Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.794575

51 (2013) 6952–6960
November

Taylor & Francis
Taylor & Francis Group

Chemical oxidation and membrane bioreactor for the treatment of household heating wastewater

Antonis A. Zorpas

Cyprus Open University, Department of Applied and Pure Science, Environmental Conservation and Management, P.O. Box 12794, 2252 Latsia, Nicosia, Cyprus
Tel. +357 22411600/99532025; Fax: +357 22411601; emails: antoniszorpas@yahoo.com, antonis.zorpas@ouc.ac.cy

Received 22 August 2012; Accepted 24 February 2013

ABSTRACT

Until now, there is limited information about the waste produced from the maintenance of the houses and or buildings central heatings. The quality of the wastewater has strong relation with the quality of water used as well as from the years of maintenance. This kind of waste is not covered by any legislation since now. The only treated methodology is the discharge of that waste in the land close to the house where the maintenance takes place. The paper describes the physicochemical characteristics of those wastewaters as well as potential appropriate treatment processes using a combination of the membrane bioreactor and Fenton oxidation techniques for the effluent discharge with the minimum environmental impact.

Keywords: Domestic heating; Central heating; Black wastewaters; MBR; Fenton; Chemical oxidation

1. Introduction

The term central heating covers hydronic heating systems with a central boiler or furnace either inside the building being heated or in the immediate vicinity. Heat is generated in the boiler. Pipes carry the heated water to the building's heat sources (radiators) and return the cooled water to the boiler again. Originally, many central heating systems were designed to be self-circulating. However, very often those systems require maintenance.

Family heating has always been of great concern to people in the cold winter period. Central domestic heating mode has been the main form of home-heating in winter. Central heating systems have the ability to provide comfort to the whole interior of a building from one point to multiple rooms. Originally, many central heating systems were designed to be self-circulating. Now, a circulator is always used to pump heat through the system. A central heating system is a closed system with either an expansion tank or open expansion vessel. A buffer tank may also be installed in the system. A wide range of fuel types are used in central heating. Coal, coke, wood, oil, gas, wood chips and wood pellets have all proven adequate fuel sources in central heating boilers (Fig. 1).

2. State of the art

2.1. Membrane bioreactor

Membrane bioreactor (MBR) technology is a promising method for water and wastewater treatment because of its ability to produce high-quality effluent that meets water quality regulations [1,2]. Due to the

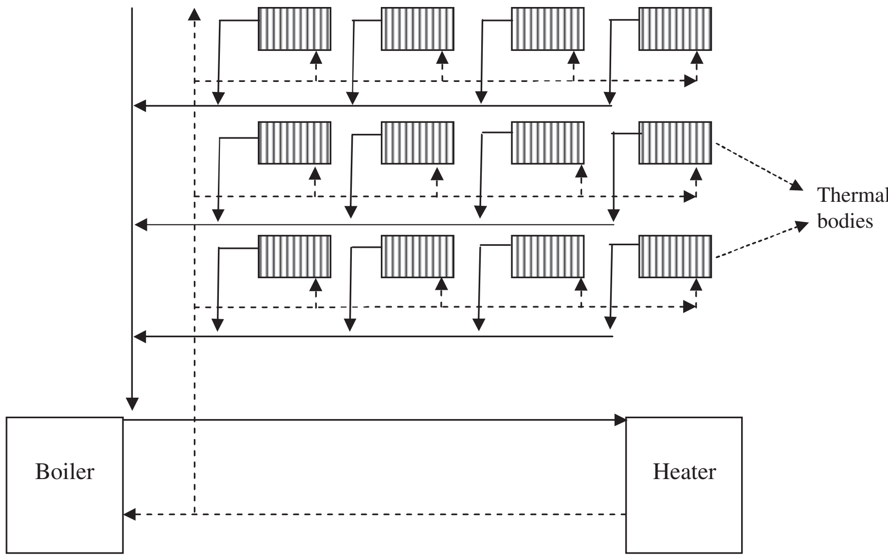

Fig. 1. Typical central heating system.

intrinsic complexity and uncertainty of MBR processes, basic models that can provide a holistic understanding of the technology at a fundamental level are of great necessity. The MBR is a system that combines biological treatment with membrane filtration into a single process. The first reported application of MBR technology was in 1969, when an ultrafiltration membrane was used to separate activated sludge from the final effluent of a biological wastewater treatment system and the sludge was recycled back into the aeration tank [1,3]. Since then, the MBR system has evolved, and research on MBR technology has increased significantly, particularly in the last five years [1,4]. The advantages of the MBR system over conventional biological treatment processes spur the growing interest in MBR technology for water and wastewater treatment. MBR treatment of municipal wastewater yields high-quality water with reported removal percentages of 95, 98 and 99% (or greater) for chemical oxygen demand (COD), biochemical oxygen demand (BOD) and suspended solids (SS), respectively [1,2,5]. This is important as water quality regulations have become increasingly stringent. A MBR has greater (independent) control over the suspended solids retention time (SRT) and hydraulic retention time (HRT) because membrane filtration rather than gravitational settling is used to separate the biomass from the effluent. This allows for operation at a longer SRT and at higher loading rates, which results in less sludge production and shortens the necessary HRT. The use of membranes to separate the biomass from the effluent also eliminates the need for large clarifying basins to settle out the biomass, thus enabling the system to be more compact [1].

2.2. Oxidation using Fenton reactions

Fenton reaction was discovered about 100 years ago, but its application as an oxidizing process for destroying toxic organics was not applied until the late 1960s [6]. Fenton reaction wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water. The main advantage is the complete destruction of contaminants to harmless compounds, e.g. CO_2, water and inorganic salts. The Fenton reaction causes the dissociation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants. Recently, advanced oxidation processes (AOPs) have been proposed to treat relatively low-strength industrial wastewaters containing non-biodegradable substances toxic to microorganisms. Among them, the Fenton method is cost-effective, easy to apply and effective with relatively low-strength wastewater containing organic compounds and has been applied to the decolorization of textile wastewater [6–12].

The Fenton method consists of four stages. First, pH is adjusted to low acidity. Then, main oxidation reaction takes place at pH value of 3–5. The wastewater is then neutralized at pH of 7–8 and finally precipitation occurs [11–13]. The oxidation mechanism in the

Fenton process involves the reactive hydroxyl radical generated under acidic conditions by the catalytic decomposition of hydrogen peroxide, which reacts unselectively within 1×10^{-3} s, with organic substances (RH), which are based on carbon chains or rings and also contain hydrogen, oxygen, nitrogen or other elements. The reaction mechanism is as follows [11,12,14,15]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + ^{\cdot}OH \quad (1)$$

$$RH + ^{\cdot}OH \rightarrow R^{\cdot} + H_2O \quad (2)$$

$$R^{\cdot} + Fe^{3+} \rightarrow \text{product} + Fe^{2+} \quad (3)$$

$$Fe^{2+} + ^{\cdot}OH \rightarrow Fe^{3+} + OH^- \quad (4)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\cdot} \quad (5)$$

Only a few applications of Fenton oxidation to high-strength wastewater such as effluent from a baker's yeast industry effluent or olive oil mill wastewater have been reported [16].

The Fenton oxidative process is a method of chemical oxidation and coagulation of organic compounds. It is performed by the implementation of hydrogen peroxide (H_2O_2) and a ferrous salt (Fenton's reagent) [14,17–19]. With the addition of Fenton's reagent, first soluble organics are successfully oxidized, and then, with the coagulation procedure, insoluble organics are successfully removed. Fenton's reagent is suitable to process a wide variety of effluents regardless of their contaminant concentrations and nature. It is an economical system characterized by its simple application and possibility of using perfectly mixed tank reactors. The system can also be adapted to different volumes and conditions [13].

Compared to other AOPs, Fenton's reaction presents several advantages. H_2O_2 is environmentally friendly, since it slowly decomposes into oxygen and water. Besides, the abundance, lack of toxicity and ease of removal from water make Fe^{2+} the most commonly used transition metal for Fenton's reaction applications. Consequently, numerous research and filed studies have been carried out to take advantage of the potential benefits of the use of Fenton's reaction as a remediation process for the treatment water and wastewater [15,20,21].

The paper focus on the physicochemical characterization of unknown wastewater which is produced from the maintenance of house heating as well as on chemical oxidation and MBR methodologies applied.

3. Materials and methods

3.1. Processes description

In the last few decades, Cyprus had a record of successful economic performance and reflected in rapid growth, full employment conditions and external and internal stability; characteristic of the post-Independence period [22,23]. The underdeveloped economy, inherited from colonial rule until 1960, has been transformed into a viable economy with dynamic services, industrial and agricultural sectors and advanced physical and social infrastructure. In terms of per capita, income is currently estimated in US $13,000 during 2000 and $20,000 during 2008; it is classified as the highest income country of all the entering new EU members [22,23]. A typical house in Cyprus is about $200 \pm 20\,m^2$ which includes usually three bedrooms, two bathrooms, kitchen, living room and office as well as storage areas and garage. Approximately, up to 12–17 heat source is utilized and somewhere of 300–350 metres of pipes (diameter from 16–18 mm, producing approximately 1.2–2.5 t of liquid waste per maintenance year). Usually, the water into the heat source never changes (as many central heating systems were designed to be self-circulating), although all the constructors mention that this water must change every five years in order to retain their effectiveness. During the last 15 years, the heat source changes from copper to iron. The only treatment method that has been applied until now, any time that a central heating is maintained, is the disposal of this waste to the land or to a sewage treatment plant if exist in the area.

3.2. Samples collection

The samples were collected from several houses. Quantities of 25 L were collected from new house (which was five years: H5), a house that was about 10 years old (H10) and from two older ones (which was more than 20 years, Ha20 and Hb20). Houses H5, H10, Ha20 were use still thermal body while Hb20 use a copper thermal body.

3.3. Samples analysis

All samples were analysed [24,25] in series of parameters: pH, electronic conductivity (EC), salinity, colour, turbidity, Specific weight, total solids (TS), SS, dissolve solids (DS), total hardness, permanent hardness, transient hardness, alkalinity, carbonates (CO_3^-), bicarbonates (HCO_3^-), sulphates (SO_4^-), chlorides (Cl_2), nitrates (NO_3^-), nitrites (NO_2^-), phosphates (PO_4^-), ammonium (NH_4^+), total kjeldahl nitrogen (TKN), COD, biological oxygen demand (BOD_5), sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), Iron (Fe), cooper (Cu), zinc (Zn) and chromium (Cr). The heavy metal concentrations were measured by atomic absorption spectroscopy using a Perkin-Elmer 2,380 spectrophotometer. Seed germination and root length test were performed on water extracts obtained by mixing 10 g of each sample with 20 mL of dis-distilled water (DDW), for 2 h. Suspensions were centrifuged at 5,000 rpm for 30 min before being filtered through Whatman No 1 filter paper. Then, 10 mL of each test solution was pipetted into a sterilized plastic petri dish. Also, one blank with only DDW was carried out. Twenty lettuce seed were placed in each petri dish and incubated at 22˚C in the dark for 7 days. The Germination Index (GI) was calculated according to the following formula, [26]:

$$GI = \frac{(\%G)(\%L)}{100} \text{ where } \%G = \text{Grow index} \quad (6)$$

$$\%L(\text{Root length}) = \frac{(\text{Root length of treatment})}{(\text{Root length of control})} \times 100 \quad (7)$$

3.4. Treatment methodology

The proposed treatment methodology involves the use of (a) MBR and (b) the implementation of Fenton as decrypted below.

3.4.1. Membrane bioreactor

A batch, cylindrical reactor combined with an immersed membrane module, was employed in this study. The batch reactor was made of plexiglass and the membrane module consisted of hollow fibres from PVDF with a nominal pore size of 0.04 μm and a total membrane surface area of 0.047m^2. The experimental apparatus is shown in Fig. 2. The membrane was connected to a suction pump that operated under constant suction pressure of -25 kPa. Constant aeration of 5 L min^{-1} was provided to the membrane module in order to minimize fouling, while 8 L/min of fine bubble aeration was provided in order to maintain the sample under suspension. The MBR system was operated at steady state conditions with a HRT equal with 7 days. The wastewater was placed into the batch reactor from a balance tank (in order to have a stable flow) and 45 min of filtration was performed at a constant suction pressure of -25 kPa. Samples were taken at intervals of 15, 30 and 45 min for metal determination. This experiment was repeated at least three times. Prior to the conduction of each filtration experiment, the membrane module was chemically cleaned by placing the membrane module in 1000 ppm of NaOCl solution (as free Cl_2) for at least 1 h and the initial clean water membrane permeability was determined.

3.4.2. Fenton Process

The aim of the experimental procedure was to determine the influence of some basic process parameters on the effectiveness of the oxidation treatment in terms of colour removal and COD. These parameters are dilution of wastewater, heptahydrated ferrous sulphate concentration, H_2O_2 concentration and sulphuric acid concentration. These parameters are referred to as "controlling parameters" of the system. The effect of the controlling parameters on the optimization performance was estimated by performing a 24 factorial experiment. In general, by using a second factorial design, *n*-controlling parameters interrelate to an optimization parameter through an appropriate linear model. Their significance can also be estimated and

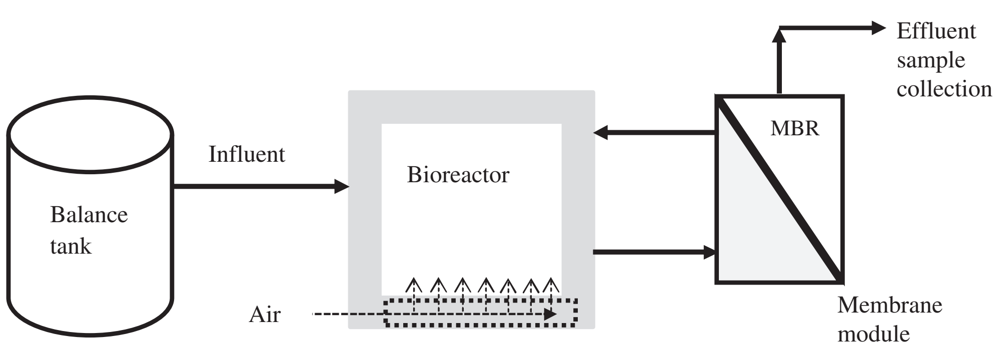

Fig. 2. Experimental procedure.

Table 1
Controlling parameters and their levels in the factorial experiment.

	Controlling parameters		Variation intervals		
	Units	Representation as	+1 Level	0 Level	−1 Level
Wastewater dilution	%	X_1	0	10	25
$FeSO_4·7H_2O$ addition	$g L^{-1}$	X_2	2.0	2.5	3.0
H_2O_2 (30%) addition	$mL L^{-1}$	X_3	1.0	1.50	2.50
HNO_3 (98%) addition	$mL L^{-1}$	X_4	0.40	0.20	0.60

assessed [11,12,27,28]. Then, the most significant variables are altered stepwise, aiming at the determination of the optimum experimental conditions. The levels of the controlling parameters are given on Table 1. The experimental area of the factorial design was predetermined in previous preliminary trials. In the 24 factorial designs, 16 experiments were carried out. Four extra experiments in the centre of the design (level 0) were also conducted for statistical purposes. Each experiment was repeated three times and the results presented are the mean values.

The wastewater was subject to Fenton oxidation treatment. The oxidation was carried out batch wise at 25˚C in an agitated (300 rpm) glass reactor of 1L capacity, equipped with temperature and pH control for 90 min. Next, HNO_3 (98%) and Fenton reagent were added. When ferrous salt, $FeSO_4·7H_2O$, was used, the H_2O_2 was of 30% concentration. After oxidation, vigorous stirring, neutralization with lime, coagulation with a weak anionic polyelectrolyte (2,540 Praestol, 0.01%) and flocculation in a jar test apparatus, the sample was filtered and the supernatant liquid was analysed in terms of colour and COD.

4. Results and discussion

Physicochemical characteristics of the central heating wastewaters from the four houses and the

Table 2
Physico-chemical characteristics of the collected samples.

Parameter	H5	H10	Ha20	Hb20	Water quality
pH	6.53 ± 0.03	5.74 ± 0.02	3.37 ± 0.04	3.61 ± 0.04	7.52 ± 0.02
EC, mS/cm	910 ± 0.12	825 ± 0.09	701 ± 0.08	687 ± 0.10	950 ± 12
Salinity, ppm $CaCO_3$	412 ± 0.11	386 ± 0.10	342 ± 0.09	322 ± 0.09	415 ± 7
Colour	7 ± 1	13 ± 1	23 ± 1	22 ± 1	0
Turbidity ftu	0.2 ± 0.1	0.4 ± 0.1	0.7 ± 0.1	0.8 ± 0.1	0
Specific weight, gr/ml	1.008 ± 0.018	0.994 ± 0.016	0.998 ± 0.051	1.108 ± 0.032	0.987 ± 0.011
TS, ppm	850 ± 27	975 ± 49	1,050 ± 105	1,247 ± 69	±
SS, ppm	263 ± 35	274 ± 41	356 ± 50	405 ± 36	±
DS, ppm	455 ± 72	512 ± 66	621 ± 63	640 ± 42	±
Total hardness, ppm $CaCO_3$	31.4 ± 5.18	70.8 ± 7.3	110.8 ± 14.3	108.1 ± 14.3	342.2 ± 12.3
Permanent hardness, ppm $CaCO_3$	17.9 ± 4.23	8.09 ± 2.1	15.1 ± 4.1	17.2 ± 7.2	220.5 ± 9.1
Transient hardness, ppm $CaCO_3$	13.1 ± 3.3	61.05 ± 10.3	95.7 ± 6.9	90.9 ± 9.6	114.5 ± 7.9
Alkalinity in phenolophthalein, ppm	0	0	0	0	0
Alkalinity in methyl orange, ppm	25 ± 2	50 ± 3	71 ± 5	75 ± 6	70 ± 2
CO_3^-, ppm	0	0	0	0	0
HCO_3^-, ppm	30.5 ± 5.2	61.01 ± 4.1	75.2 ± 6.7	76.3 ± 7.1	98.4 ± 2.2
SO_4^-, ppm	33.2 ± 4.4	44.6 ± 7.5	51.2 ± 6.2	49.6 ± 5.4	11.6 ± 1.9
Cl_2, ppm	254.2 ± 21.9	270.6 ± 22.1	238.8 ± 18.9	217.5 ± 17.3	287.6 ± 4.3
NO_3^-, ppm	0.04 ± 0.01	2.2 ± 0.08	4.5 ± 1.6	5.1 ± 1.1	6.6 ± 0.8
NO_2^-, ppm	0.01 ± 0.005	0.02 ± 0.004	0.03 ± 0.006	0.01 ± 0.005	0.01 ± 0.005
PO_4^-, ppm	0.02 ± 0.005	0.07 ± 0.01	0.08 ± 0.01	0.07 ± 0.01	0.05 ± 0.01
NH_4^+, ppm	2.78 ± 0.54	1.21 ± 0.71	1.57 ± 0.63	1.92 ± 0.42	0.15 ± 0.06
COD, ppm	110.2 ± 7.9	248.4 ± 15.7	210.4 ± 7.8	208.7 ± 12.1	32.1 ± 1.2
BOD_5, ppm	2.2 ± 0.9	3.6 ± 1.2	3.01 ± 0.91	3.5 ± 1.4	0.7 ± 0.1

drinking water quality are presented in Table 2. pH varies from 3.37 ± 0.04 to 6.53 ± 0.04. Samples from Ha20 and Hb20 presented with pH 3.37 and 3.61 respectively. Conductivity presented to be low but Hb20 has the lowest consecration up to 687 mS/cm. Colour and turbidity are a very significant parameter for those wastewaters. Ha20 and Hb20 presented with high turbidity than the H5as they had never be maintained. These impurities may include clay, silt, finely divided inorganic and organic matter, soluble colour organic compounds and plankton and other microscopic organisms. COD for all the samples (expect H5) is at the range of 200–250 ppm. H5 presented with COD up to 110 ppm. Due to chemical used, the hardness and the conductivity of the samples are lowest from the water used.

Alkalinity and hardness are very high in the oldest houses Ha20 and Hb20 than the new ones which seem to be very logical as the equipment was never maintained in the past and the water never changed. Nitrates, nitrites, phosphates and ammonium are very low for all the samples and were attributed to the drinking water quality of the city that has very low content of these substances. It is obvious from Table 3 that Hb20 has higher concentration of Cu as the thermal bodies used in the building were constructed from cupper than iron used in the other houses. For all the samples, there is a continuous increasing of metals in the wastewater with the sample. Fig. 3 presents the GI. The GI characterized the toxicity of the wastewater when is intended to be used for irrigation. It is important to mention that, if a sample with a GI 0 < GI < 26 is characterized as very phytotoxic, when 27 < GI < 66 the water is characterized as phytotoxic, 67 < GI < 100 the sample is characterized as non-phytotoxic and if the GI >101 then the sample is characterized as phyto-nutrient according to Zorpas [26]. In this study, GIs were higher than 150.

Turbidity is a principal physical characteristic of water and is an expression of the optical property that

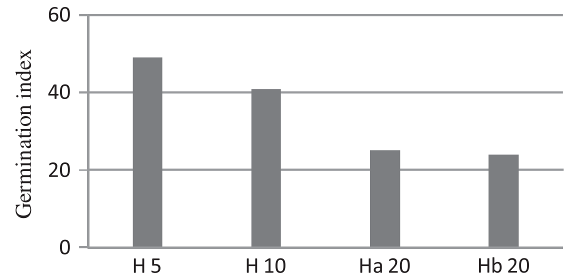

Fig. 3. GI for wastewater samples collected from the central heating system of four buildings in Cyprus.

causes light to be scattered and absorbed by particles and molecules rather than transmitted in straight lines through a water sample. It is caused by suspended matter or impurities that interfere with the clarity of the water. Table 4 presents the results from the batch experiment of the implementation of MBR. COD is reduced up to 95%. Zhang et al. [28] mention that a COD removal was up to 97% from the implementation of a stainless steel membrane module with a 0.2 μm nominal pore diameter, in domestic sewage treatment. MBR presented high efficiency in the removal of heavy metals and nutrients: 100% removal of Cr, Zn, Cu and Fe while the other metals vary from 80–97% or removal.

Fenton processes are suitable to treat a wide variety of effluents irrespective of their concentration and origin, and are characterized by their simple and versatile operation. Usually, the application of Fenton decreases the COD from 60–80% and the colour from 85–100%. Rivas et al. [29] estimated that the application of Fenton in a heavy-polluted waste from olive oil solid residue was up to 90% in residence times between 1 and 8 h. Zorpas and Costas [11] and Zorpas and Inglezakis [12] found out that the application of Fenton in a heavy-polluted waste from olive oil mills reduces the COD up to 75% and the colour more than

Table 3
Trace elements and heavy metals.

Parameter	H5	H10	Ha20	Hb20	Water quality
Na, ppm	170.1 ± 5.3	159.3 ± 9.3	198.3 ± 17.9	175.1 ± 12.3	195.7 ± 3.6
K, ppm	15.3 ± 2.4	12.6 ± 3.1	10.1 ± 6.1	12.3 ± 5.5	4.3 ± 0.8
Ca, ppm	18.5 ± 3.3	23.4 ± 5.1	55.5 ± 8.1	47.3 ± 7.4	75.2 ± 5.9
Mg, ppm	6.2 ± 1.2	7.7 ± 2.1	16.3 ± 9.2	12.2 ± 2.1	8.7 ± 1.1
Fe, ppm	0.17 ± 0.09	1.12 ± 0.75	4.33 ± 1.13	3.98 ± 0.87	0.06 ± 0.01
Cu, ppm	1.66 ± 0.36	2.11 ± 0.55	4.26 ± 1.02	15.3 ± 3.9	2.3 ± 0.01
Zn, ppm	1.12 ± 0.22	1.98 ± 0.41	3.09 ± 0.78	3.14 ± 1.21	1.09 ± 0.02
Cr, ppm	0.032 ± 0.004	0.041 ± 0.015	0.051 ± 0.011	0.048 ± 0.011	Not detected

Table 4
Physico-chemical characteristics of treated wastes with MBR and MBR effectiveness.

Parameter	H5	H10	Ha20	Hb20
pH	7.02 ± 0.03	7.14 ± 0.02	6.47 ± 0.04	6.59 ± 0.04
EC, mS/cm	10.3 ± 0.07	12.5 ± 0.04	13.1 ± 0.06	12.6 ± 0.15
Salinity, ppm $CaCO_3$	5.4 ± 0.41	6.23 ± 0.12	5.18 ± 0.14	6.99 ± 0.16
Color	0	0	0	0
Turbidity, ftu	0	0	0	0
TS, ppm	2.05 ± 0.09	2.35 ± 0.04	3.52 ± 0.07	3.06 ± 0.06
SS, ppm	0.96 ± 0.06	0.88 ± 0.05	0.94 ± 0.03	0.99 ± 0.06
DS, ppm	0.55 ± 0.02	0.49 ± 0.03	0.67 ± 0.05	0.46 ± 0.03
Total hardness, ppm $CaCO_3$	27.1 ± 1.2	50.8 ± 3.9	78.9 ± 4.1	67.1 ± 3.9
Alkalinity in methyl orange, ppm	25 ± 2	50 ± 3	71 ± 5	75 ± 6
CO_3^-, ppm	0	0	0	0
HCO_3^-, ppm	10.5 ± 2.6	23.2 ± 1.9	32.8 ± 3.5	29.4 ± 3.9
Cl_2, ppm	2.5 ± 0.7	4.8 ± 2.1	3.1 ± 1.3	4.2 ± 1.1
COD, ppm	18.9 ± 2.6	31.8 ± 4.6	26.9 ± 3.5	29.6 ± 3.3
BOD_5, ppm	0.98 ± 0.19	1.1 ± 0.51	1.24 ± 0.77	1.14 ± 0.56
MBR efficiency for trace elements and heavy metals per each sample				
Na	80%	82%	78%	81%
K	97%	97%	97%	97%
Ca	87%	86%	86%	85%
Mg	98%	98%	98%	98%
Fe	100%	100%	100%	100%
Cu	100%	100%	100%	100%
Zn	100%	100%	100%	100%
Cr	100%	100%	100%	100%
Colour	100%	100%	100%	100%
COD	82%	87%	87%	86%

70%. Table 5 presents COD and colour removal efficiency results of the factorial experiments.

From our results, it is clear that Fenton has the ability to treat this waste efficiency and reduces the colour up to 100% and the COD (although it is not a critical parameter for this waste) up to 84%. From this data, a mathematical model was constructed. Its adequacy was checked by the Fisher criterion. According to the latter, the following ratio should follow the *F*-distribution with level of importance $p = 5\%$:

$$F = \frac{S_{ad}^2}{S_Y^2} \tag{8}$$

where S_Y^2 is the standard deviation, and S_{ad}^2 is the adequacy deviation and is calculated by the following equation:

$$S_{ad}^2 = \frac{\sum_{i=1}^{N}(Y_i - \hat{Y}_i)^2}{f} \tag{9}$$

where Y_i is the experimental *i* value, $\hat{Y}_i$ is the estimated *I* value from the model determined, *f* is the number of degrees of freedom and *N* is the number of trials.

As far as the determination of statistically important parameters is concerned, the procedure mentioned below was followed. The coefficient deviation is defined as:

$$S^2(b_j) = \frac{S_Y^2}{N} \tag{10}$$

where *N* is the number of trials.

The importance of the coefficient was checked by:

$$t = \frac{|b_j|}{S(b_j)} \tag{11}$$

where b_j is the *j* linear coefficient. "*t*" should follow the Student distribution for importance level $p = 5\%$ and degrees of freedom those of the deviation $S^2(Y)$. After the mathematical model construction and the

Table 5
Per cent of COD and Colour removal efficiency results of the factorial experiment.

Trial	X1	X2	X3	X4	% COD efficiency Ha20	% Colour efficiency in Ha20
1	+	+	+	+	72.56	98
2	−	+	+	+	84.62	100
3	+	−	+	+	71.39	96
4	−	−	+	+	70.52	100
5	+	+	−	+	71.18	99
6	−	+	−	+	74.39	100
7	+	−	−	+	72.66	100
8	−	−	−	+	77.19	100
9	+	+	+	−	79.77	98
10	−	+	+	−	72.44	98
11	+	−	+	−	74.23	96
12	−	−	+	−	71.17	100
13	+	+	−	−	74.28	97
14	−	+	−	−	76.06	100
15	+	−	−	0	74.12	98
16	−	−	−	0	81.17	100
17	0	0	0	0	76.19	100
18	0	0	0	0	75.09	99
19	0	0	0	0	75.13	100
20	0	0	0	0	76.15	100

determination of statistically important parameters, an effort to find the optimum conditions for the effectiveness of the Fenton oxidation treatment of those *y* wastewater was made. This was performed through a steepest ascent method [11,12,27].

5. Conclusion

In conclusion, this study presents the characteristic of unknown waste until now which is produced from the houses' central heating while they are maintained. One of the most significant problems that it presented in the central heating of the house is that the heating loses its performance as the water which is into the pipes and the thermal body never changes. Until now, there is no any specific regulation that may cover those kinds of wastes. Usually, those wastes have very dark colour, low pH and high total solids. However, the quality of those wastes has strong relation with the town's water. The waste can be characterized as hazardous as the pH is low and the GI is less than 50. Also, due to the fact that the water usually never changes, some metal are extract from the equipment and pass into the water. Ha20 and Hb20 indicated that if the houses' domestic heating is not maintained, then the waste is characterized as toxic and hazardous. MBR technology is more promising than the application of Fenton method for water and wastewater treatment because of its ability to produce high-quality effluent that meets water quality regulations. The implementation of the MBR for the treatment of those wastes seems to be promising methods and is characterized with significant performance.

References

[1] N.L. Ng Aileen, S.K. Albert, A mini-review of modelling studies on membrane bioreactor (MBR) treatment for municipal wastewaters, Desalination 212 (2007) 261–281.
[2] S. Zhang, Y. Qu, Y. Liu, F. Yang, X. Zhang, K. Furukawa, Y. Yamada, Experimental study of domestic sewage treatment with a metal membrane bioreactor, Desalination 177 (2005) 83–93.
[3] C.W. Smith, D. Gregorio, R.M. Taleott, The use of ultrafiltration membrane for activated sludge separation, in: Presented at the 24th Annual Purdue Industrial Waste Conference, Purdue University, West Lafayette, IN, 1969, pp. 1300–1310.
[4] W. Yang, N. Cicek, J. Ilg, State-of-the-art of membrane bioreactors: Worldwide research and commercial applications in North America, J. Membr. Sci. 270 (2006) 201–211.
[5] J. Manem, R. Sanderson, Membrane bioreactors, Water treatment membrane processes, J. Mallevialle, P.E. Odendaal and M.R. Wiesner, (Eds.), McGraw-Hill, New York, NY, 1996 pp. 17.1–17.31.
[6] C.P. Huang, C. Dong, Z. Tang Z, Advanced chemical oxidation: Its present role and potential future in hazardous waste treatment, Waste Manage. 13 (1993) 361–377.
[7] K. Swaminathan, S. Sandhya, A.C. Sophia, K. Pachhade, Y.V. Subrahmanyam, Decolorization and degradation of H-acid and other dyes using ferrous–hydrogen peroxide system, Chemosphere 50 (2003) 619–625.

[8] T.H. Kim, C.H. Park, J.M. Yang, S.Y. Kim, Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation, J. Hazard. Mater. 112 (2004) 95–103.
[9] S. Meric, D. Kaptan, T. Olmez, Color and COD removal from wastewater containing reactive black 5 using Fenton's oxidation process, Chemosphere 54 (2004) 435–441.
[10] S. Meric, H. Selcuk, V. Belgiorno, Acute toxicity removal in textile finishing wastewater by Fenton's oxidation, ozone and coagulation–flocculation processes, Water Res. 39 (2005) 1147–1153.
[11] A.A. Zorpas, C.N. Costa, Combination of Fenton oxidation and composting for the treatment of the olive solid residue and the olive mile wastewater from the olive oil industry in Cyprus, Bioresour. Technol. 101(20) (2010) 7984–7987.
[12] A.A. Zorpas, V.J. Inglezakis, Intergraded applied methodology for the treatment of heavy polluted waste waters from the olive oil industries. Appl. Environ. Soil Sci. (2011), Article ID 537814, 14 pages.
[13] R.J. Bidga, Consider Fenton's chemistry for wastewater treatment, Chem. Eng. Prog. 91(12) (1995) 62–66.
[14] Y.W. Kang, K.Y. Hwang, Effects of reaction condition on the oxidation efficiency in the Fenton process, Water Res. 34 (2000) 2786–2790.
[15] X.R. Xu, Z.Y. Zhao, X.Y. Li, J.D. Gu, Chemical oxidative degradation of methyl tert-butyl ether in aqueous solution by Fenton's reagent, Chemosphere 55 (2004) 73–79.
[16] M. Altinbas, A.F. Aydin, M.F. Sevimli, I. Ozturk, Advanced oxidation of biologically pretreated baker's yeast industry effluents for high recalcitrant COD and color removal, J. Environ. Sci. Health. Part A 38 (2003) 2229–2240.
[17] H.J.H. Fenton, Oxidation of tartaric acid in the presence of iron, J. Chem. Soc. 65 (1894) 899–911.
[18] A.P. Murphy, W.J. Boegli, A Fenton-like reaction to neutralize formaldehyde waste solution, Environ. Sci. Technol. 23 (1989) 166–169.
[19] S.H. Gau, F.S. Chang, Improved Fenton method to remove recalcitrant organics in landfill leachates, Water Sci. Technol. 34(7–8) (1996) 455–462.
[20] A.A. Burbanoa, D.D. Dionysioua, M.T. Suidana, T.L. Richardson, Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reaction, Water Res. 39 (2005) 107–118.
[21] M.I. Badawy, M.Y. Ghaly, Advanced oxidation processes for the removal of organo-phosphors pesticides from wastewater, Desalination 194 (2006) 166–175.
[22] A.A. Zorpas, C. Coumi, M. Drtil, I. Voukkali, Municipal sewage sludge characteristics and waste water treatment plant effectiveness under warm climate conditions, Desalin. Water Treat. 36 (2011) 1–15.
[23] A.A. Zorpas, M. Drtil, C. Coumi, I. Voukkali, P. Samaras, Operation description and physicochemical characteristics of influent, effluent and the tertiary treatment from a sewage treatment plant of the Eastern region of Cyprus under warm climates conditions. A seven year project, Desalin. Water Treat. 22 (2010) 244–257.
[24] APHA, AWWA-WPCF, Standard Methods for the Examination of Water and Wastewater, 10th ed., American Public Health Association, Washington, DC, 1995.
[25] A.A. Zorpas, A.G. Vlyssides, M. Loizidou, Physical and chemical characterization of anaerobically stabilized primary sewage sludge, Fresenius Environ. Bull. 7 (1998) 383–508.
[26] A.A. Zorpas, Sewage sludge compost evaluation in oats, pepper and eggplant cultivation. Dyn. Soil Dyn. Plants. Global Science Book 2(2) (2008) 103–109.
[27] Y.P. Alder, E.V. Markova, Y.V. Granovsky, The Design of Experiments to Find Optimal Conditions, Mir Publisher, Moscow, 1995.
[28] S. Zhang, Y. Qu, Y. Liu, F. Yang, X. Zhang, K. Furukawa, Y. Yamada, Experimental study of domestic sewage treatment with a metal membrane bioreactor, Desalination 177 (2005) 83–93.
[29] F.J. Rivas, F.J. Beltrán, O. Gimeno, J. Frades, Treatment of olive oil mill wastewater by Fenton's reagent, J. Agric. Food. Chem. 49 (2001) 1873–1880.