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Original Article

Protein removal from fish mince washwater using ohmic heating

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Abstract

A static ohmic heating system was developed to remove protein from fish mince (threadfin bream) washwater collected from a surimi production plant in order to improve water quality. The samples were heated under different electric field strengths (EFS, 20, 25, and 30 V/cm) until reaching the desired temperature (50, 60, and 70°C), and further held at that temperature for a certain time (0, 15, and 30 minutes). Heating the samples to 70°C resulted in a better protein removal when compared to 50 and 60°C. After heating to 70°C, the samples were centrifuged. The analysis of the supernatant obtained shows the reduction of protein, COD, BOD, TS, and TDS to 42%, 25%, 23%, 44%, and 61%, respectively. The electrical conductivity of the samples showed a linear relationship with temperature and the temperature demonstrated a parabolic relationship with heating time. EFS and holding time have no significant effect on protein removal.

Keywords: electrical conductivity, ohmic heating, protein, surimi, wash-water, waste recovery

1. Introduction

Production of surimi requires a number of washing processes in order to remove undesired organic substances from fish mince. Proteins, fats, and other organic substances contained in wastewater result in high values of chemical (COD) and biochemical oxygen demand (BOD), which have an impact on the environment, and incur high costs for water treatment. A general water treatment method using microorganisms is simple, but requires a large area and a lengthy period of time. This might limit the production capacity if land resources are limited.

It is known that protein in water becomes coagulated under heating. Ohmic heating is a method to heat materials by the passage of electrical energy through them. Typically, the substance is placed in a cell that is electrically connected to the power supply. The power supply will generate electric field strength (EFS) across the cell. Typically, the EFS determines how fast the heating rate is. Stronger EFS means higher heating rate. During heating, an electric current flows into the substance via the electrodes. Because of the internal resistance of the substance, the electrical energy is converted to heat energy. Under conventional methods, heating occurs from a heated surface to interior locations. However, in ohmic heating, heat is generated internally due to its internal resistance, as mentioned above, so the subject is heated quickly and uniformly (Maneeyen, 2004). Other advantages of using ohmic heating are: it requires a simple system and low capital investment; it offers clean technology since no chemical additives are used in the process; it is a highly energy-efficient method (Huang *et al.*, 1997).

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Threadfin bream (*Nemipterus spp.*), a demersal fish, has been one of the important raw materials in Thai surimi production for several years. The surimi obtained is white, providing smooth texture with a good flavor and strong gel-formability (Holmes *et al.*, 1992; Morrissey and Tan, 2000). In Thailand, 102, 121, and 113 thousand metric tons of threadfin bream were caught from the Gulf of Thailand and the Indian Ocean in 2000, 2002, and 2003, respectively (Department of Fisheries, 2003-2005). These numbers reflected the rising demand for using threadfin bream in the production of fish products, including surimi. Studying the properties of fish mince wash-water from threadfin bream by using ohmic heating became of interest since there is only limited information available and it was considered that ohmic heating might be an alternative for wastewater treatment for Thai surimi production plants, especially small to medium size factories, due to its simplicity and low investment costs.

The objectives of this research were to develop a static ohmic heating system and to apply the system to remove protein from fish mince washwater collected from a local surimi production plant. The effect of EFS, temperature, and holding time on the recovery of protein, as well as the relationship between the electrical conductivity and temperature were investigated for the further development of a continuous ohmic heating system in the future.

2. Material and Methods

2.1 The ohmic heating system

The static ohmic heating system consisted of an ohmic cell, an ordinary manual on-off variable transformer (0-240 Volts), a digital recordable power meter (Yokogawa model WT110), and a mercury thermometer. The ohmic cell (see Figure 1) was made from an acrylic tube with a length and internal diameter of 300 mm and 50 mm, respectively. Two circular 316 stainless steel electrodes (50 mm diameter) were fixed at each side of the cell with the distance of 75 mm between each other. A removable plug was used as a guide for a thermometer, which can be removed during filling of the sample. A variable transformer was used to generate the desired EFS (10, 20 and 30 V/cm), and a digital meter was used to record the voltage across the cell and the electric current every 10 seconds.

2.2 System accuracy

The system accuracy was verified by using standard solution of 0.1M NaCl with a working temperature ranged from 20 to 70°C. The experiments were conducted two times, including one replication.

2.3 Sample collection

The fish mince washwater was obtained from a surimi production plant in Samuthsakorn Province. The factory purchased threadfin bream from a domestic supplier. Most of the fish were caught from the Gulf of Thailand during October 2006 and February 2007. The sizes of fish varied from approximately 10 to 30 units per kilogram. Whole threadfin breams were headed, gutted, washed, and minced through the meat-bone separator before being washed in the first washing tank, and subsequently dewatered and washed in other washing tanks following production standards. In this experiment, the washwater from the first washing tank was collected, filled in plastic bottles and kept cool in a foam box containing ice during transportation to the laboratory. The experiment was performed within two hours after the sample was collected.

2.3 Ohmic heating experiment

In each experiment, the sample, having a temperature of 8-10°C, was poured into the cell until the cell was flooded with a small amount of sample to allow air bubbles that occurred during pouring to float to the surface. The excess sample and air bubbles were removed by using a syringe to ensure the precision of the electrical conductivity measurements. Then the plug was put onto the cell (see Figure 1) and the thermometer was attached to the plug to measure the sample temperature. The sample was then left at room temperature (~30°C) for a few minutes until the temperature rose to about 16-18°C, which is close to the temperature of the wastewater outside the factory. After that, the sample was heated under the specific EFS, with 10, 20, and 30 V/cm, until reaching the desired temperatures, 50, 60, and 70°C. Then the variable transformer was turned off. During the heating process, the temperature, voltage, and current were recorded every 10 seconds. In order to study the effect of holding time, the transformer was turned on when the temperature of the sample dropped 1°C below the desired temperature, and was turned off again when the sample temperature reached the desired value, until reaching the required holding time of 0, 15, and 30 minutes. At the end of each experiment, the heated sample was centrifuged at 12,000 rpm for 10 minutes. The supernatant was collected and analyzed for the remaining protein, TS (total solid), TDS (total dissolved solid), COD, and BOD values. The experiment was repeated one time using the same parameters.

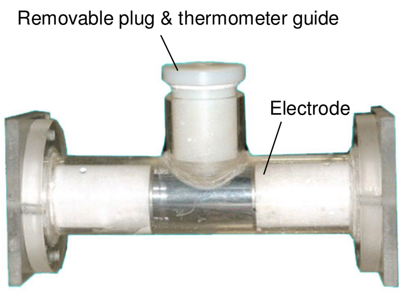

Figure 1. The static ohmic cell

2.4 Calculation of electrical conductivity

With the assumption that there is no voltage drop across the wiring and connectors in the circuit, the electrical conductivity of the washwater (s) can be calculated by using Equation (1):

$$\sigma = (I/V).(L/A) \quad (1)$$

Where "V", "I", "L", and "A" represent the voltage drop across the cell in volts, the electric current passed through the sample in amperes, the distance between two electrodes in meters, and the cross section area of the electrode in square meters, respectively.

2.5 The analysis of treated washwater

The remaining protein in the treated sample was analyzed by using a Kjeldahl analyzer with the conversion factor of 6.25, according to Association of Official Analytical Chemists (AOAC) standard method 973.48 (Association of Official Analytical Chemists, 1995). TS and TDS were measured following the American Public Health Association standard methods (American Public Health Association, 1998). COD and BOD of the samples were measured according to AOAC standard method 973.46 and 973.44 (Association of Official Analytical Chemists, 1995), respectively.

3. Results and Discussion

3.1 System accuracy

The graph between the electrical conductivity of 0.1 M NaCl and temperature is shown in Figure 2. The "σ_{exp}" represent the values of the electrical conductivity of the solution that were obtained from the experiment, and "σ_{Lobo}" is the reference value obtained from Lobo equation (Lobo, 1984). The plot indicates that the measured values at low temperatures were close to the reference values. However, when the temperature was higher, the measured values became lower. At 70°C, "σ_{exp}" was 6.3 % lower than the reference value. The difference might come from the rising internal resistance in the circuit wiring and connectors between the digital meter and the cell. The electric current passed through the circuit, wires, and connectors made from metal, resulting in heat. The internal resistance of the circuit became higher according to the temperature dependence of the resistance of the metal (Mott and Jones, 1958). These internal resistances caused an increase of the voltage drop across them, V_i, thereby reducing the voltage drop across the cell. Discrepancies in calculation of the electrical conductivity (Equation 1) occurred since the voltage read from the digital meter, which should be equal to the voltage drop across the cell, was higher than the actual value.

However, since the resistance of the fish mince washwater is approximately 4 times higher than that of the NaCl standard solution, the ratio of V_i to the voltage drop across the cell containing washwater should be theoretically 4 times lower than the ratio of V_i to the voltage drop across the cell containing NaCl solution. Therefore, the discrepancies of the measured electrical conductivity of washwater should also be 4 times lower than 6.3% at 70°C.

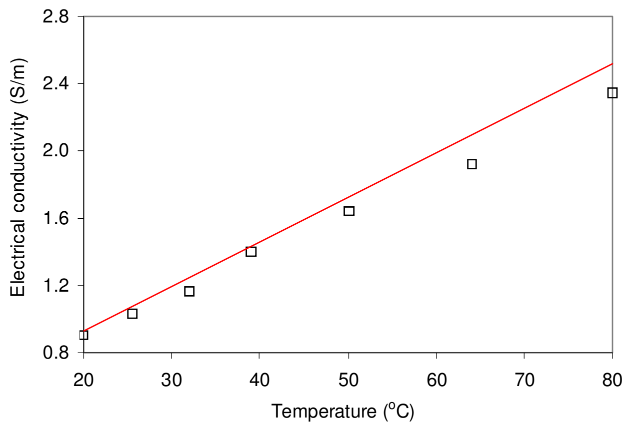

Figure 2. Electrical conductivity of 0.1 M NaCl solution obtained from: (a) --, reference values from Lobo's equation, (b) □, experiments.

3.2 Electrical conductivity of fish mince washwater

For this study, the samples were collected from a surimi plant. The initial protein concentration in each sample varied from 4.26 to 8.86 g/L. From our observation in the factory, the size of the fish used in the production varied depending on the market availability and changed from day to day, i.e., from 10 to 30 units/kg. The variety of the raw material might result in different initial protein concentrations in the collected samples. Moreover, the volume of the water used in the washing process was not strictly controlled and this would also affect the initial protein concentration. Figure 3 shows the electrical conductivity values (σ) of six samples of fish mince washwater at different temperatures. The linear relationship between σ and temperature was similar to the results found in several previous ohmic heating experiments using different food materials (e.g. Palaniappan and Sastry, 1991; Sukprasert, 1998; Zareifard *et al.*, 2003; Castro *et al.*, 2004). It was also found that the higher the initial protein concentration in the sample the greater the value of electrical conductivity. However, in the sample with a protein concentration of 5.32 g/L, the electrical conductivity was noticeably higher than that with 6.34 g/L. Although variations in the fish material related to seasonal changes might affect the electrical conductivity properties of the fish mince washwater, the main cause that had an impact on variations in the electrical conductivity would more likely be the different levels of hardness of the water used in the washing process, which was not strictly controlled in the real production situation.

In order to obtain a general equation, the characteris-

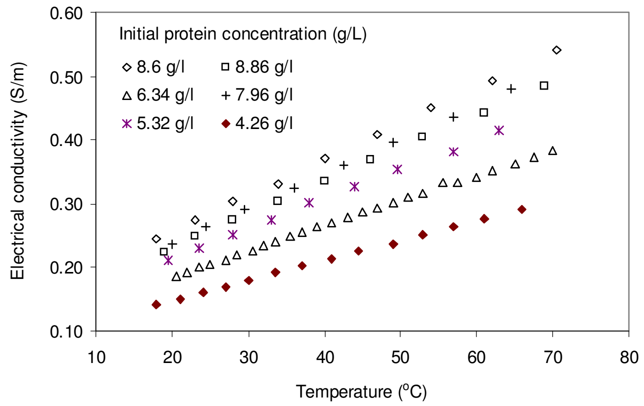

Figure 3. Electrical conductivity at 20°C of samples contained different concentrations of the initial proteins. "1" was the predicted equation.

tic electrical conductivity, σ^*, and the characteristic temperature, T^*, defined as per Equation (2-a) and (2-b), were determined.

$$\sigma^* = (\sigma / \sigma_{20}) - 1 \qquad (2\text{-a})$$

$$T^* = (T / 20) - 1 \qquad (2\text{-b})$$

where σ and σ_{20} are the electrical conductivity of the washwater at any temperature T (in degree Celsius) and at 20°C, respectively. Interestingly, it was found that independent from the initial protein concentration, the relationship between σ^* and T^* was the same as shown in Equation (3) (Figure 4). This relation was considered to be useful for the further development of the continuous ohmic heating system.

$$\sigma^* = 0.4885 T^* \qquad (3)$$

3.3 The effects of temperature on solids removal

With increasing temperature, like heating, proteins become denatured and coagulated (Volkin and Klibanov,

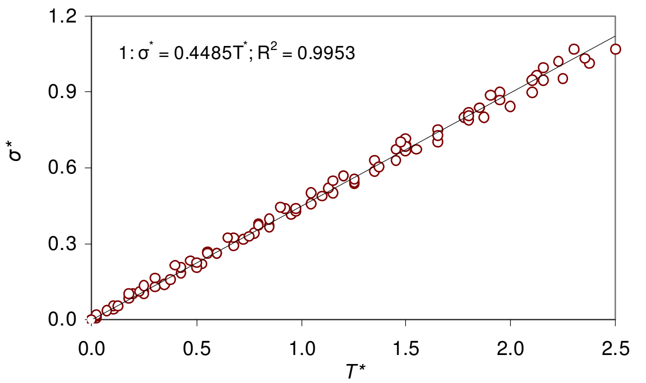

Figure 4. The plot between characteristic electrical conductivity and characteristic temperature. "1" was the predicted equation.

1990; Damodaran, 1996). Different levels of protein remain after the heating process up to the different temperatures. These remaining proteins have been centrifuged. Figure 5 shows the remaining protein in the supernatant. For the supernatant collected from a sample that was heated up to 50°C, the remaining protein was 62.59% ± 4.07%. For those heated to 60°C and 70°C, the remaining protein was reduced to 49.02% ± 4.07% and 41.90% ± 3.72%, respectively. Haard (1995) reported that only 65-75% of the sarcoplasmic proteins from demersal fishes were coagulated under heating. This was similar to the results obtained from the experiment here. It was also found that heating a sample up to 80°C reduced only slightly the amount of remaining protein compared to heating up to 70°C (38.96% and 41.90%). Huang *et al.* (1997) performed ohmic heating experiments using fish mince washwater prepared from frozen Pacific whiting fish mince and also recommended that the highest heating temperature was 70°C.

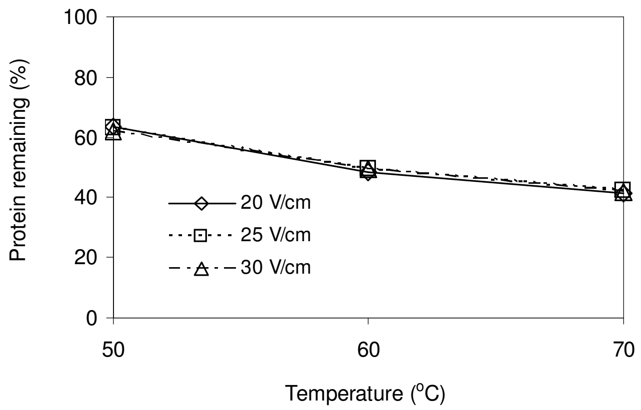

Figure 5. The remaining proteins in supernatant collected from samples after heated to 50, 60 and 70°C under the electric field strength of: Ж, V/cm; Δ, 25 V/cm; , 30V/cm.

The temperature also significantly affected the amount of the remaining COD, BOD, TS (total solid), and TDS (total dissolved solid) as shown in Figure 6 and Figure 7 (for all with a standard level of significance $p<0.05$). The initial COD values of the samples were extremely high, in the range of 6,451 to 10,477 mg/L. These values were comparable to the COD values reported by Lin et al. (1995). After ohmic heating and centrifugation, the COD values of the supernatant were reduced to 46.20%, 31.67%, and 25.03%, while the BOD values were reduced to 50.7%, 31.87%, and 23.42% after the washwater was heated up to 50, 60 and 70°C, respectively. Since BOD and COD values are the important factors that determine water quality, the use of ohmic heating can rapidly improve the surimi wastewater quality through reduction of both values by more than 75%. The reduction of BOD and COD should result in the reduction of further wastewater treatment costs. As ohmic heating requires much shorter time compared to traditional wastewater treatment, it shows a potential to be used as a wastewater pre-treatment in terms of time and cost reduction. In addition, protein recovered from the wash-water was clean, since no chemical additives were used in the process. This means that the factory could earn income from this by-product protein. However, as the electric power consumption is a major cost factor the overall obtained maximum benefit must be considered. Using ultra-filtration an 89 to 94% reduction of COD values from frozen fish mince washwater was achieved after Lin *et al.* (1995), which is higher than the reduction of COD by ohmic heating. However, ohmic heating might be one alternative of water treatment for small surimi plants, since it requires only a technological simple system and relatively low capital investment.

The amounts of 41%, 51%, and 56% of TS and 22.58%, 32.14% and 38.91% of TDS were removed after the washwater sample was heated up to 50, 60, 70°C, respectively, and then centrifuged (Figure 7). Huang *et al.* (1997) reported that 92.1% of total suspended solids were removed by using ohmic heating. This agreed with our study and indicated that there were some heat stable proteins remaining in the treated washwater, which was supported by the observation of remaining protein in the sample after it was heated up to 70°C.

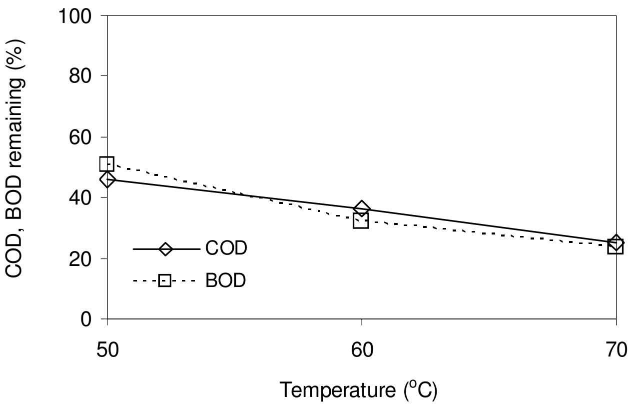

Figure 6. COD and BOD (in %) retained in supernatants collected from samples ohmically heated to 50, 60, and 70°C.

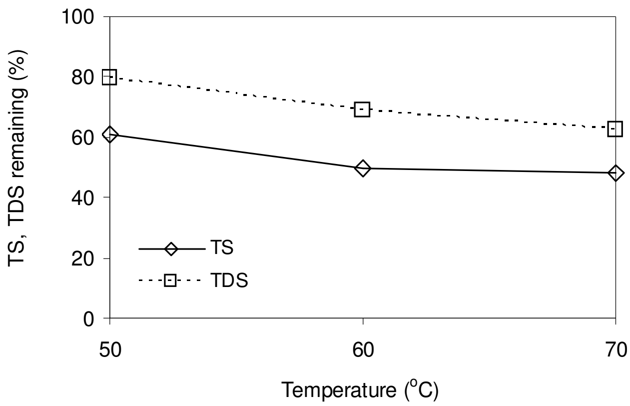

Figure 7. The remaining TS (Total Solid) and TDS (Total Dissolved Solid) in supernatants collected from samples ohmically heated to 50, 60, and 70°C.

3.4 The effects of EFS on protein removal

Even though the EFS had no significant effects on the remaining protein ($p<0.05$), it affected the heating time. The graph between the temperature of the sample under different EFS and heating time is shown in Figure 8. It clearly demonstrates that the relationship between the temperature and heating time could be explained by a parabolic model. Theoretically, with the assumption of no heat loss in the experiment, the heating rate (q) was proportional to the square of the EFS (∇V) as per Equation (4) (Sastry and Palaniappan, 1992).

$$q = (\nabla V)^2 . \sigma \tag{4}$$

Let q_{20}, q_{25}, and q_{30} represent the heating rate when the sample was heated under the EFS of 20, 25, and 30 V/cm, respectively. From Equation (4), it is expected that the ratio q_{20}/q_{25} and q_{20}/q_{30} should be equal to 0.64 and 0.44. The two values obtained from the experiment were 0.61 and 0.42, which were approximately 5% lower than the theoretical values. The differences should be the result of heat loss during ohmic heating. Under lower EFS, the heating time was longer. Longer time allowed more heat loss from the system. Consequently, the ratio of the heating rate under a lower electric field to a higher one would be lower than the theoretical value.

Although using higher EFS offered a shorter heating time, too, a higher EFS resulted in undesirable results such as burning on the electrode surface (Wongsa-Ngasri, 1999) or the occurrence of electrolytic hydrogen-gas being produced resulting in a sudden drop of the electrical conductivity (Palaniappan and Sastry, 1991). However, no such negative effects were observed using EFS of 30 V/cm. This indicated that this magnitude of EFS should be applicable to the ohmic heating of threadfin bream fish mince washwater.

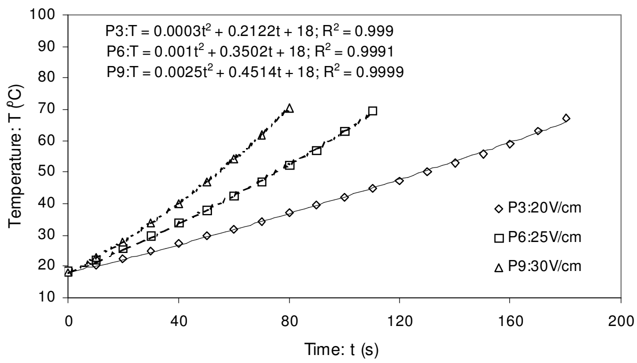

Figure 8. The effects of electric field strength on the heating time required to heat the samples from approximately 20 to 70°C: ◊, 20 V/cm; □ 25 V/cm; Δ, 30 V/cm. "3", "6", "9" were the predicted equation of temperature (T) under an electric field strength of 20, 25, and 30 V/cm, respectively.

3.5 The effects of holding time on protein removal

Holding time had no significant effects on the protein removal ($p<0.05$). However, slightly more protein was reduced (6%) after the sample was held at a constant temperature of 50°C for 15 minutes (Figure 9). At higher temperatures, the holding time did not assist in any further protein removal. Moreover, a holding time of 15 and 30 minutes resulted in the same capability of protein removal from the sample at every heating temperature. Neucere and Cherry (1982) reported a decrease in the percentage of water-soluble protein in peanut seeds under wet heating at 100°C with a holding time of 45 minutes or longer. However, since the heating at temperatures higher than 70°C did not result in an increased protein recovery, there was no useful gain to hold the washwater at a constant temperature after the reaching the designated temperature value.

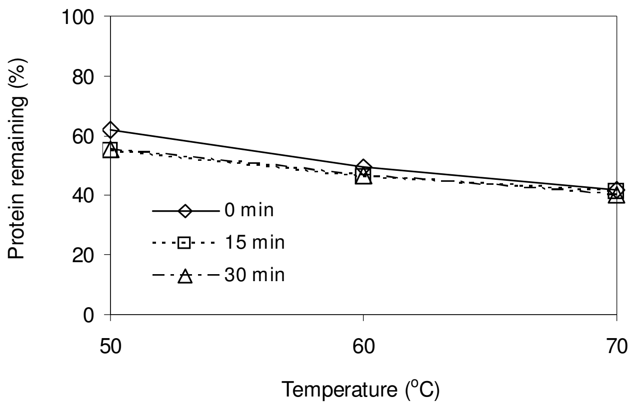

Figure 9. The amount of proteins remained in the supernatants collected from the samples heated to 50, 60, and 70°C, and held at the same temperature for a certain period of time: ◊, 0 minute; □, 15 minutes; Δ, 30 minutes.

4. Conclusion

Samples collected from a local surimi production plant were used in this study. The results reveal that the electrical conductivity depended on the initial protein concentration in the sample. Though the initial protein concentration in each sample was very different from each other and varied over a wide range, only one linear relationship between the electrical conductivity and the temperature is found, which can be described by "$\sigma^*=0.4885T^*$". After heating, the protein becomes coagulated and could be easily removed from the liquid phase. Protein in the supernatant is reduced to 62.59% ± 4.07%, 49.02% ± 4.07%, and 41.90% ± 3.72% after the samples were heated to 50, 60, and 70°C, respectively. After heating to 50, 60, and 70°C, the COD values of the supernatant were reduced to 46.20%, 31.67%, and 25.03%, the BOD values were reduced to 50.70%, 31.87%, and 23.42%, the TS was reduced to 60%, 50%, and 48%, and the TDS was reduced to 80%, 69%, and 63%, respectively. Heating time was proportional to the inverse of the square of the EFS. Heating under EFS of 30 V/cm would not result in any arcing phenomena or any drop in the electrical conductivity at high temperatures. Holding the sample at a constant temperature resulted in no further reduction of the protein content in the samples, except at 50°C. In summary, the results show the potential of using ohmic heating as a rapid method to improve fish mince washwater quality in terms of COD and BOD reduction.

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