**MATERIALS AND METHODS**

**Pump Water**

Pump water collected from a fishing industry was used to mimic real treatment conditions. In general, most plants use sea water to transport fish.

| Parameter          | Unit | Value   |
|--------------------|------|---------|
| Initial TSS        | mg/L | 12,360  |
| Oils and fats      | mg/L | 520     |
| pH                 | --   | 6.13    |
| Conductivity       | mS   | 40.10   |
| Initial turbidity  | NTU  | 9,260   |
| BOD                | mg/L | 8,290   |
| COD                | mg/L | 32,971  |

Table 1. Chemical and biological characteristics of the effluent
Sea water has high concentration of salts, which leads to its high conductivity, a parameter directly affecting the electric current. (see Table 1).

**Electrocoagulation Reactor**

A transparent acrylic batch reactor with dimensions of 20 cm × 30 cm × 35 cm (width, length, and height, respectively) was used, with a capacity for treating 10 L of wastewater. A total of 10 aluminum electrodes were used (5 as the anode and 5 as the cathode), whose size was 10 cm in width and 10 cm in length, thus covering an area of 100 cm². A considerable volume was available for sludge collection, given the accumulation of significant amounts of such sludge in the reactor. Figure 1 below illustrates the electrode configuration in the reactor.

**Experimental Tests**

Two factors were considered in the experimental pump water tests: current intensity and treatment times. This was done in three stages at current intensities of 7, 10, and 13 A and the samples were taken at 0, 20, 30, and 40 minutes. DR1900 Hach portable spectrophotometer was used to measure the TSS concentration. The removal percentage of total suspended solids (TSS) was determined using equation (4), as shown below:

\[
y = \%R = \left( \frac{[\text{SST}_f] - [\text{SST}_i]}{[\text{SST}_i]} \right) \times 100
\]

where: \(\%R\): Removal Percentage of TSS,  
[\(\text{SST}_f\)]: Final concentration of TSS,  
[\(\text{SST}_i\)]: Initial concentration of TSS

**Sludge Analysis**

The sludge collected during electrocoagulation had liquid consistency and was centrifuged at 3000 g for 20 minutes, before disposing the supernatant. The resulting precipitates were dried at 70°C for 16 hours in a forced air convection heater and dust ground for analysis. The ash content was determined by following FAO recommendations [Food and Agriculture Organization of the United Nations, 1986], in a muffle furnace at 500 °C until constant weight; sodium chloride (NaCl) by argentometry using an automatic titrator (Easy Cl Titrator de Mettler Toledo); phosphorus (P) using the 965.17 Association of Official Analytical Chemists (AOAC) photometric technique; potassium (K), iron (Fe), and zinc (Zn) using Atomic Absorption spectrometry (AA) 975.03 AOAC acetylene air flame; and Al was quantified by AA, as per the instructions of the Perkin Elmer equipment, using a nitrous-acetylene oxide torch on diluted ashes in 1 N hydrochloric acid (HCl).
Experimental Design using Response Surface Methodology (RSM)

RSM was used, based on a full $3^k$ factorial design, with two factors [electrical current intensity ($x_1$) and treatment time ($x_2$)] and three levels ($-1$, $0$, $+1$) (see Table 2). Nine experiments were performed with their nine replicates and two core points. RSM is composed of mathematical techniques applied for the improvement and optimization of complex systems [Choi et al., 2020; Basri et al., 2007]. This method is used to assess the effects of different parameters and their interactions in the response of the system. [Choi et al., 2020; Xu et al., 2015].

Equation (5) denotes the second order polynomial equation used in RSM, which evaluates each of the independent variables at its three levels.

$$y_i = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j$$

where: $y_i$ is the response variable; $x_i$ and $x_j$ are the independent variables; and $b_0$, $b_i$, $b_{ii}$ and $b_{ij}$ are the compensation terms, linear coefficients, quadratic coefficients, and interaction coefficients, respectively [Khan et al., 2019]. Design Expert 11.1 software was used to assess the interaction between the factors and the response variable as well as to obtain the analysis of variance (ANOVA) at 95% confidence level.

RESULTS AND DISCUSSION

Results from the RSM

Table 3 contains the $3^k$ factorial response surface design, considering the factors, current intensity ($x_1$) and treatment time ($x_2$) with the mentioned 3 levels over 20 experiments. Using multiple regression analysis, the response ($y$) was correlated with the design factors ($x_1$, $x_2$) using the second order polynomial [see equation (5)].

To assess the significant variables, the p and F values of the response variables, using ANOVA, are shown in Table 4. The results indicated that current intensity ($x_1$) and treatment time ($x_2$) had a significant impact at 95% confidence level ($p < 0.05$) on the TSS removal. A model value of F of 32.89 and a probability $>F$ of less than 0.0001 implies that this model is statistically significant. The high values of $R^2$ close to 1 reveal a satisfactory agreement between the results obtained and those predicted [Sefatjoo et al., 2020; Dil et al., 2019]. The quadratic regression model for TSS removal ($y$), in terms of the coded factors, is shown in Table 5.

Figure 2 indicates the predicted values versus experimental values obtained for TSS removal. The resulting data points were observed to be well distributed near a straight line, thereby indicating a good correlation. Figure 3 depicts the three-and two-dimensional response surface graphs, in terms of two independent factors, which provide a clearer understanding of the primary effects of the interaction. [Dil et al., 2019].

Optimization of Electrocoagulation for TSS removal

One of the main objectives of this study was to find the optimal parameters for maximization of TSS removal. For this purpose, the variables, current intensity and time, were optimized using RSM to obtain maximum efficiency for TSS removal. The optimal values obtained for the current intensity and time were 13 A and 30 minutes, respectively, which resulted in a maximum TSS removal of 99.9%. The experimental value of TSS removal using the optimal conditions was 98.36%, which is extremely close to the optimized value and, hence, confirms the importance of the model.

Effect of Current Intensity

The efficiency of contaminant removal through electrocoagulation is directly proportional to the current intensity, as explained by the Faraday’s Law [Azarian et al., 2018; Nariyan et al., 2017]. Generally, on increasing the current intensity, the removal efficiency is also increased.
Current intensities of 7, 10, and 13 A were used over a fixed surface area of 100 cm$^2$ of the aluminum electrodes, connected in parallel. In Figure 3 a) and b) it can be observed that the TSS removal efficiency increases rapidly as the current increases from 7 to 10 A. The corresponding removal percentage increases from 67% to 88%, respectively. On the contrary, when the current intensity increases from 10 to 13 A, the removal percentage only increases slightly.

Similar results were obtained by [AlJabery et al., 2020] and [Karichappan et al., 2014], indicating a rapid increase in TSS removal as the current increases. This is explained by the increase of the Al$^{3+}$ cations and the consequent Al(OH)$_3$ particles released by the anode when the current density increases [Deveci et al., 2019; Deghles and Kurt, 2016]. However, the application of a high current intensity can cause a decrease in the removal efficiency [Holt et al., 2002]. This may be attributed to the observation that the rate of hydrogen gas released from the cathode increases despite the increase in the amount of Al delivered to the medium. As the amount

| Table 3. Experimental design |
|---------------------------------|
| | Current intensity (A) | Time (minutes) | TSS removal (%) |
| Run | Block | Levels | $X_1$ | $X_2$ | Experimental | Predicted |
| 1 | 1 | -1 | -1 | 7 | 20 | 61.00 | 65.89 |
| 2 | 1 | 0 | -1 | 10 | 20 | 82.00 | 81.88 |
| 3 | 1 | 1 | -1 | 13 | 20 | 97.00 | 94.73 |
| 4 | 1 | -1 | 0 | 7 | 30 | 97.00 | 90.55 |
| 5 | 1 | 0 | 0 | 10 | 30 | 98.00 | 99.56 |
| 6 | 1 | 1 | 0 | 13 | 30 | 99.00 | 96.39 |
| 7 | 1 | -1 | 1 | 7 | 40 | 98.00 | 98.54 |
| 8 | 1 | 0 | 1 | 10 | 40 | 99.00 | 99.55 |
| 9 | 1 | 1 | 1 | 13 | 40 | 99.00 | 103.38 |
| 10 | 1 | 0 | 0 | 10 | 30 | 99.00 | 98.54 |
| 11 | 2 | -1 | -1 | 7 | 20 | 63.00 | 64.89 |
| 12 | 2 | 0 | -1 | 10 | 20 | 84.00 | 80.88 |
| 13 | 2 | 1 | -1 | 13 | 20 | 95.00 | 93.73 |
| 14 | 2 | -1 | 0 | 7 | 30 | 94.00 | 89.55 |
| 15 | 2 | 0 | 0 | 10 | 30 | 96.00 | 98.56 |
| 16 | 2 | 1 | 0 | 13 | 30 | 97.00 | 98.55 |
| 17 | 2 | -1 | 1 | 7 | 40 | 96.00 | 97.54 |
| 18 | 2 | 0 | 1 | 10 | 40 | 97.00 | 102.38 |
| 19 | 2 | 1 | 1 | 13 | 40 | 99.00 | 95.39 |
| 20 | 2 | 0 | 0 | 10 | 30 | 98.00 | 97.54 |

| Table 4. Statistical analyses of variance using the Response Surface Methodology (RSM) Quadratic Model |
|---------------------------------|
| Source | Sum of Square | df | Mean Square | F | p |
| Block | 5.00 | 1 | 5.00 |
| Model | 2267.57 | 5 | 453.51 | 31.32 | <0.0001 |
| $X_1$: Current intensity (A) | 494.08 | 1 | 494.08 | 34.12 | <0.0001 |
| $X_2$: Time (min) | 936.33 | 1 | 936.33 | 64.67 | <0.0001 |
| $X_1X_2$ | 512.00 | 1 | 512.00 | 35.36 | <0.0001 |
| $X_1^2$ | 11.52 | 1 | 11.52 | 0.79 | 0.3885 |
| $X_2^2$ | 285.48 | 1 | 285.48 | 19.72 | 0.0007 |
| Residual | 188.23 | 13 | 14.88 |
| Lack of Fit | 185.73 | 11 | 16.88 | 13.51 | 0.0709 |
| Pure Error | 2.50 | 2 | 1.25 |
| Cor Total | 2460.80 | 19 |

$R^2 = 92.34\%; R^2_{adj} = 89.39$
of hydrogen bubbles increases, they stick more readily to the crystals of the coagulant and are rapidly deposited on the reactor surface by flocculation [Bayar et al., 2011]. This causes flocculation and does not allow the coagulant to be mixed with the contaminants for removal. Furthermore, the efficiency of the current intensity is directly related to the pH. At low pH values, an increase in current intensity causes efficiency to decrease [Deveci, 2019; Phalakornkule et al., 2010]. Hence, electrocoagulation using aluminum electrodes should be operated under neutral or higher conditions to obtain optimal results [Deveci et al., 2019; Adhoum et al., 2004].

**Effect of Treatment Time**

The increase in the reaction time is directly proportional to the removal of the contaminant. As it may be observed in Figure 3, TSS removal efficiency increases as the treatment time increases to 30 minutes. Thereafter, removal efficiency tends to be constant. This is consistent with the findings of [Saad, 2019] and [Al-Qodah, 2018], who asserted that removal tends to be constant after 28 minutes, because the rate of generation of cationic metal ions increases with increasing reaction time, which implies an improvement in the efficiency of removal of the contaminant [Priya and Jeyanthi, 2019; Nawarkar and Salkar, 2019]. However, long reaction time accelerates the reaction and destabilizes the colloids that eventually reduce the zeta potential of the particles. This zeta potential should be close to zero to achieve maximum efficiency for the removal of the contaminants [Priya and Jeyanthi, 2019]. At the same time, OH⁻ ions are produced at the cathode, which increases with increase in reaction time, resulting in the formation of aluminum–hydro complexes and flocs [Montero et al., 2007]. A prolonged reaction time influences the loss of mass of the electrode and the cost of the process; hence, there is a need to determine the optimal time for the treatment.

**Effect on the Sludge Obtained**

The ash content in the sludge is around 20%, and a third of it comprises salt from the seawater used for pumping and is directly related to the amount of salt water that was not removed during centrifugation and is trapped in the precipitate. The higher current intensity associated with the longer treatment time could carry over some metal compounds into the already formed sludge. The contents of Fe, K, Zn, and P in the sludge were not significantly different among the several treatment processes, although it is noteworthy that lower currents coincided with lower concentrations of the metals (see Table 6). On the other hand, the concentration of Al in the sludge clearly increased due to the formation of salts from the sacrificial electrode, and this concentration had a direct relationship with both the current intensity and time for electrocoagulation. The concentration of Al in the sludge must be taken into account

**Table 5. Statistical parameters obtained using RSM for total suspended solids (TSS) removal (%)**

| Response          | R² (%) | Adj – R² (%) | p     | Quadratic model for response based on least squares |
|-------------------|--------|--------------|-------|---------------------------------------------------|
| TSS removal (%)   | 92.34  | 89.39        | 0.0000| $y = -115.73 + 13.3929x_1 + 8.17857x_2 - 0.266667x_1x_2 - 0.162698x_1^2 - 0.0771429x_2^2$ |

(TSS removal, %); $x_1$ (Current intensity, A); $x_2$ (Time, min)
when considering a possible use of the sludge as feed or fertilizer, because of the toxicity associated with the innate metal [Vitorello et al., 2005].

**CONCLUSIONS**

This study proved that electrocoagulation using Al electrodes is effective in removing TSS from pump wastewater generated in the processing of fishmeal. Analysis of the experimental design indicated that the current intensity and treatment time influenced the removal of TSS. The value of $R^2$ obtained for TSS was 92.32%, which indicates good conformance with the second order regression model. The optimal operating conditions for TSS removal were $I = 13$ A and $t = 30$ minutes. Using these conditions, 99.9% removal efficiency for TSS was obtained. However, it should also be noted that the Al content in the sludge increased in treatment processes at higher current intensities over longer time.

### Table 6. Dry content of ash, salts, and metals in sludge from electrocoagulation of pump water

| Run | Block | Current intensity (A) | Time (min) | Ashes% (dry content) | NaCl% (dry content) | Al% (dry content) | Fe% (dry content) | K% (dry content) | Zn ppm (dry content) | P% (dry content) |
|-----|-------|-----------------------|------------|-----------------------|---------------------|------------------|-----------------|----------------|---------------------|-----------------|
| 1   | 1     | 7                     | 20         | 19.00                 | 6.55                | 1.88             | 0.34            | 0.41           | 240                 | 2.56            |
| 2   | 1     | 10                    | 20         | 29.67                 | 6.55                | 1.95             | 0.33            | 0.42           | 261                 | 2.37            |
| 3   | 1     | 13                    | 20         | 19.03                 | 6.11                | 1.77             | 0.31            | 0.40           | 259                 | 2.27            |
| 4   | 1     | 7                     | 30         | 19.37                 | 6.33                | 1.92             | 0.33            | 0.41           | 264                 | 2.65            |
| 5   | 1     | 10                    | 30         | 20.05                 | 6.99                | 1.78             | 0.30            | 0.42           | 269                 | 2.65            |
| 6   | 1     | 13                    | 30         | 19.27                 | 6.21                | 1.67             | 0.31            | 0.38           | 256                 | 2.12            |
| 7   | 1     | 7                     | 40         | 20.09                 | 6.13                | 2.01             | 0.31            | 0.40           | 260                 | 2.65            |
| 8   | 1     | 10                    | 40         | 20.04                 | 6.26                | 2.03             | 0.30            | 0.40           | 267                 | 2.37            |
| 9   | 1     | 13                    | 40         | 20.12                 | 6.24                | 2.01             | 0.30            | 0.41           | 250                 | 2.37            |
| 10  | 1     | 10                    | 30         | 21.00                 | 6.05                | 2.14             | 0.29            | 0.40           | 247                 | 2.46            |
| 11  | 2     | 7                     | 20         | 19.29                 | 6.92                | 1.53             | 0.31            | 0.40           | 224                 | 2.06            |
| 12  | 2     | 10                    | 20         | 11.97                 | 7.00                | 1.86             | 0.34            | 0.45           | 255                 | 2.44            |
| 13  | 2     | 13                    | 20         | 17.30                 | 6.01                | 1.55             | 0.36            | 0.36           | 278                 | 2.05            |
| 14  | 2     | 7                     | 30         | 21.38                 | 6.66                | 1.84             | 0.25            | 0.44           | 256                 | 2.53            |
| 15  | 2     | 10                    | 30         | 22.79                 | 7.48                | 1.56             | 0.22            | 0.42           | 309                 | 2.30            |
| 16  | 2     | 13                    | 30         | 18.72                 | 6.14                | 1.35             | 0.28            | 0.35           | 212                 | 1.90            |
| 17  | 2     | 7                     | 40         | 20.71                 | 5.74                | 2.00             | 0.28            | 0.39           | 263                 | 2.39            |
| 18  | 2     | 10                    | 40         | 20.30                 | 5.42                | 2.28             | 0.37            | 0.41           | 207                 | 2.58            |
| 19  | 2     | 13                    | 40         | 20.55                 | 7.02                | 2.02             | 0.24            | 0.41           | 250                 | 2.19            |
| 20  | 2     | 10                    | 30         | 23.00                 | 5.92                | 2.59             | 0.30            | 0.42           | 243                 | 2.58            |
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