APPLICATION OF FENTON REAGENT ON EFFLUENT OF THE EDIBLE OIL AND GHEE INDUSTRY FOR THE REMOVAL OF ORGANICS AND HEAVY METALS

Namra Noor[1] and Mohammad Nafees[2]

[1]Department of Environmental Sciences, the University of Peshawar, Khyber Pakhtunkhwa, Pakistan

[2]Department of Environmental Sciences, the University of Peshawar, Khyber Pakhtunkhwa Pakistan

Abstract

This study aimed to apply Fenton's reagent to the effluent of edible oil and ghee mills for the evaluation of the removal of heavy metals. Primarily, Fenton regent (iron sulfate and hydrogen peroxide) is used for the oxidation of organics present in wastewater. In this manuscript, it is evaluated for the removal of heavy metals to see whether there is an increase or decrease in heavy metal contents. For this purpose, wastewater samples were collected from the main outlet drain of the industry. The sample was analyzed for physical, chemical, and heavy metals before and after treatment. Fenton reagent was applied, in which different doses of $FeSO_4/H_2O_2$ (Fenton) were prepared, i.e., 0.5:1 to 2:4 mol $FeSO_4$ and H_2O_2, respectively, and were applied to 100 mL of wastewater samples. The percentage removal of turbidity and COD was 94.7% and 97.8%, respectively. The percentage removal of Ni and Pb was 99% and 25%, respectively. A significant difference was found between and among the groups according to the post-hoc LSD comparison. It is therefore concluded that Fenton can be used effectively for the treatment of effluents by edible oil and ghee mills. The recommended dose was identified as 2:4 mol of $FeSO_4/H_2O_2$.

Keywords: Fenton Reagent, COD, Heavy Metals, Reflux Condensation, wastewater treatment

Introduction

The increase in population has resulted in a rise in the demand for goods, which in turn has led to rapid industrialization. Industrial waste production has increased due to the growth of industrial facilities. The quality and quantity of wastewater generated depend on the type of industry (Nafees, 2007). Wastewater is among the diverse types of waste that cities produce in large amounts. The quality of these wastes depends on their source, the way in which they are collected, and the treatment they receive. The ultimate destination of these wastes is also highly varied (Mateo-Sagasta et al., 2015). On a daily basis, the effluents generated from domestic and industrial activities constitute the main cause of pollution in receiving water bodies, which is a great burden on water quality management. Some of these pollutants are pathogenic microorganisms, phosphorus and nitrogen, hydrocarbons, heavy metals, endocrine disruptors, and organic matter (Akpor et al., 2014). Among other industries, the oil and ghee industry is also a key factor in polluting the environment by producing waste effluents, emissions, and sludge. Pakistan is considered a larger manufacturer of vegetable ghee and cooking oil. All over the country, almost 115 industrial units have been installed. The estimated production is about 2.8 million tons. Beside other industries, the oil and ghee industry is the highest producer of organic pollutants in effluent, i.e., in terms of biological oxygen demand (BOD) and chemical oxygen demand (COD), with the release of heavy metals like lead, zinc, iron, copper, nickel, etc., and a large quantity of organic solvents (Ahmad et al., 2014). The surface water in Pakistan is being disturbed at a shocking rate. The pollution mainly occurs due to untreated industrial waste effluent, including ghee mills. Ghee mill effluents include sewage as well as organic sludge that contribute to pollution (Nafees, 2010). Wastewater with high organic material adversely affects the dissolved oxygen (DO) level of the water bodies and poses a risk to fish species dependent on a high DO level (Khan et al., 2018). Besides this, the release of heavy metals from industries can also accumulate in the tissues of fish. Heavy metals not only affect the immune system of fish but also contaminate the food chain, with ultimate effects on the human population (Bashir et al., 2017). To cope with industrial effluents, various treatment facilities are available. Such processes as ozonation, chlorination, permanganate oxidation, wet air oxidation (WAO), supercritical water oxidation (SCWO), and ultraviolet radiation are effective against organic pollutants, but no such effect is found on heavy metals. Recently, Fenton reagent has been introduced for quick removal of organic loads from industrial effluents. It is a new technique with high efficiency and high efficacy against organic contents (BOD and COD). Research studies revealed that, in comparison to other methods, Fenton is quite reasonable (Yoo et al., 2001). Recently, Fenton was tried in the tannery industry, containing a high organic load, and was found to be very effective (Schrank et al., 2005). The Fenton process is a popular treatment method in all advanced oxidation processes (AOPs). It is the combination of hydrogen peroxide (H_2O_2) and iron (Fe_2, II) and releases highly reactive hydroxyl radicals (OH). The OH radicals have a high oxidation capacity and react with organic contaminants to form the final products like carbon dioxide (CO_2), water (H_2O), and inorganic ions. This process works in normal external conditions, such as room temperature and atmospheric pressure (Sangami, et al., 2017). The Fenton reagent is being evaluated during the initial stages of development. Research has been applied by various researchers to industries such as textile mills, pharmaceuticals, food, and so on. Despite the presence of organic matter in ghee mill effluent, Fenton is not utilized. Most studies have been carried out for the removal of COD from industrial wastewater using secondary and tertiary treatment technologies in the form of various physical and chemical processes or combinations of both, such as sedimentation and filtration of various types (Ahmad et al., 2014). This study has been designed for the purpose of applying Fenton reagent to ghee industrial effluent with the objective of knowing about the efficacy of Fenton against organic as well as heavy metal contents.

Methodology

A total of six composite samples were taken in three months. Each composite sample consists of 12 grab samples collected at a 30-minute interval. Samples were taken in 1.5-liter cleaned and dried bottles and then brought for analysis to the laboratory. A sample was analyzed for physical, chemical, and selected heavy metals by following the standard method of analysis (APHA, 2005). Fenton reagent was applied in a 500-ml flask by taking a 100-ml sample. Different doses of Fenton regent ($FeSO_4/H_2O_2$) ranged from 0.5:1 to 2:4 moles, respectively. Molar solutions of ferrous sulfate and hydrogen per chloride were prepared separately and then applied to samples with 1:2 of the prepared solutions. pH was adjusted with a calibrated pH meter (APHA, 2005). The above experiments were performed in a controlled laboratory environment.

Results

The targeted edible oil and ghee industry produces 200 tons per day of oil and ghee (150 tons of ghee and 50 tons of oil). It consumes 400 cubic meters of water per day and produces 300 cubic meters of wastewater per day, which is drained directly into an outside effluent drain and indirectly thrown into the River Kabul. This contaminated water has threatened aquatic life. Some studies revealed in 2018 that the main contributor to water pollution is the oil and ghee industry (Afzal et al., 2018). Studies on the applicability of the Fenton and Fenton-like reactions in the ghee and oil industries have not been published till date.

Analytical results of untreated wastewater

The color of the wastewater was cloudy, which is objectionable. pH is an important parameter of water and wastewater quality for many reactions. The average values for untreated wastewater were in the range of 7-8. EC is the parameter that indicates the water quality and its functions. The values of EC are not defined in Pak. NEQSs are dependent on the total dissolved solids present in the wastewater effluent. The average values were measured for untreated samples as 1450–1500 mg/L. TDS was measured within the range of 700–759 mg/L for an untreated wastewater sample. Likewise, the average values for turbidity of the untreated sample were found in the range of 200–235 NTU. Whereas, the average values for COD were very high (2933–3000 mg/L) and were above the permissible limits of 150 mg/L for wastewater. Some heavy metals were evaluated, like Cu, Pb, Fe, and Ni, and the average values for these metals were 0, 0.68, 0, and 0.015 mg/L. the values defined by Pak. NEQSs for Cu, Pb, Fe, and Ni are 1, 0.5, 2, and 1 mg/L. Studies have evaluated that, beside other industries, the oil and ghee industry is the major contributor to water pollution (Ahmad et al., 2014).

Edible oil and ghee mill wastewater after treatment with Fenton Reagent

The average values found with the application of different doses for pH were 6.20, 6.21, 6.30, and 6.74. For EC with dose application, the values were 653, 841, 3230, and 4250 µs/cm. Likewise, the average values of turbidity with the application of Fenton's reagent at different doses were found to be 156 to 11 NTU. Furthermore, the average mean TDS values for doses ranging from 0.5:1 to 2:4 mol were 325 to 2130 mg/L. whereas the average values of COD with the application of different doses of Fenton were noted as 313 to 62 mg/L. Heavy metals are considered to be environmental pollutants. Some of them are carcinogenic and lethal and disturb aquatic life. The values for copper (Cu) were observed at 0 mg/L, and lead (Pb) was reduced from 0.62 to 0.51 mg/L and were within Pak-NEQSs limits. The average values for iron (Fe) were found to be 0.50–3.89 mg/L, which were beyond the permissible limits due to the application of Fenton as it contains iron, which was used as a catalyst. While the concentration of nickel (Ni) was also reduced from 0.013 to 0 mg/L. Post-hoc LSD comparisons for pH, EC, turbidity, TDS, and COD showed that results for untreated wastewater were significantly different from 0.5:1 to 2:4 mol at $p < 0.05$.

Table 1. Physico-Chemical parameters and Heavy metals evaluation in wastewater, untreated and treated average samples (Fenton Reagent), Edible Ghee and oil industry

Parameters	Untreated sample Values (Average)	NEQSs	Treated samples doses $FeSO_4/H_2O_2$ (Average)			
			0.5mol/1mol (5ml/10ml)	1mol/2 mol (5ml/10ml)	1.5mol/3mol (5ml/10ml)	2mol/4 mol (5ml/10ml
pH	7.6	6-9	6.20	6.21	6.30	6.74
Temp (°C)	20	__	15	15	15	15
EC (us/cm)	1500	__	653	841	3230	4250
Turbidity (NTU)	231	__	156	113	61	11
TDS (mg/L)	759	3500	325	419	1610	2130
COD (mg/L)	2933	150	313	283	108	62
Cu(mg/L)	0	1.00	0	0	0	0
Pb (mg/L)	0.68	0.5	0.62	0.56	0.50	0.51
Fe (mg/L)	0.00	2.0	0.50	1.35	1.62	3.89
Ni (mg/L)	0.015	1.0	0.013	0.005	0.001	0.00

Discussion

AOPs are physical-chemical treatment procedures that cause the organic medium to degrade by producing a lot of highly oxidizing free radicals. One of the most popular AOPs, the Fenton reaction, has received extensive research attention for its potential use as a supplemental step in wastewater treatment. In an acidic medium (pH between 2.5 and 3.0), hydrogen peroxide (H_2O_2) serves as the oxidizing agent, while Fe2+ ions act as catalysts in the reaction that produces the hydroxyl radical (•OH) (Gode et al., 2019). (Liu and Li, 2018) conducted a study on the use of Fenton in pharmaceutical wastewater. Through the application of different doses of Fenton, its findings regarding pH ranged from 6.80 to 6.00. (Perrira et al., 2020) conducted a study on cosmetic wastewater treatment using the Fenton process. With the effect of various doses of Fe_2+ and H_2O_2, the efficiency of electrical conductivity (EC ms/cm) increased to 79%. (Perrira et al., 2020) conducted a study on cosmetic wastewater treatment using the Fenton process. With the effect of various doses of Fe2+, the efficiency of turbidity removal was found to be 60.6%. While with the variation of H_2O_2 the removal efficiency of turbidity was 61.5%. (Vasquez-Medrano et al., 2018) revealed a study on how the application of Fe/H_2O_2 doses under acidic conditions decreases the organic pollutant content in wastewater. The increase in Fe2+ enhances the treatment efficiency but contributes to the high concentrations of total dissolved solids. Furthermore, (Shetty and Verma 2015) explained a study on wastewater treatment in the pharmaceutical industry by applying different doses of Fenton reagent ($FeSO_4/H_2O_2$), and the efficiency of maximum COD removal was found to be 85% at a 1:3 dose.

Table 2: Average Percent Removal Efficiency

S No	Parameter	Concentration in sample	Concentration in treated sample	Percent decrease
1	COD (mg/L)	2933 mg/L	62	97.8%
2	Turbidity(NTU)	231 NTU	11	94.7%
3	Ni (mg/L)	0.015	0.001	99.9%
4	Pb (mg/L)	0.68	0.51	25%

Conclusion

The effective reduction was observed by applying 2:4mol dose of Fenton reagent. The percentage removal of turbidity and COD in wastewater was about 94.7% and 97.8%, respectively. In the case of heavy metals like nickel (Ni) and lead (Pb), they were removed by 99.9% and 25%, respectively. If the waste water sample contains the mentioned heavy metals, Fenton reagent is useful to remove them. For a more comprehensive and precise study, segregation and characterization of sludge should be done.

Table 3. ANOVA comparison for untreated and treated samples between and within the groups

		Sum of Squares	Df	Mean Square	F	Sig.
pH	Between Groups	4.324	4	1.081	267.601	.000
	Within Groups	.040	10	.004		
	Total	4.365	14			
Turbidity	Between Groups	86613.600	4	21653.400	21653.400	.000
	Within Groups	10.000	10	1.000		
	Total	86623.600	14			
TDS	Between Groups	8165298.000	4	2041324.500	2041324.500	.000
	Within Groups	10.000	10	1.000		
	Total	8165308.000	14			
EC	Between Groups	32639576.400	4	8159894.100	8159894.100	.000
	Within Groups	10.000	10	1.000		
	Total	32639586.400	14			
COD	Between Groups	18178604.400	4	4544651.100	4544651.100	.000
	Within Groups	10.000	10	1.000		
	Total	18178614.400	14			
Cu	Between Groups	.004	4	.001	13.840	.000
	Within Groups	.001	10	.000		
	Total	.005	14			
Pb	Between Groups	1.186	4	.296	3696.441	.000
	Within Groups	.001	10	.000		
	Total	1.187	14			
Fe	Between Groups	20.697	4	5.174	2511.728	.000
	Within Groups	.021	10	.002		
	Total	20.717	14			
Ni	Between Groups	2.223	4	.556	269.701	.000
	Within Groups	.021	10	.002		

Acknowledgments: The author is grateful to the honorable managers and plant managers in charge of the visited industry for their help in presenting relevant data. I am also thankful to the Central Resource Laboratory, Department of Environmental Science, University of Peshawar, for their kind support in chemical analysis.

References

1. Afzal, M. S., Ashraf, A., and & Nabeel, M. (2018). Characterization of industrial effluents and groundwater of Hattar industrial estate, Haripur. Advances in Agriculture and Environmental Science: Open Access (AAEOA), 1(2), 70-77
2. Ahmad, W., Hussain, R., Nafees, M., and & Hussain, A. (2014). Optimization of wastewater treatment process in industry "a case study of Hattar Industrial Estate Haripur". Pakistan Journal of Analytical & Environmental Chemistry, 15(1), 7.
3. Akpor, O. B., Otohinoyi, D. A., Olaolu, D. T., & Aderiye, B. I. (2014). Pollutants in wastewater effluents: impacts and remediation processes. International Journal of Environmental Research and Earth Science, 3(3), 050-059.
4. American Public Health Association (APHA). Standard Methods for the Examination of Water and Wastewater, 21 (2005) 259. doi: 10.4236/aim.2016.611081
5. Bashir, A., Nafees, M., and& Khan, N. (2017). Study of Chattri Dam for Selected Metal Concentrations in Water, Sediments and Fish Species. Journal of Agriculture Research & Technology, 10(3), DOI: 10.19080/ARTOAJ.2017.10.555788
6. Göde, J. N., Souza, D. H., Trevisan, V., & Skoronski, E. (2019). Application of the Fenton and Fenton-like processes in the landfill leachate tertiary treatment. Journal of environmental chemical engineering, 7(5), 103352.
7. Khan, M. H., Muhammad, N., Nafees, M., Khan, S., and& Ullah, U. (2018). Spatial distribution and pollution source (s) apportionment in adjacent tributaries of River Panjkora. Journal of Biodiversity and Environmental Sciences, 12(5), 391-403
8. Liu, F., & Li, J. (2018, May). Application of Fenton Process in Industrial Wastewater Treatment Plant. In IOP Conference Series: Earth and Environmental Science (Vol. 146, No. 1, p. 012023). IOP Publishing
9. Mateo-Sagasta, J., Raschid-Sally, L., & Thebo, A. (2015). Global wastewater and sludge production, treatment and use. Wastewater: Economic asset in an urbanizing world, 15-38.
10. Muhammad, N., Nafees, M., Hussain, R., Khan, M. H., Jehan, S., and&Ullah, U. (2018). Pollution and energy reduction strategy in soft drink industries. Environmental Science and Pollution Research, 25(28), 28153-28159
11. Nafees, M. (2010). Role of Kabul River in Socio-economic Activities and Associated Environmental Problems. Central Asia (1729-9802), (67)
12. Nafees, M. (2017). Reduction in Organic Waste through Recovery from Waste Paper Recycling Mill. Pakistan Journal of Analytical & Environmental Chemistry, 18(2), 136-142.
13. Pereira, L. M. G., de Oliveira Ferreira, M. E., de Brito, N. N., &Ostroski, I. C. (2020). Cosmetic wastewater primary treatment by Fenton process and final polishing adsorption. Revista Eletrônicaem Gestão, Educação e TecnologiaAmbiental, 24, 13
14. Sangami, S., and& Manu, B. (2017). Fenton's treatment of actual agriculture runoff water containing herbicides. Water Science and Technology, 75(2), 451-461
15. Schrank SG, Jose HJ, Moreira RFPM, Schroder HFr (2005). Applicability of Fenton and H_2O_2/UV reactions in the treatment of tannery wastewaters. Chemosphere, 60: 644–655
16. Shetty, R., &Verma, S. (2015). Fenton's reagent for the treatment of pharmaceutical industry wastewater. International Journal of Science and Research, 4(7), 3093-3096.
17. Vasquez-Medrano, R., Prato-Garcia, D., & Vedrenne, M. (2018). Ferrioxalate-mediated processes. In Advanced Oxidation Processes for Waste Water Treatment (pp. 89-113). Academic press
18. Yoo, H. C., Cho, S. H., and Ko, S. O. (2001). Modification of coagulation and Fenton oxidation processes for cost-effective leachate treatment. Journal of Environmental Science and Health, Part A, 36(1), 39-48, 940-947.