RESEARCH ARTICLE

Characterization of pistachio processing industry wastewater and investigation of chemical pretreatment

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ABSTRACT

This study was carried out in two stages; in the first stage of the study, wastewater characterization of wastewater originating from the pistachio industry was primarily completed, and in the second stage, chemical pre-treatment studies were completed. Pistachio wastewater used in the study was obtained from a pistachio processing factory located in Gaziantep province. In chemical treatment studies, montmorillonite clay, AlCl3, Al2(SO4)3, Fe2(SO4)3 and FeCl3 were used as coagulants. As a result of chemical treatability tests, AlCl3 was determined to be the best coagulant. With AlCl3 at optimum dosage and optimum pH value, 99.6% suspended solid (SS) removal efficiency, 65.8% chemical oxygen demand (COD) removal efficiency and 85.5% total phenol (TP) removal efficiency were obtained.

Keywords: Pistachio industry wastewater, chemical treatment, coagulation, flocculation, precipitation

1. INTRODUCTION

Currently, dangerous material containing different structures and concentrations sourced in a variety of industrial and agricultural activities continuously pollute the environment. In spite of the contribution of these pollutants to modern life, most may accumulate in water, soil or air and if precautions are not taken to protect the environment and appropriate technologies are not used, an imbalance problem will occur leading to negative outcomes for the environment. Pollutants in receiving water environments may cause esthetic pollution and toxicity, just as basal accumulation may disrupt living conditions for aquatic organisms. Additionally, due to oxygen consumed by biological degradation or decomposition this may lead to dangerous situations for human groups or other living organisms using this aquatic environment. Though it appears that complete removal of environmental pollution is impossible when examined in terms of current technological and economic facilities and environmental awareness, on one hand further pollution of the environment should be prevented, while on the other it is necessary to ameliorate pollution that is present. Wastewater from the pistachio processing industry is among pollutants requiring treatment in order not to harm receiving environments in Turkey.

Pistachio processing industry wastewater is wastewater as a result of processing 10 or more species of the Pistacia genus Pistacia vera L. (pistachio). The products have commercial value and are sold as dried nuts and nuts are accepted as an edible fruit [1]. With cultivation dating to ancient times, pistachio was first cultivated by Hittites living in southeast Anatolia and is known to have spread to Rome in the 1st century and then to Spain and later France. The transition to America occurred in 1853-54 [2].

Pistachio grows in suitable microclimates at the 30-45° parallels in the northern and southern hemispheres of the earth. Countries producing pistachio globally are found in the northern hemisphere generally [3, 4, 5]. In Turkey, 94% of production comes from the southeast Anatolian region, with pistachio cultivation in 56 provinces according to latest statistics [6]. In 1990, pistachio was produced from 33 343 ha area and this reached 70 087 ha in 2018. Parallel to this increase in production area, there has been a large increase in fruit
production; production was 40,000 tons in 1990 and reached 240,000 tons in 2018 [5]. Additionally, pistachio cultivation entered a new era with the Southeast Anatolia Project (GAP). With irrigation conditions, the opportunity to cultivate pistachio developed, and new facilities will be offered in addition to present facilities and hence, production amounts will increase further in future years.

The maturity period for pistachio is the second half of August to the beginning of September in hot regions like Gaziantep and Şanlıurfa. Harvesting in these regions begins at the end of August and continues until the end of September. In Turkey, the mechanization level for pistachio harvesting and processing is at very low levels and these processes are based on hand labor.

Industries processing pistachio have variations in product amount linked to pistachio amounts in winter and summer seasons. The result of investigations and research identified that the roasting and stripping stage uses mean 100 m³ water daily and that 1 ton of pistachio produces 20 m³ wastewater. This proportion may vary linked to the size of the processing facility. Pistachio industry wastewater contains high organic matter content, organic matter with high pollutant qualities like dense suspended solids and polyphenols. Literature research revealed a limited number of studies about treatment of wastewater from industries processing pistachio [10, 11].

The coagulation-flocculation process is used for removal of ions dissolved in water, color, turbidity and suspended solid matter, harmful bacteria and proteins, material creating flavor or odor, algae and plankton during treatment of drinking water and wastewater [12]. Coagulation is fully linked to the dosage of coagulant and pH of the medium. For aluminum salts, optimum coagulation occurs at pH 5-7, while for iron salts it occurs at pH 4-10. In these types of coagulation processes, colloids are held within hydrated polymeric structures. The most commonly used coagulant in water and wastewater treatment processes is alum \((Al_2(SO_4)\cdot18H_2O)\), with alum flocs least soluble at pH 7. Below pH 7.6, flocs have positive load, while above pH 8.2 the load is negative. Iron salts are commonly used as coagulant. Insoluble aqueous iron oxide forms in the interval from pH 3-13. At acidic pH values, flocs have positive load, while at alkaline pH values flocs have negative load, with mixed loads in the interval pH 6.5-8. The presence of anions in the medium affects the degree of flocculation. Sulfate ions increase flocculation in acidic conditions, while they lower it in alkaline conditions. Chloride ions increase flocculation degree by an amount at both acidic and basic pH values [13].

This study was carried out in two stages; in the first stage of the study, wastewater characterization of wastewater originating from the pistachio industry was primarily completed, and in the second stage, chemical pre-treatment studies were completed. There are limited studies related to treatment of wastewater from industries processing pistachio in the literature. Studies about this topic will contribute to the Turkish and global literature in addition to offering a technological and economic choice for treatment of pistachio processing industry wastewater in Turkey.

2. MATERIALS AND METHODS

2.1. Chemical material, clay and wastewater

All chemicals used in the study were obtained commercially (Merck and Sigma quality). Clay used to assist coagulants and as adsorbent was natural clay from Namman county in Erzurum quarried by Anka Nanoteknoloji Ltd. The mineral was initially dried naturally, then in a 110 °C oven for 4 hours, then ground and sieved using ASTM standard sieves and clay with 0.5 mm dimensions was used in this study. Pistachio wastewater used in the study was obtained from a pistachio processing factory located in Gaziantep province.
2.2. Experimental system

The first section of the study used a jar test setup for pre-treatment. The jar test was completed with slow mixing of 25 rpm to rapid mixing of 300 rpm. For the jar test setup, each 800 mL flask contained 10% diluted pistachio wastewater and the dilution rate was noted during calculations. pH was set with NaOH and H₂SO₄. Coagulation-flocculation processes were completed with a variety of chemicals. After the precipitation process, samples taken from the supernatant portion were observed for removal of %COD, %SS and %TP of organic pollutants. The jar test setup used in the study is given in Fig 2.

Fig 2. Experiment setup

2.3. Chemical analysis

During the study, samples prepared according to methods stated in the standard methods were heated in a thermostator (WTW marka CR3000 model) for 2 hours at 148±2°C and absorbance values were read at 600 nm with a spectrophotometer (Spekol 1100, Carl Zeiss Technology) to identify COD concentrations [14]. For SS measurements, measurements were taken spectrophotometrically with a Spekol 1100 (Carl Zeiss Technology) brand spectrophotometer at 525 nm wavelength. Additionally, to confirm accuracy, measurements were taken gravimetrically as stated in the standard methods [14]. Total phenol was detected with the Folin-Ciocalteau method [15] with phenol concentration measured spectrophotometrically using the 4-aminoantiprin method [16]. NH₃ concentration was examined with a Thermo Orion brand 290 A+ ion selective electrode. Additionally, it was investigated colorimetrically with Merck brand commercial kit number 14752 with a spectrophotometer. Oil and grease measurements were performed using a ‘oil-grease petrol-hydrocarbon’ measurement device (Wilksir HATR-T2). The pH and temperature in the reactors were recorded and measured continuously with the aid of a WTW brand multiline P4 model multiparameter measuring device according to electrometric methods. According to the membrane electrode method, the dissolved oxygen amount in the sample was read by dipping the oximeter probe into the sample [14]. Nitrate and nitrite concentration measurements were taken with a Dionex ICS 3000 brand ion chromatography device. Phosphate analysis used ammonium vanadomolybdate with absorbance measurements read at 400 nm wavelength with a spectrophotometer. Total organic carbon and total nitrogen measurements were performed using a Teldyne-TeKmar Apollo 9000 TOC-TN analysis device.

3. RESULTS AND DISCUSSION

3.1. Characterization of pistachio wastewater

The results of studies found that wastewater from the pistachio industry contained high degree of pollutants and hence should definitely be treated before discharge into the receiving environment. Discharge should occur after standards for receiving environments stated in the Water Pollution Control Directive (WPCD) are met. Wastewater from the pistachio industry were obtained in two different periods and from different operations, with the analysis results for identification of pollutant parameters contained in wastewater shown in Table 1.

3.2. Chemical treatment of wastewater from pilot facility

The first procedure in the study left wastewater obtained from pistachio processing facilities to precipitate without any treatment for different durations. After the simple precipitation procedure, results for samples taken from the upper sections of the wastewater are shown in Fig 3. As seen in the graph given in Fig 3, removal efficiency rapidly increased up to 1 hour and then no particular change was observed. At the end of the first hour of the chemical precipitation procedure, SS, COD, TSS, turbidity and oil-grease removal efficiencies were 82%, 26%, 63%, 70% and 65% with these values reaching 89%, 40%, 62%, 82% and 68%, respectively, at the end of 12 hours. The obtained results show the wastewater has good simple precipitation features, and application of a preliminary precipitation procedure will have significant positive effect on the treatability of the wastewater.
Table 1. Characterization of wastewater obtained from the pistachio industry

| Parameters measured | Unit  | 1st Period | 2nd Period |
|---------------------|-------|------------|------------|
| TCOD                | mg L⁻¹ | 20 891     | 15 700     |
| SCOD                | mg L⁻¹ | 9 137      | 4 520      |
| PCOD                | mg L⁻¹ | 11 754     | 11 184     |
| SS                  | mg L⁻¹ | 9 600      | 6 100      |
| TSS                 | mg L⁻¹ | 16 384     | 11 710     |
| TOC                 | mg L⁻¹ | 3 410      | 3 225      |
| TN                  | mg L⁻¹ | 125.5      | 116        |
| BOD (Final BOD)     | mg L⁻¹ | 3 742      | 3 074      |
| Total phenol        | mg L⁻¹ | 1 750      | 354.34     |
| Phenol              | mg L⁻¹ | 52.26      | 13.45      |
| Ammonia             | mg L⁻¹ | 1.31       | 1.02       |
| Oil-grease          | mg L⁻¹ | 11.37      | 9.6        |
| pH                  | -      | 5.99       | 5.5        |
| Temperature         | °C     | 18         | 18         |
| Conductivity        | ms cm⁻¹ | 2.69       | 2.67       |
| Turbidity           | NTU   | 995        | 990        |
| Cl⁻                 | mg L⁻¹ | -          | 290.67     |
| NO₃⁻                | mg L⁻¹ | -          | 0.61       |
| SO₄²⁻               | mg L⁻¹ | -          | 37.32      |
| PO₄³⁻               | mg L⁻¹ | -          | 6.7        |
| Na⁺                 | mg L⁻¹ | -          | 337.79     |
| NH₄⁺                | mg L⁻¹ | -          | 2.58       |
| K⁺                  | mg L⁻¹ | -          | 650.8      |
| Mg⁺                 | mg L⁻¹ | -          | 24.18      |
| Ca²⁺                | mg L⁻¹ | -          | 121.127    |

Fig 3. SS, COD, TSS, turbidity and oil-grease removal efficiencies with different precipitation durations.
3.3. Effect of coagulant type on treatment efficiency

Studies investigating the effect of coagulant type on removal efficiency in chemical treatment experiments for wastewater were completed by adding different coagulant material to wastewater in reactors in the experiment system shown in Fig 2. In the experiments, 500 mL wastewater placed in 6 flasks with 800 mL volume and dosed the wastewater with the chosen coagulants. For pH setting, 1 N H$_2$SO$_4$ or 1 N NaOH was chosen. After the precipitation procedure, samples taken from the upper section of wastewater had COD, SS and TP removal efficiencies calculated. Within the scope of these experiments, montmorillonite clay, AlCl$_3$, Al$_2$(SO$_4$)$_3$, Fe$_2$(SO$_4$)$_3$ and FeCl$_3$ were used. Also, the best pH interval, optimum coagulant type and dosage were investigated.

In the first stage of the chemical coagulation study, studies were performed to determine the appropriate precipitation duration under the same conditions. In this study, 1 g L$^{-1}$ coagulant dosage was added to each jar, with the pH value of 6.5. The jars were stirred at 300 rpm for a rapid mix period of 3 minutes and it was followed by a slow mix period of 15 minutes at 25 rpm. After that, the samples were taken at different precipitation times of 30 minutes, 1 hour, 2 hour and 3 hours and analyzed for SS, COD and TP to determine the removal efficiencies. The results were shown in Fig 4.

As shown in Fig 4, at the end of the 30 min precipitation procedure, AlCl$_3$, Al$_2$(SO$_4$)$_3$, FeCl$_3$ and FeCl$_3$ can be seen to cause a significantly positive difference in turbidity. When Fig 4 is investigated, experiments performed at pH 6.5 with 1 g L$^{-1}$ coagulant dosage obtained highest removal efficiencies for SS and COD of 99.8% and 71.3% with FeCl$_3$, while highest removal efficiency for TP was determined as 81.5% with AlCl$_3$. Studies observed that high removal efficiency was observed up to 30 min; however, there was no further removal after 30 min. As a result, the ideal precipitation duration was determined as 30 min. Reduction of surface load in jar test experiments performed without the addition of coagulant material did not have repulsion potential in electrical double layer due to the presence of electrolytes with opposite charge in the medium and it is thought the desired treatment efficiency could not be obtained as a result. In the study, the treatment efficiency for montmorillonite clay and Fe$_2$(SO$_4$)$_3$ were clearly observed to be low. As a result, in remaining studies, the use of these two coagulants was discontinued.

3.4. Effect of coagulant dosage on removal efficiency

In this stage the effect of coagulant dosage was investigated in chemical coagulation studies and experiments continued with the three coagulants of AlCl$_3$, Al$_2$(SO$_4$)$_3$ and FeCl$_3$ with best efficiency in the first stage. Each reactor had 0.5, 1 and 2 g of coagulant material added with pH set to 6.5 and mixing rate was 3 min of rapid mixing at 300 rpm, then 15 min of slow mixing at 25 rpm and then 30 min precipitation procedure. The SS, COD and TP removal efficiencies for the coagulant type and amount can be seen in Fig 5.
Fig 5. Effect of different AlCl₃, Al₂(SO₄)₃ and FeCl₃ dosage on SS, COD and TP removal efficiency

Fig 5 shows that AlCl₃ had highest SS, COD and TP removal efficiencies with 2 g L⁻¹ coagulant of 99.6%, 72.4% and 82.6%; for Al₂(SO₄)₃ highest SS, COD and TP removal efficiencies were obtained with 2 g L⁻¹ of 98.8%, 72.4% and 79.5%; while for FeCl₃ the highest SS, COD and TP removal efficiencies were obtained with 2 g L⁻¹ of 99.8%, 69.8% and 79.2%, respectively. The use of higher amounts of coagulant than the optimum coagulant dose causes other unwanted problems during wastewater treatment. Considering the wastewater amount and experimental setup, there was very little difference between coagulant doses in these experiments in laboratory conditions. If it is considered that in real applications kilograms of coagulant are used, the importance of the identification of optimum coagulant dose is understood. As a result, when Fig 5 is investigated, the optimum dosage for the three coagulants was identified as 1 g L⁻¹.

3.5. Effect of pH change on treatment efficiency

To research the effect of pH variation, coagulants with 1 g L⁻¹ dosage were used with rapid mixing at 300 rpm for 3 min, slow mixing at 25 rpm for 15 min and 30 min precipitation with experiments performed with pH values from 1-12. For pH setting, 1 N H₂SO₄ or 1 N NaOH solutions were used to set the pH to values from 1-12. Fig 6 shows the variations over time for SS, COD and TP removal efficiencies for the appropriate pH interval of the coagulants used (AlCl₃, Al₂(SO₄)₃ and FeCl₃).

As seen in Fig 6, during pH optimization, for AlCl₃ the SS removal efficiency was 99.6%, COD removal efficiency was 65.8% and total phenol removal efficiency was 85.5% at the optimum pH 6. For Al₂(SO₄)₃, SS removal efficiency was 98.4%, COD removal efficiency was 58.1% and total phenol removal efficiency was 78.8% at the optimum pH value of 6. Finally, for FeCl₃ the SS removal efficiency was 99.3%, COD removal efficiency was 63.4% and total phenol removal efficiency 91.8% at the optimum pH of 8. If the pre-treatment of pistachio processing industry wastewater using chemical coagulant matter operates
at low pH, flocs with better precipitating properties were obtained. At high pH, weak flocs formed and it was determined that suspended matter was found in the supernatant portion. As a result, the desired treatment efficiency could not be reached at high pH values. Due to chemical treatability studies, AlCl$_3$ provided better results with maximum SS, COD and TP removal efficiencies found with coagulant dosage 1 g L$^{-1}$, pH 6, mixing rate of 300 rpm for 3 min and 25 rpm for 15 min and 30 min precipitation.

4. CONCLUSIONS

Though Turkey is 3$^{rd}$ in the world in terms of pistachio processing industries, the number of companies with production from modern facilities is very few. Wastewater from these industries contribute significantly to pollution of natural environments. In this study, chemical precipitation was used to determine the optimum treatment conditions for treatability of pistachio processing industry wastewater with high COD content.

The significant toxic pollutant of pistachio processing industry wastewater was firstly characterized and in the second stage chemical pre-treatment studies were performed. The chemical treatability studies used clay, AlCl$_3$, Al$_2$(SO$_4$)$_3$, Fe$_2$(SO$_4$)$_3$ and FeCl$_3$ as coagulants. The results of the chemical treatability experiments identified AlCl$_3$ as the best coagulant. At optimum dosage and optimum pH, AlCl$_3$ provided 99.6% SS removal efficiency, 65.8% COD removal efficiency and 85.5% TP removal efficiency. The results obtained from the experiments and recommendations are listed below:

- When pre-treatment studies applied a simple precipitation procedure, the SS removal efficiency was 82%, COD removal efficiency was 26%, TSS removal efficiency was 43%, turbidity removal efficiency was 70% and oil-grease removal efficiency was 65% at the end of one hour. These results show that wastewater has good simple precipitation properties. It was understood that if preliminary precipitation is applied, there will be significant positive effect on treatability of the wastewater.

- Chemical treatability studies used montmorillonite clay, AlCl$_3$, Al$_2$(SO$_4$)$_3$, Fe$_2$(SO$_4$)$_3$ and FeCl$_3$ as coagulants. At the end of experiments, optimum coagulant dosages, optimum precipitation duration, optimum pH values and the obtained COD, SS and TP removal efficiencies were determined. Detection of optimum coagulant dosage used 0.5, 1 and 2 g L$^{-1}$ coagulant, identification of optimum precipitation duration used 30 min, 1 hour, 2 hour and 3 hours and optimum pH detection used values from pH 1-12 for chemical treatment experiments. The results of the chemical treatability experiments found optimum dosage was 1 g L$^{-1}$ for the three coagulants and optimum pH values were 6 for AlCl$_3$ and Al$_2$(SO$_4$)$_3$ and 8 for FeCl$_3$. At optimum dosage and pH values, AlCl$_3$ provided 99.6%, Al$_2$(SO$_4$)$_3$ provided 98.4% and FeCl$_3$ provided 99.3% SS removal efficiency with pH values of 6 for AlCl$_3$ and Al$_2$(SO$_4$)$_3$ and 8 for FeCl$_3$. At optimum dosage and optimum pH values AlCl$_3$ gave 65.8%, Al$_2$(SO$_4$)$_3$ gave 58.1% and FeCl$_3$ gave 63.4% for COD removal efficiencies. At optimum dosage and optimum pH values AlCl$_3$ gave 85.5%, Al$_2$(SO$_4$)$_3$ gave 78.8% and FeCl$_3$ gave 91.8% for TP removal efficiencies. The coagulant providing best results compared to other chemicals was identified as AlCl$_3$.

- For selection of chemicals to be used as coagulant, though the highest removal was obtained with AlCl$_3$, it was concluded that AlCl$_3$ may not be suitable at high pH values due to not forming stable structures. However, the desired efficiency can be reached for pre-treatment at low pH. When compared with other chemicals, the most appropriate coagulant for COD, SS and TP removal is AlCl$_3$. After AlCl$_3$, the order is FeCl$_3$, Al$_2$(SO$_4$)$_3$, clay and Fe$_2$(SO$_4$)$_3$. After the coagulation-flocculation procedure for pistachio wastewater, it can be seen that high removal efficiencies were achieved from the color of the discharge water.

- It is thought this study will be a guide to more comprehensive treatment studies for pistachio processing industry wastewater.

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