A comparative Study for Grey Water Using Ozonation and Ultrasonic Irradiation Processes.

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Abstract:  
Grey water is considered a type of wastewater which bring damage to human health and environmental if disposed improperly. This lead to research an efficient treatment method to reduce the damage. The methodology used for grey water treatment was ozonation and ultra sonication. PH, ozone dose, temperature and time were the factors effecting the overall performance of the treatment process for the two forms of grey water(car wash water and Domestic water). both the COD & oil content were measured to determine the effectiveness of the process. for carwash sample ,the COD and oil content were 95%,96.5% at 0.52 mg/l ozone dose , at 55 min duration time and ph=9. As for the domestic water , the COD and oil content were 96.5%,96% at 0.52 mg/l ozone dose , at 55 min duration time and ph=9. The removal was lower for ultrasoniation .for carwash sample ,the COD and oil content were 94% and 74%  at 45Co , at 55 min duration time and ph=9. As for the domestic water , the COD and oil content were 97% and 96 % at 55 min duration time and ph=9.  
Finally, treatment of greywater with ozone has proven to be more efficient than ultrasound  

Keywords: Grey water, Ozonation , Ultra sonication , COD, Oil, Domestic water, Car wash wate.

INTRODUCTION:  
Some people point out that population growth in Iraq is the main cause of water scarcity, as the current population growth rate in Iraq is about 15%, which is one of the largest in the world. With this population growth, and with a corresponding increase in food demand, the agricultural policy of the previous government was aimed at achieving food self-sufficiency [1]. So the agricultural sector turns into the largest water consumer, and there are three main obvious reasons that lead to interdependence and interdependence to increase water demand: population growth, development needs, and excessive water consumption. Traditional ground and surface water sources are becoming increasingly vulnerable to human, natural and industrial pollution. The most appropriate and cost-effective alternative approach to rural areas is the reuse of greywater [2]. Grey water is one type of domestic wastewater, which can be classified into: grey water, black water. It is household wastewater in all its aspects - including water from the bathroom, shower, and hand basins to kitchen sinks and washing machines - in addition to car wash water, except that it does
not contain any water derived from the toilet [3]. One of the main solutions seen as a new source of water is greywater treatment for reuse in areas with insufficient water. Treatment methods can be divided into three categories, depending on efficiency and economic costs (physical, chemical, and biological) [4]. The chemical method is more effective than other methods and includes treatment (ozone and ultrasound). The ozone cycle is a safe way to deal with greywater, because ozone is soluble in water and can easily degrade to other roots, including hydroxide, OH, HO3, HO4 and o (super oxide). These roots can bind to any organic compound in grey water, and ozone is also characterized by a rapid color removal process that produces no toxic products or clay deposits [5]. Ultrasound has also proven in the past several years to be an effective way to analyze organic fluid residues in less toxic compounds and in some cases to fully mineralize the compounds [6], as an advanced method of oxidation to remove a wide range of pollutants and treat greywater. Acoustic is an alternative technology for disinfection in low-quality water. High-energy inputs for effective disinfection and high temperatures produced in water are major disadvantages of ultrasound disinfection [7].

In this study, the highest COD and oil was removed from ozone and ultrasound treatment methods, and a comparison was made based on water quality. The effect of the ozone dose, solution pH, contact time and temperature were taken into account to find the optimum conditions.

- **Aim of This Work**
  The goal is to treat gray water with ultrasound and ozone treatment and compare them to get the best efficiency of removing pollutants in order to reduce risks to human health and the environment and therefore can be reused for other purposes such as irrigation and in industrial and other matters, especially in countries that suffer from a shortage of water.

- **Grey water Treatment Methods.**
  1-pretreatment (Filtration).
  Grey water was taken from car wash station and domestic water from home. This wastewater is fed to the system after a pre-treatment method to maintain the perfect wastewater properties for advance treatments. Poly spun filter and carbon black was used as a pre-treatment step, Figure (3), to reduce the amount of impurities that affect the ongoing process and efficiency removal.

![Fig 1. pretretment (Filtration).](image)

2- **Ozone treatment.**
Ozonation has been studied for elimination of contaminant generally, natural and recalcitrant organic compounds specifically from wastewater. This process is characterized by the high
oxidation potential and no potentially carcinogenic by-products formation, which is toxic to microorganisms in the following biological treatment in conventional oxidation processes (pre-treatment).

**Advantages:**
- Ozone is more effective than chlorine in destroying viruses and bacteria.
- The ozonation process utilizes a short contact time (approximately 10 to 30 minutes). There are no harmful residuals that need to be removed after ozonation because ozone decomposes rapidly.
- After ozonation, there is no re-growth of microorganisms, except for those protected by the particulates in the wastewater stream.

**Disadvantages:**
- Low ozone dosage may not effectively inactivate some viruses, spores, and cysts.
- Ozonation is not economical for grey water with high levels of suspended solids (SS), biochemical oxygen demand (BOD), chemical oxygen demand, or total organic carbon.

**3- Ultrasound treatment.**

Over the past years, ultrasound has been applied effectively as one of the advanced oxidation processes to remove a wide range of pollutants and in wastewater treatment. It has proven to be an effective way to break down organic liquid waste into less toxic compounds and is able to fully mineralize the compounds in some cases.

**Advantages:**
- Ultrasound treatment has proven to be an effective way to break down organic liquid waste and convert it into less toxic compounds.

**Disadvantages:**
- Ultrasound treatment is limited due to its high cost.
- Ultrasound treatment This treatment is usually excluded independently due to the high energy it requires.
Fig 3. Power sonic 405

• EXPERIMENTAL SECTION

Materials
Deionized water (H2O) was purchased from the Water Treatment Center, Ministry of Science and Technology, Iraq, sodium hydroxide (NaOH, 97%) and hydrochloric acid (HCl, 98%) from Scharlau Spain, and two samples of greywater were used. Water samples (Domestic water and car wash water) were taken. Domestic water was taken from the local house in Baghdad (Iraq), and car wash water from a car wash station in Baghdad (Iraq).

Table (1): Characteristics of grey water from refinery effluents inlet the treatment processes.

| Tests          | COD (PPM) | OIL (PPM) | PH  | TURB (NTU) | TDS (PPM) | Ca (PPM) | Mg (PPM) | Cl (PPM) |
|----------------|-----------|-----------|-----|------------|-----------|----------|----------|----------|
| Car wash water | 350       | 285       | 6.7 | 220        | 873       | 200      | 72       | 189      |
| Domestic water | 320       | 86        | 6.8 | 190        | 696       | 145      | 57       | 131      |

• Procedure
The wastewater sample is fed to the system after a pre-treatment method to maintain the perfect wastewater properties for advance treatments. Polyspun filter and carbon black was used as a pre-treatment step, to reduce the amount of impurities that affect the on going process and efficiency removal.

1-Experimental Procedure for ozonation only
The next procedure has been followed in experimental runs: One liter of water sample was placed in cylinder. The solution’s acidity is regulated by using NaOH or HCL solutions (0.1M) different PH was studied (3,5,7,9) Ozone

Table (2): Characteristics of grey water from refinery effluents outlet the pretreatment processes.

| Tests          | COD (PPM) | OIL (PPM) | PH  | TURB (NTU) | TDS (PPM) | Ca (PPM) | Mg (PPM) | Cl (PPM) |
|----------------|-----------|-----------|-----|------------|-----------|----------|----------|----------|
| Car wash water | 189       | 44        | 6.7 | 30         | 650       | 135      | 30       | 115      |
| Domestic water | 173       | 13        | 6.6 | 16         | 340       | 90       | 20       | 75       |
concentrations (0.27, 0.3, 0.35, 0.45, 0.52) changed from the device setting) enters the reactor in the form of fine bubbles through the diffuser which located at the bottom of the reactor.

The ozone setup unit is shown in Fig. 1.

a. Duration time for treatment was changed as a separate variable.
b. The samples are kept in a dark space to avoid disintegration of the pollutant by the rays of the sun.
c. Collected samples are subjected to analytical methods, such as chemical oxygen demand (COD) and oil content tests as fast as can.

Fig 4. Ozone treatment Setup unit

2-Experimental Procedure for ultrasonication only

The following procedure was followed in the experimental operation where one liter of water sample was placed in the device, then the temperature of the sample was changed by the device, then the ultrasound machine was started to process the water sample, then the treatment period was changed as a separate variable, then the samples were saved in a dark place to avoid the disintegration of the polluted sun, then the collected samples are subjected to analytical methods, such as chemical oxygen demand (COD) and oil content tests as soon as possible.

Fig 5. Ultrasound treatment setup unit

- Thermal Analysis

The COD test was performed by testing the profluent tests when been dealt with. An oxidizing specialist, as ( K2Cr2O7 ), was added to the gathered examples and left to 120 min and a temperature of 150 °C for assimilation in (Lovibond COD reactor RD 125). Processed examples were left to chill off at room temperature, at that point broke down in a photometer (MD 200 COD VARIO Photometer). The level of COD effectiveness expulsion from the rewarded arrangement by the oxidation procedure was assessed from the accompanying condition:

\[
\text{COD Removal efficiency} = \frac{\text{Solution before treatment} - \text{Solution after treatment}}{\text{Solution before treatment}} \times 100\%
\]
\[ \text{CODo} - \text{CODf} \times 100 \]

Where COD\text{\textcircled{o}} is the initial value of COD concentration (in mg/l) at \( t = \) zero time, COD\text{\textcircled{f}} is the value of COD concentration (in mg/l) after \( t \) time ozonation.

- **RESULTS AND DISCUSSION**

1 Factors Affecting on ozonation process

1.1 Effect of pH

Since pH is a major functional parameter that significantly impacts ozonation efficiency (Chu W., 2000). Acidic, neutral, and base conditions have been defined as representing a pH 5, 7, 9, and 11. The oil content and COD value were tested when pH is changed and the time for treatment was 55 min. The oil content and COD value were tested when pH is changed and the time for treatment was 55 min at 0.27 mg/l. It was found that the best removal efficiency of COD was 95% at pH=9, while 94%, 90% and 84% were removal efficiencies of pH= 7.5and 3 respectively. For the oil content, removal efficiencies became 79.7%, 70.2 %, 57% and 42% for pH= 9, 7, 5 and 3 respectively. So in general as shown in figure 4.1, the carwash water removal efficiency of ozone at 55 min contact time increases when the pH value increase from 3 to 9.

![Fig 6. COD and Oil content removal % at different pH value carwash water.](image)

Figure 7 when domestic wastewater is used for the treatment, similar behavior for the COD and oil content removal efficiency. It was found that the best removal efficiency of COD\text{\textsubscript{\text{in}}} was 96.5% at pH=9, while 96%, 94.8% and 94% were removal efficiencies of pH= 9and 3 respectively. For the oil content, removal efficiencies became 96%, 95 %, 92.4% and 91% for pH= 9, 7, 5 and 3 respectively.

![Fig 7. COD and Oil content removal % at different pH value for domestic water.](image)

A possible explanation of this phenomenon is that the concentration of \( \text{OH}^- \) ions increased with the pH value of the solution. Higher pH value promoted the decomposition of ozone, producing more \( \bullet \text{OH} \) radicals for the effective oxidization or degradation of organic acids, thus a higher COD removal rate was obtained[8].

1.2 Effect of ozone dose
It was found that the best removal efficiency of COD in was 94% at 0.52 mg/l, while 88%, 91%, 92% and 94% were removal efficiencies of 0.3, 0.35, 0.46 and 0.52 mg/l respectively. For the oil content, removal efficiencies became 74%, 77%, 85%, 92% and 96.5% for 0.27, 0.3, 0.35, 0.46 and 0.52 mg/l respectively, so in general as shown in Figure 8, the removal efficiency of ozone at 55 min contact time increases when the dose value increase from 0.27 to 0.52 mg/l. This is overuse were the increase in ozone dose the amount of treated organic material and oil content increase but in general the 0.52 mg/l is the optimum dose for the removal.

![Fig 8: COD and Oil content removal % at different ozonation dose value.](image)

The effect of ozonation dose on the domestic water was shown in Figure 5. The oil content and it was found that the best removal efficiency of COD in was 96% at 0.52 mg/l, while 81%, 84%, 90% and 96% were removal efficiencies of 0.3, 0.35, 0.46 and 0.52 mg/l respectively. For the oil content, removal efficiencies became 64%, 69%, 71%, 86% and 99% for 0.3, 0.35, 0.46 and 0.52 mg/l.

![Fig 9: COD and Oil content removal % at different ozonation dose value](image)

An increase in the dose of weight means an increase in the concentration of the effective OH root in the oxidation of organic pollutants, as well as an increase in the rate of interaction of oxygen or the OH root with other pollutants that enter into the calculations of the total oxygen requirement or that consume oxygen in wastewater. In other words, an increase in weight means increase in oxygen and free radical active, and this is also reflected in the increased rate of oxidation of hydrocarbon contaminants, represented by oil.

1.3 effect of time
Since experimental work has been carried out in a batch mode, time is one of the considerable variables. The reduction of COD at 55 min for 0.52 mg/l ozone dose and optimum pH = 9 were studied. The result for carwash water as shown in Figure 10, after 10 min the removal for the one distributor was 92% while for two was 94.2%. 
Fig 10: Effect of time on COD removal efficiency for carwash water
The result for domestic wastewater as shown in figure 4.4. The removal of the COD was increased with time, the major removal happens in the first 10 min. Where the removal was 97% for COD while for oil content was 89%. At 55 min.

Fig 11. Effect of time on COD removal efficiency for domestic wastewater
The results showed that over 70% removal efficiency was at high concentrations of pollutants at first 10 min of the reaction (Sevimli, 2002), explained increasing exposure time will have a slight effect but still considerable effect of treatment. When ozone dose rate and/or time were increased, the utilization ratio decreased because the most organic compounds were decomposed beyond 25 min as contacted time. In contrast, when reaction time increased, ●OH has better chance to react with contaminant.

2 Factors Affecting on Ultrasonic process
2.1 Effect of Contact Time
The ultra sonication treatment was studied using ultrasonic bath with constant frequency. The reduction of COD and oil content was measured at 55 min and optimum pH =9 were studied. The result of the COD removal percent was shown in figure 12. after 10 min the COD removal increased rapidly to 82% and the removal increases as the time of treatment increase. the removal values was 76.88 and 93.8% for 25, 40, 55 min. The max removal reached was at 55 min.
Fig 12.: Effect of time on COD removal efficiency
The results showed that 93.8% removal efficiency was at high concentrations of pollutants at 55 min. The result were similar to Nasseri [9], were the removal in his case was reached to 94% after 60 min with similar behavior. The reduction of oil content at 55 min and optimum pH 6.7 was also studied. The result as shown in figure 7, the removal of oil increase with time until it reach to the max removal at 55 min were the removal was 71.1%. In general, the removal of COD and oil. The explanation of this phenomena is when Ultrasound passes in a liquid leads to the acoustic cavitation phenomenon such as formation, growth, and collapse of bubbles (cavitation), accompanied by generation of local high temperature, pressure, and reactive radical species (\(\cdot \)OH, \(\cdot \)OOH) via thermal dissociation of water and oxygen. These radicals penetrate into water and oxidize dissolved organic compounds. Hydrogen peroxide (H2O2) is formed as a consequence of \(\cdot \)OH and \(\cdot \)OOH radical recombination in the outside of the cavitation bubble [10].

Fig 13. Effect of time on oil content removal efficiency
Fig 14 shown the removal efficiency of domestic wastewater. The behavior and the explanation were similar to the carwash water. The result of the COD removal percent was shown in figure 4.6. after 10 min the COD removal increased rapidly to 79% and the removal increases as the time of treatment increase. The removal values was 81, 85 and 90.1% for 25, 40, 55 min. The max removal reached was at 55 min. While for oil content, after 10 min the oil removal increased rapidly to 60% and the removal increases as the time of treatment increase. The removal values was 63, 68 and 70.6% for 25, 40, 55 min. The max removal reached was at 55 min.

Fig 14: Effect of time on oil content and COD removal efficiency

2.2 Effect of pH
Different PH value have been studied in the ultrasound process. Acidic, neutral, and base conditions have been defined as representing a pH 3.5, 7 and 9. The oil content and COD value were tested when PH is changed and the time for treatment was 55 min. It was found that the best
removal efficiency of COD was 94% at pH=9, while 92%, 80% and 70% were removal efficiencies of pH= 7.5 and 3 respectively. For the oil content, removal efficiencies became 74%, 71%, 52.8% and 35.7% for pH= 9, 7, 5 and 3 respectively. So in general as shown in figure 9, the removal efficiency of ozone at 55 min contact time increases when the PH value increase from 3 to 9.

Figure 16 show the effect of PH when using domestic wastewater on COD and Oil removal. It was found that the best removal efficiency of COD was 98% at pH=9, while 96%, 94.8% and 92.84% were removal efficiencies of pH= 9 and 3 respectively. For the oil content, removal efficiencies became 96%, 95.4%, 92% and 86% for pH= 9, 7, 5 and 3 respectively.

The difference in pH may be correlated with the presence in waste water of organically active compounds more prone to pH 7 to 9 oxidation. The pH-value effect could be interpreted as influencing the distribution in waste water of the current state of organic compounds. It is common knowledge that pH can influence the physico-chemical properties of acid solutions, and therefore the pH can affect the ultrasound decomposition of the solution. The formation of salt in the acid medium reduces the vapor pressure of the reactants so that they cannot reach the present bubbles and thus have a slight effect on ultrasound [11].

2.3 Effect of temperature

The effect of temperature on the ultrasound have been studied on the removal of COD and oil content of the water sample. As shown from figure 14 for the carwash water, the COD removal
was 94% at 45°C which was the high removal value followed by 93.8% for 40°C and 90% ,82% for 30 and 20°C respectively. The increase of operating temperature effect the COD removal value were the removal increases slightly with the increase of temperature at 55 min treatment.

**Fig17: effect of temperature on ultrasound treatment**

For the oil content, removal efficiencies became 74%, 71 %, 52% and 35% for 45, 40,30 and 20 °C respectively. For the oil removal the increase of temperature effect significantly on the oil removal value were the highest removal recorded was at 45°C. to explain this phenomena Solubility of oxygen decrease when temperature increases in wastewater. so when temperature rising from 20°C To 45°C Will release the dissolved oxygen in wastewater that led to more oxidation and then reduction of organic pollutants besides high level of temperature enhancing other side reaction of the different chemical compounds which cause minimization of organics then COD concentration will be decrease .for the Domestic water In this the Effect, Domestic water results are close to those for car wash water.

3- **Comparison Between car wash water and Domestic water.**

From the represented figures above, a comparison has been made depending on the efficiency removal for The same condition. Figure (14) (15) illustrate the difference in removal efficiencies of car wash water and Domestic water, at initial concentrations of nearly (350) ppm COD),(285ppm oil) for car wash water and (320 ppm COD),(86ppm oil) for Domestic water. Domestic water removal efficiency appear to have better response to the applied conditions during Processing methods than efficiency of real due to the The degree of degradation highly depends on the type and amount of pollutant presents in grey water And that Domestic water has less pollutants than car wash water. also Solution pH as explained before has a significant effect.

**Fig(18) Effect of PH on COD efficiencies for car wash water and Domestic water.**
**Conclusion**

At the end of reviewing the examined tests and discussing the results, the following conclusions have been established:

1. Ozonation process has been successfully degrade most of the organic compounds located in grey water. The oil content and COD value were tested when PH is changed and the time for treatment was 55 min at 0.52 mg/l. It was found that the best removal efficiency of COD was 97% at 55 min. For the oil content, found that the best removal efficiency of oil was 89 at 55 min.

2. The ultra-sonication treatment was studied using ultrasonic with constant frequency. The reduction of COD and oil content was measured at 55 min and optimum pH =9, found that the best removal efficiency of COD was 91.5% at 55 min, also found that the best removal efficiency of oil was 70.6% at 55 min.

3. After comparing the results of the different treatments together for the two samples (Domestic water and car wash water), the Domestic water sample achieved the highest percentage of removing pollutants (94%), then the car wash water (90%).

4. The rate of organic compounds degradation by ozone increased at alkaline conditions through the participation of hydroxyl radicals, therefore pH seems to have an important role in the process. Ozonation shows a minimum degradation at acidic condition (pH3) and a maximum at neutral to base (pH≥7).

5. It was established that the increase in contact time was instrumental in increasing Efficiency removal starts from 10 minutes to 55 minutes, and then the effect becomes slight.

6. The effect of temperature on the ultra-sonication treatment been studied on the removal of COD and oil content of the water sample. found that the best removal efficiency of COD and oil at 45 °C. which is the max removal.

7. Ozone dose is important to determine the optimal amount of ozone needed to treat the water sample. In general, the removal efficiency increases the ozone at 55 minutes of contact time when the dose value increases from 0.27 to 0.52 mg / l. In general, 0.52 mg / L is the optimal dose for removal.

8. Reuse of greywater offer a potential option for water demand management that can contribute to the reduction of freshwater consumption for irrigation, particularly in the rural area.

**Recommendation for Future Work**

1. This study should be conducted in an advanced manner, as it is possible to apply it extensively in Iraq and obtain potential funding for it.

2. Large scale units are advised to be constructed when the project is applied and a coverage ability for agriculture sector should be examined.
3—Further tests may be applied to future water parameters such as TSS, detergents, etc., to study the ability to expand the purposes of reusing treated wastewater.

4—Study and develop wastewater standards for reuse in other areas such as irrigation according to quality requirements, taking into account safe practice guidelines.

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