

Optimizing energy from an economic and environmental point of view in the treatment of industrial caustics (Bander Imam petrochemical complex)

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ABSTRACT

Previous research has shown that increasing the level of functional activity, including walking, reduces the probability of chronic back pain in the future. Therefore, this study aimed to the effect of walking exercise on stability indices, pain and disability in patients with chronic nonspecific LBP. In this randomized clinical trial, 36 subjects with nonspecific LBP were included. The subjects were randomly divided into a routine exercise group and walking group. Exercises were conducted three times per week for six weeks. Overall, stability indices were measured with the Biodex balance system. In the walking group, the overall dynamic stability index significantly changed from 1.85 ± 0.544 to 0.483 ± 0.222 , the mediolateral dynamic stability index significantly changed from 0.955 ± 0.206 to 0.233 ± 0.118 , and the anteroposterior dynamic stability index significantly changed from 1.41 ± 0.609 to 0.399 ± 0.216 . There is no significant difference in the static and dynamic stability index between routine and walking groups. The positive effects of walking exercise on postural control reactions were shown, so we suggest that in addition to routine exercises, walking exercise should also be considered in subjects with chronic nonspecific LBP.

Keywords: Energy optimization, Industrial caustics, Bandar Imam petrochemical complex, Economic aspect, Environmental aspect

Introduction

Access to clean and healthy water is one of the most basic human needs to live on earth. For this reason, wastewater is one of the most valuable water resources available today. Water quality is affected by pollution caused by human activities such as agriculture, mining and energy production [1]. On the other hand, fossil fuels are one of the most important branches of energy supply that have benefited mankind for many years. Increasing environmental pollution, global warming, and climate change are the most important side effects of using these fuels, which make people think about green and clean energy [2]. Among the types of wastewater, industrial wastewater is more important due to its high consumption and variety of pollutants. Pollutants such as carbon dioxide, nitrogen oxides, sulfur dioxide, volatile organic compounds, heavy metals, are not easily decomposed and can pollute groundwater if improperly discharged into the environment [3]. Therefore, it is necessary to

remove these pollutants from the wastewater before the final discharge to the environment. Based on operating conditions, operating units and types of processed materials, different wastewaters are produced. Some wastewaters must be treated separately because their combination with other wastewaters makes treatment difficult [4]. One of the most important materials used in oil and gas refineries is sodium hydroxide solutions. Sodium hydroxide, also known as caustic, is used in petroleum and other industries such as food, pulp and paper, tanning, wood preservatives, and hygiene [5]. Olefin units include processes in the oil and gas industry that use caustic materials. In olefin units, sodium hydroxide is often used to remove organic sulfur compounds, hydrogen sulfide, and carbon dioxide from hydrocarbon streams such as natural gas and liquid petroleum gas. Additionally, sodium hydroxide solution is used to remove acidic components such as chrysalis, mercaptans, and naphthenic acids from streams. In addition, caustic is also used to separate sulfur compounds from furnace exhaust gases, which are

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one of the most important adverse factors in the process [6, 7]. Also, caustic is used as a carbon dioxide gas absorber in light oil cuts, as a sulfide absorbent in the treatment of various oil cuts, and for dewatering hydrocarbon flows. In addition, it is used in industrial processes such as gas scrubbing and oil sweetening [8]. Other uses of this solution include scrubbing gasoline, kerosene, and distilled oils [9]. Although caustic is a very valuable material, the residual and soluble materials produced from the consumption of caustic in the oil and gas industry are known as two hazardous industrial wastes. Used caustic is very toxic and has an unpleasant smell. This wastewater has a high pH (pH > 12), high sulfide concentration (1-4% by weight), and high salinity (5-12% sodium by weight) and is classified as hazardous under the US Resource Conservation and Recovery Act. Wastes, therefore, must be treated before discharge [10, 11]. In addition, depending on the type of industry, caustic used can also contain thiol, amine, phenol, hydrogen sulfide and mercaptan, which are compounds that sit on the surface of the skin, are easily absorbed into the bloodstream and cause adverse effects on the body [12]. On the other hand, petrochemical products are considered as an integral part of human life, and various petrochemical products with their many applications have a great contribution in meeting the daily needs of human beings, which include the manufacture and production of pharmaceuticals, health materials, textiles, electronic industries, etc. cited. More than 500 different processes are used in petrochemical industries. Therefore, the potential of these industries to pollute the environment is evident. Also, with the increasing expansion of petrochemical products in the world, the importance and necessity of controlling the pollution caused by these industries is undeniable. From the environmental aspects of petrochemical industries, we can mention the production of various process effluents. Caustic wastewater from olefinic units is an example of this type of wastewater, since these wastewaters have a high pollution load, they should be effectively treated before releasing them into the environment [13]. Currently, in our country, there is no comprehensive management related to the caustic waste used, so the researchers are looking to investigate their environmental and economic aspects. In general, caustic treatment methods are divided into three biological, chemical and thermal methods [14, 15]. Although most industries use the neutralization method to dispose of this waste, this method has a harmful effect on the environment due to the release and leaving of toxic compounds. Therefore, it is necessary to find alternative methods such as membrane-based methods [16], electrochemical removal method [17] and electrocoagulation method [18] in which the toxic substances in this wastewater are converted into harmless compounds [16]. The key limiting points of various proposed methods for caustic treatment include cost, operational complexity, high consumption of chemicals, as well as transportation and safety issues. Advanced oxidation methods such as chemical oxidation, Fenton, photofenton, processes based on ultraviolet radiation, photocatalytic oxidation-

regeneration and sonolysis are among the new methods based on the oxidation of purified compounds [19].

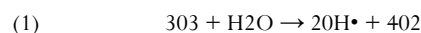
Barge et al [21] investigated the purification of spent caustics using wet air oxidation processes and catalytic wet air oxidation processes. They used a heterogeneous catalyst, FeSO₄, which is cheap and abundant. They obtained a COD decomposition of about 68% at 100 °C for 1 h, while a COD decomposition of 94% was achieved using a FeSO₄ catalyst under the same operating conditions. In another study, Bargh et al [22] investigated the refining of caustic cresyl using a ruthenium catalyst supported by multi-walled carbon nanotubes (Ru/CNT). The purification process was carried out in a slurry reactor for 2 hours. They achieved 61% COD decomposition at 175°C.

Materials and Methods

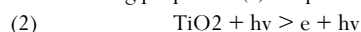
New methods have been developed for the biological treatment of waste caustic. Caustic oxidation of sulfide waste is carried out in aerobic reactors containing sulfide-oxidizing bacteria. Biological methods are widely used in the treatment of many wastewaters, but they are not suitable for wastewaters with chemical oxygen requirements greater than 10,000 mg/L. Also, micro-organisms need a lot of time to break down pollution, and due to biomass poisoning and sludge production, it is not a suitable method for this type of waste.

Incineration is used to process wastewaters with COD greater than 100,000 mg/L. Although this method is not recommended due to high energy consumption and release of toxic compounds such as furan and dioxin [1]. In the meantime, chemical methods are more common, which are introduced in detail.

Ozone is a strong oxidizer with an oxidation potential of 2.07 V. Under controlled conditions, hydroxyl radicals are produced from ozone. There are various complex mechanisms in explaining the production of hydroxyl radical, and the general reaction of this radical production is given below:



Hydroxyl radical is also produced in the presence of catalyst or oxidants and by photons. The common catalyst here is titanium oxide (TiO₂). Titanium oxide is excited and an empty space in the electron shell with oxidizing properties (h) and an electron with reducing properties (e) are produced.



With the reaction of OH and H₂O on the surface of the catalyst, these vacancies and electrons are hydroxyl radicals



It is produced:

In the presence of oxidants such as ozone or hydrogen peroxide with ultraviolet radiation, the hydroxyl radical

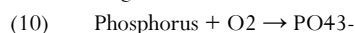
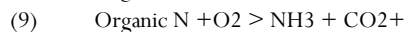
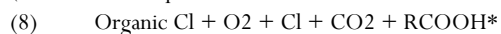
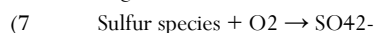
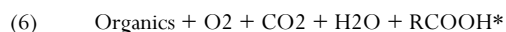


it is produced.

Among the existing metals, iron is most used in the production of hydroxyl radicals in the presence of hydrogen peroxide. In this method, which is known as Fenton's process, H₂O₂ reacts with +Fe²⁺ to produce hydroxyl [11].

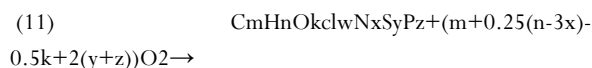
In the WAO process, according to the following reactions, organic compounds are converted into CO₂, water and short-chain biodegradable organic acids due to oxidation with air. The main advantage of this process is that they last. Elemental sulfur is converted into sulfate, halogens into halides and phosphors, phosphates, pollutants remain in the liquid phase, and nitrogenous pollutants are converted into ammonia, nitrate and nitrogen gas according to the feed composition and reaction conditions. Ammonia is produced, which is removed and controlled by using a suitable catalyst or using a suitable absorbent [18].

The remaining inorganic compounds are also oxidized according to the general reactions below.



The main reactions are similar to the burning process in that any compound that is burned in the WAO process can be oxidized in water. The WAO process is also used for the processing of aqueous wastes, slurries and sludges in which the concentration of organic compounds is high [13, 16, 19]. Another advantage that the WAO process has over burning is that in this process, insoluble organic compounds are converted into simpler and soluble compounds, which are finally oxidized to carbon dioxide and water, and none of the toxic and polluting compounds such as nitrous oxide Sulfur oxide, hydrochloric acid, dioxin furan and ash are not produced.

In general, the material balance is as follows, the amount of released energy is about 435 kJ per mole of reacted oxygen [20].



Results and Discussion

Chemical oxidation:

In this method, to remove pollutants from the wastewater, the oxidizer is directly combined with the wastewater at ambient temperature and pressure. The most common oxidizers in this method are chlorine, chlorine dioxide, oxygen, ozone permanganate persulfate, and hydrogen peroxide. **Table 1** shows the advantages and disadvantages of some oxidizers. In addition to the cost of these types of processes, another problem that exists in these processes is the production of intermediate

and toxic products, which must be separated by methods such as surface absorption.

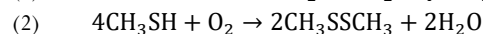
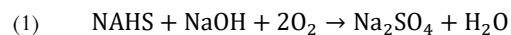
To prevent this problem, the compounds in the wastewater that produce these intermediate products must be separated from the wastewater before adding the oxidant, and the amount of the oxidant must also be controlled.

Advanced chemical oxidation:

Advanced chemical oxidation involves the production of hydroxyl radicals, which have high oxidizing power. Unlike other methods, instead of transferring these materials from one state to another, this method has the ability to remove organic and inorganic pollutants including aromatic carboxylic acids. This method was initially used in the early 80s to purify water, but later it is used to purify wastewater with high chemical oxygen requirements, where pollutants are converted into harmless carbon dioxide water and mineral salts. However, with the production of intermediates that are resistant to oxidation, this method alone is impractical. Therefore, this method is used as a pre-process of biological treatment.

Assumptions and simulation tools:

Chemical oxidation has been chosen to purify industrial caustics in this research. This purification will be done by oxygen or moist air. Keep in mind that in the third chapter, the chemical process related to this process was described and the items related to the cycle were identified in the corresponding image. In this simulation, there are two main equations which are as follows:



These two equations are the most important equations related to the design of the main reactor of the caustic or industrial leachate purification process. In these two equations, it is stated how the industrial leachate will be transformed into purified water from materials with high PH.

Figure 1 shows the cycle considered for this process. In this process, industrial leachate or caustic feed stream is first mixed with air or aerated. In this process, we need a pump to provide the flow related to the leachate and to flow it to combine with air. A compressor is also required to compress the air so that it is ready to be mixed with the leachates. Next, air and sap are mixed together using a mixer. A heat exchanger is used to increase the temperature of the leachate. The pre-heating of the leachate in this converter will be using the product obtained in the reactor, thus saving as much as possible in the use of thermal energy and reducing the thermal power of the cycle. Next, to enter the reactor, the leachate flow must first reach a suitable temperature level, for which a heater is used. In this heater, the temperature of the leachates reaches a suitable level for chemical reactions. Next, using a cooler or chiller, the temperature of the reactor product is reduced, and then it breaks its pressure by passing through a choke valve, and finally it enters the flash drum or separator to separate the dangerous gases, which are also acidic, from the cycle product.

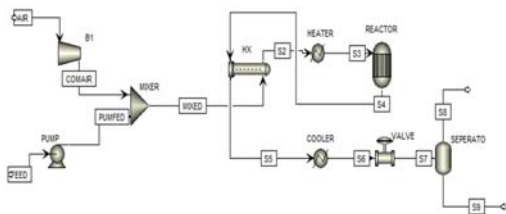


Figure 1. The cycle related to the simulation of industrial caustic purification process

The characteristics of the inlet air flow are specified in the figure below. 500 kg/h of primary air enters the cycle with a temperature of 25 and a pressure of 1 bar. This natural air also contains nitrogen gas. Here, the air has the task of accelerating the chemical reactions of the reactor, and the aeration of the leachates before reaching the reactor will prepare the mixture for the reaction in the reactor.

After designing the process with the proposed specifications, the initial results obtained for the currents in this process will be according to **Table 1**. All the physical, chemical and thermodynamic information related to all flows are specified in this table.

Table 1. Specifications of process flows after simulation

	Units	AIR	COMAIR	FEED	MIXED	PUMFED	S2
Description							
From			B1		MIXER	PUMP	HX
To		B1	MIXER	PUMP	HX	MIXER	HEATER
Stream Class		CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN
Phase		Vapor Phase	Vapor Phase			Liquid Phase	
Temperature	C	25.00	384.61	25.00	58.71	24.60	100
Pressure	bar	1.00	10.00	1.00	10.00	10.00	10.00
Molar Vapor Fraction		1.00	1.00	0.00	1.00	0.00	1.00
Molar Liquid Fraction		0.00	0.00	1.00	0.00	1.00	0.00
Molar Solid Fraction		0.00	0.00	0.00	0.00	0.00	0.00
Mass Vapor Fraction		1.00	1.00	0.00	1.00	0.00	1.00
Mass Liquid Fraction		0.00	0.00	1.00	0.00	1.00	0.00
Mass Solid Fraction		0.00	0.00	0.00	0.00	0.00	0.00
Molar Enthalpy	cal/mol	-1.97	2652.87	-68945.31	-3167.31	-68931.60	-3167.31
Mass Enthalpy	cal/gm	-0.06	82.91	-3813.71	-102.61	-3812.95	-102.61
Molar Entropy	cal/mol-K	0.02	1.24	-38.92	-0.98	-38.95	-0.98
Mass Entropy	cal/gm-K	0.00	0.04	-2.15	-0.03	-2.15	-0.03
Molar Density	mol/cc	0.00	0.00	0.02	0.00	0.05	0.00
Mass Density	gm/cc	0.00	0.01	0.44	0.01	0.96	0.01
Enthalpy Flow	cal/sec	-8.54	11514.64	-26484.11	-14964.21	-26478.85	-14964.21
Average MW		32.00	32.00	18.08	30.87	18.08	30.87
Mole Flows	kmol/hr	15.63	15.63	1.38	17.01	1.38	17.01
Mass Flows	kg/hr	500.00	500.00	25.00	525.00	25.00	525.00
Volume Flow	l/min	6452.15	1428.65	0.95	1200.76	0.43	1200.76

Also, the continuation of the specifications of the flows related to the simulation is also according to the table below. The output flow from the reactor is 525 kg/h, which has increased according to the equations of 1 and 2 percent of leachate after this reactor. Finally, the available vapors have a flow rate of about 517 kg/h, which are separated from liquids in the drum. **Table 1** also shows that in the used heat exchanger, the leachate flow has increased

the absolute temperature by about 50 degrees Celsius. This increase in temperature helps to reduce the amount of thermal power required by the heater and actually optimize and save on the amount of energy consumption and environmental issues related to excessive use of energy.

Table 2. Characteristics of different flows in the simulation

	Units	S3	S4	S5	S6	S7	S8	S9
Description								
From		HEATER	REACTOR	HX	COOLER	VALVE	SEPERATO	SEPERATO
To		REACTOR	HX	COOLER	VALVE	SEPERATO		
Stream Class		CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN	CONVEN
Phase							Vapor Phase	Liquid Phase
Temperature	C	140.00	140.00	140.00	40.00	21.49	40.00	40.00
Pressure	bar	10.00	10.00	10.00	10.00	1.00	1.00	1.00

Molar Vapor Fraction		1.00	1.00	1.00	0.92	0.94	1.00	0.00
Molar Liquid Fraction		0.00	0.00	0.00	0.08	0.06	0.00	1.00
Molar Solid Fraction		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass Vapor Fraction		1.00	1.00	1.00	0.96	0.96	1.00	0.00
Mass Liquid Fraction		0.00	0.00	0.00	0.04	0.04	0.00	1.00
Mass Solid Fraction		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Molar Enthalpy	cal/mol	-3882.81	-3900.10	-3900.10	-5453.61	-5453.61	-3278.94	-68702.93
Mass Enthalpy	cal/gm	-125.79	-126.33	-126.33	-176.66	-176.66	-105.12	-3808.32
Molar Entropy	cal/mol-K	-2.54	-2.55	-2.55	-6.80	-2.56	0.19	-38.07
Mass Entropy	cal/gm-K	-0.08	-0.08	-0.08	-0.22	-0.08	0.01	-2.11
Molar Density	mol/cc	0.00	0.00	0.00	0.00	0.00	0.00	0.05
Mass Density	gm/cc	0.01	0.01	0.01	0.01	0.00	0.00	0.95
Enthalpy Flow	cal/sec	-18344.61	-18423.74	-18423.74	-25762.35	-25762.35	-15111.55	-7917.37
Average MW		30.87	30.87	30.87	30.87	30.87	31.19	18.04
Mole Flows	kmol/hr	17.01	17.01	17.01	17.01	17.01	16.59	0.41
Mass Flows	kg/hr	525.00	525.00	525.00	525.00	525.00	517.52	7.48
Volume Flow	l/min	972.37	972.24	972.24	679.70	6497.66	7193.95	0.13

The output flow from the heater has a temperature of about 140 degrees Celsius to prepare it to enter the reactor, but in relation to the cooler or cooling converter used in the cycle, it should be said that it has the duty to set the temperature between 30 and 40 degrees Celsius at the outlet.

Equilibrium numbers in chemical reactions will be the most important output for the correct simulation of a reactor. The equilibrium numbers obtained for the simulated reactor are according to the table below. In this table, the K number, which is the equilibrium constant in chemical reactions or the kinetic number of the reaction, is specified for each element.

Table 3. Equilibrium numbers related to reactor reactions

Component	F	X	Y	K
SODIU-01	2.75E-05	2.47E-01	3.09E-11	1.25E-10
WATER	8.12E-02	1.35E-01	8.12E-02	6.02E-01
SODIU-02	6.84E-05	6.15E-01	9.19E-10	1.49E-09
DIMET-01	6.80E-06	1.49E-05	6.80E-06	4.56E-01
OXYGE-01	9.19E-01	3.13E-03	9.19E-01	2.93E+02

Usually, classical chemical treatment involves adding an oxidizing agent to water containing pollution to oxidize it. Chemical oxidation has been widely used in the treatment of hazardous organic materials. Nowadays, by using technology, it is possible to effectively and safely use the oxidation process on

the scale of large projects by monitoring the process parameters. This is mainly due to ease of access and economic issues. **Table 3** shows the specifications of chemical reaction equations simulated in the software.

Table 4. Chemical equations and their parameters

Rxn No.	Reaction extent kmol/hr	Heat of reaction	Reference component	Stoichiometry
1	0.001164			NAHS + SODIU-01 + 2 OXYGE-01 --> WATER + SODIU-02
2	5.78E-05			4 METHY-01 + OXYGE-01 --> 2 WATER + 2 DIMET-01

The method of treating wastewater or industrial leachate has various advantages; one of these important advantages is the possibility of reducing energy consumption and increasing productivity in these processes. One of the most important

parameters for the energetic and environmental optimization of this process is the use of a pre-heating converter before the leachate enters the reactor space.

But two important parameters that play an important role in this process, the first is the air flow and the next is the temperature of the flash drum. The amount of Na_2SO_4 in the exhaust gases of the flash drum can be changed by changes related to the flow rate of the incoming air. This gas, which is a neutral gas, reduces the destructive and irreparable environmental effects of leachates and gases created from it, and are one of the products of the reactor. Therefore, reducing or increasing its amount can be effective in reducing environmental effects. Using sensitivity analysis, we will optimize the ratio of air flow rate to leachate flow rate. The following figure displays the output results for this sensitivity analysis.

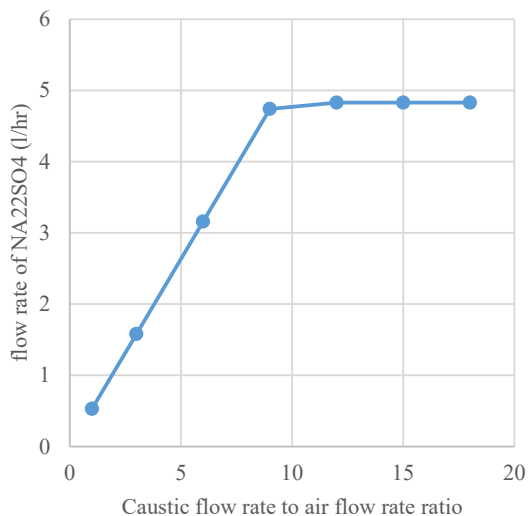


Figure 2. Sensitivity analysis in order to determine the optimal value of the ratio of air to leachate

With the increase of the amount of air flow compared to the leachate, the amount of produced Na_2SO_4 also increases to some extent, but after this ratio exceeds the number 9, we do not see a significant increase in the amount of Na_2SO_4 produced. So, in order to increase energy efficiency and reduce environmental damage, the ratio of leachate flow to air in this process should be considered equal to 9.

Figure 3 also provides an analysis of the amount of $C_2H_6S_2$ produced at different flash drum temperatures. This gas is also one of the production products of the reactor and its increase indicates a better performance in industrial leachate treatment. According to the obtained results, the best temperature for the flash drum is the same temperature of 140 degrees Celsius related to the reactor in order to obtain the highest amount of $C_2H_6S_2$ production.

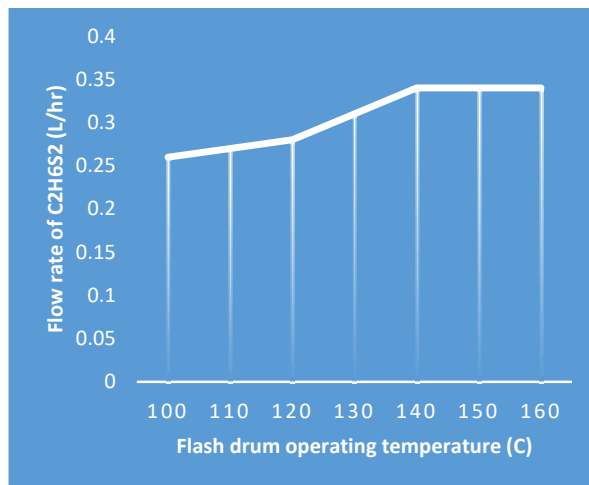


Figure 3. Amount of $C_2H_6S_2$ produced at different flash drum temperatures

Conclusion

Advanced chemical oxidation includes the production of hydroxyl radicals that have high oxidizing power. Unlike other methods, instead of transferring these materials from one state to another, this method has the ability to remove organic and inorganic pollutants including aromatic carboxylic acids. This method was initially used in the early 80s to purify water, but later it is used to purify wastewater with high chemical oxygen requirements, where pollutants are converted into harmless carbon dioxide water and mineral salts. However, with the production of intermediates that are resistant to oxidation, this method alone is impractical. Therefore, this method is used as a pre-process of biological treatment.

The presence of nitrate, nitrite in the advanced oxidation system that produces hydroxyl radicals with ultraviolet (UV) rays causes a decrease in efficiency because nitrates and nitrites absorb UV rays and reduce the production of hydroxyl radicals. Therefore, the amount of oxidation decreases. The turbidity of the solution also has the same effect as nitrate and nitrite on the oxidation efficiency because it prevents the penetration of UV rays into the solution. In this method, strong oxidizers such as ozone and hydrogen peroxide are used. Of course, compounds like ozone are also dangerous and its excessive use causes environmental problems. In general, the efficiency of advanced chemical oxidation depends on the type of oxidation process, physical and chemical properties of the pollutant and operating conditions.

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Conflict of interest: None

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Ethics statement: None

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