



## Elimination of Chloroform (CHCl<sub>3</sub>) from Drinking Water via a Synergistic Effect of Stripping, Oxidation and Adsorption Process in Air Lift Loop Reactor

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### A B S T R A C T

In this work, a modified internal loop airlift reactor has been designed to remove the organic pollutants in synthetic wastewater at an efficient and inexpensive treatment technique by means of a synergistic effect combining of (oxidation, stripping and adsorption). The validation of the current style was experimentally examined in the treatment of synthetic Wastewater contained chloroform. The experimental testing rig was implemented at various air flow rates range (5-20) (L/min), with total variable residence period (5-60 min) with a different molar ratio of CHCl<sub>3</sub> to H<sub>2</sub>O<sub>2</sub> i.e. 1:10, 1:15 and 1:20. The results showed that the best molar ratio of chloroform to hydrogen peroxide was 1:20 for the air flow rate 18 L/min and extended retention period (60 min) having the uppermost results (83.3%) to remove chloroform from the contaminated effluent water. This design complements the research objectives with high efficiency through the synergy of stripping, oxidation and adsorption processes to remove contaminated chloroform from wastewater. This work contributes to a part of the solution of the environmental problems of the contaminated water before recycling, reuse or released to our safe environment.

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## INTRODUCTION

One of the main objectives of the industrial wastewater is to remove or reduce concentrations of the remaining organic pollutants in wastewater to the extent permitted by national and international organizations. Many approaches of removing these pollutants have received increasing attention in recent years because of the difficulty of treating them in water networks, in addition to the problems related to health if allowed to leak into the human environment. The presence of a complex mixture of organic compounds in raw surface waters is natural due to the interaction between chlorine and natural organic matter. For example, there is humic acid and fulvic acid which is generated from trichloromethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform); which are as byproducts of the water sterilization process and is carcinogenic and undesirable. Chloroform is one of them and its presence in high levels in drinking water can cause serious damage to kidneys and liver over time [1, 2], and the presence of trihalomethanes (THMs) in drinking water is a big threat to the human environment. Therefore, the World Health Organization set the maximum permissible limits for the amount of chloroform in water 30 µg/L, while the US Environmental Protection Agency has placed interim rules of

the permitted level of 40 µg/L of the (THMs) as a byproducts of water disinfection process outputs [4]. The new approach of the European Commission has proposed a specific value of 40 µg/L for chloroform [5]. The new orientation of the European Commission is a proposal to establish a specific value of 40 µg / L chloroform. The system is subjected to testing by treating one of the most widespread organic pollutants chloroform, to determine the ability and practical efficiency of the synergistic system of the processes of stripping, oxidation, and adsorption of dissolved organic matter dissolved in drinking water. The removal of pollutants (dangerous and toxic chemicals) from wastewater or drinking water sources have become an important issue since pollutants have negative effects on the environment. In general, many different and classified methods as physiochemical and biological processes that have advantages and disadvantages [6, 7]. Trying to develop a system and a scenario that aims to collect the good features of each individual process and implement them through one system is a real challenge due to the high solubility of organic pollutants in the water, making the process of treatment or removal ineffective [8]. Membrane separation process is costly, present technology of water remedy like filtration via activated carbon, microbiological methods, and ozonation are not enough to strip out pollutants from the contaminated water

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[9, 10]. Byproducts of hazardous bromines and biodegradable organic carbon make the treatment by ozone or ozone peroxide ineffective.

The introduction of bacteria through biological treatment via the packed bed reactor, while the contaminated water pass through packed media may cause many problems, such as clogging the bed and making channeling via bypassing flow, leading to an ineffective handling process [11, 12].

The resistant behaviors of ether compounds make the biodegradation processes ineffective [13]. Therefore, there is a need to seek an alternative design to effectively remove organic pollutants from water to a less hazardous compound and a cost-effective system. In this study, a modern system of synergistic mutually reinforcing operations of (oxidation, stripping, and adsorption) is implemented to destroy the chloroform pollutants from wastewater. Variation of the significant factors have been studied such as the molar ratio of  $\text{CHCl}_3$  to  $\text{H}_2\text{O}_2$ , air flow rate, and residence time. The purpose of this research was to fruition the feasibility of employing a new styling of a synergistic incorporate system of (oxidation, stripping, and adsorption) for the removal of Chloroform from wastewater.

## EXPERIMENTAL DETAILS

### Materials

**Activated carbon** The commercial granular effective carbon was obtained from an (instructional company) with a purity of 99.9% and surface area  $1050 \text{ (m}^2/\text{g)}$ , and solid density  $1.153 \text{ (g/mL)}$  to be used as an absorbent material. The GAC solid carbon was ground and sieved into three sizes extends  $75\text{-}250$ ,  $250\text{-}600$ , and  $600\text{-}1190 \text{ }\mu\text{m}$ , the sieved activated carbon of granular shape was used in the current study to check the ability of particle size ranges as adsorbent material in the adsorption process. The GAC was washed via distilled water to extract all remaining fine particles and then dried by the furnace.

**Molecular sieves ( $5\text{\AA}$ ) pellets 1/8 inch** It is one of the best materials which it retains the chemical substance inside a porous structure for molecular sieves, which is synthesized and equipped from Sigma-Aldrich, Inc. and has its chemical composition  $0.8 \text{ K}_2\text{O} : 0.2 \text{ Na}_2\text{O} : 1 \text{ Al}_2\text{O}_3 : 2.0 (+ \text{ or } -) 0.1 \text{ SiO}_2 : x \text{ H}_2\text{O}$ .

**Hydrogen peroxide** Hydrogen peroxide was supplied (as strong oxidizing agent creates free radicals) from (GmbH Olloweg Germany) in 35% concentrate.

**Chloroform** The primary solution of chloroform was prepared by dissolve one gram of chloroform [which is supplied by Sigma-Aldrich, Inc, chemical formula  $\text{CHCl}_3$ , with 99.8% purity, its molecular weight 119.4 and with solubility in water  $0.005 \text{ mL/mL (v/v)}$ ] in one liter of distilled water to make its concentration  $1000 \text{ mg Chloroform/L}$ , then diluted to the desired concentrations of 10, 20, 50, 100 and  $150 \text{ mg/l}$ . The acidity of the primary solution was adjusted to the desired acidity (7.5-8) by using 0.1M for both, hydrochloric acid and sodium hydroxide.

### Experimental setup

Figure 1 illustrates the sequence of the scenario of the synergistic processes as planned as the initial design. The effect of details of the engineering dimensions of the reactor parts on how it three spontaneously processes occur is generally appeared in Figure 2. The idea of using one device like the airlift loop reactor to conduct stripping, oxidation and adsorption operations were carried out using various operating conditions and study the performance of the operating system via the treatment and removal of one chemical pollutant (phenol) form drinking water.

Experiments are performed using the internal airlift loop reactor described in Figure 2c, it contains two coaxial Plexiglas tubes outer with inside diameter  $0.15\text{ m}$  and height of  $1.5 \text{ m}$  and the inner tube has a diameter of  $0.075 \text{ m}$  and  $1.20 \text{ m}$  length. The working volume of the reactor is  $25 \text{ L}$ . The internal tube of the reactor was fixed with three screw

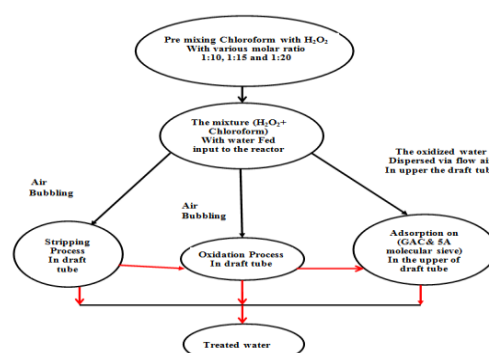


Figure 1. Schematic arrangement of synergistic process

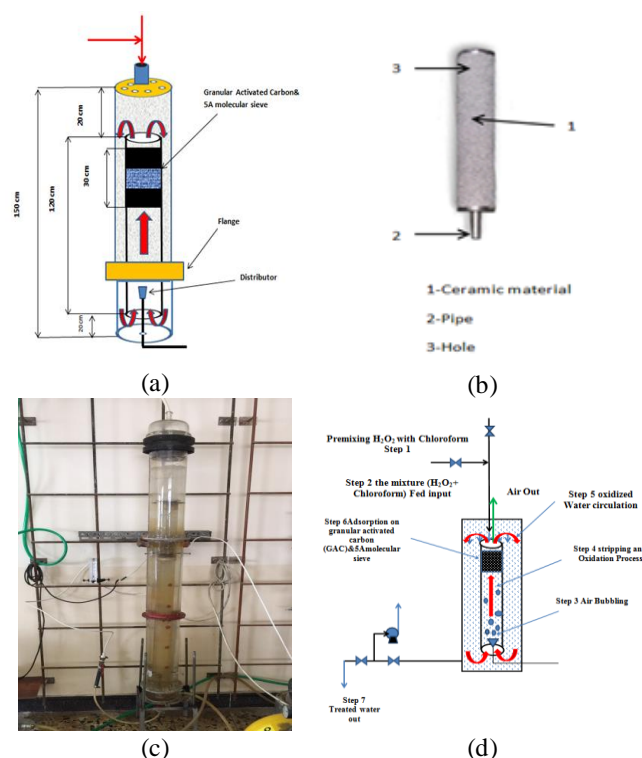


Figure 2. Experimental set up segments: styling and screenplay concerning the synergistic method

braces at the top and the bottom end of the column so as to locate it in a central position at any space above the base. The upstairs side also includes bed (7.5 × 30 cm) having a permeable adsorbent article (granular activated carbon (GAC) and 5Å molecular sieves are utilized to adsorb the chloroform pollutant from the wastewater (Figure 2a). The gas dispenser (Figure 2b) was manufactured from multi-slot ceramic material which has equivalent size diameter equal to 0.15 mm and available flow area of 80% located at the middle of the lower end of the internal tube.

The chloroform is fed to the lift loop reactor after pre-mixing it with contaminated water using ground gravity and controlling the flow rate via gate valves as illustrated in Figure 3. Various range of air rates (2-18) L/min exercised through the experiments. Experiments are carried out at laboratory temperature (30 ± 2 °C).

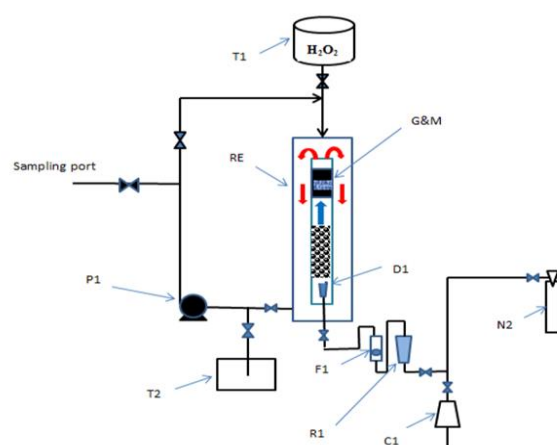
### Experimental procedure

The preparatory sample of contaminated synthetic water contains a concentration of 150 ppm of contaminated organic chloroform. 1000 mL of hydrogen peroxide was added as an oxidized factor to 4 liters of water in the feed container at 25°C due to make the molar ratio for chloroform to hydrogen peroxide equal to 1/20. At the same time 0.2 kg of granular activated carbon and 5A molecular sieves with occupied size (173.5 cm<sup>3</sup>) to the bed assigned to the padding at the upper end of the inner tube. In order to reach the steady state, the pumping of contaminated synthetic water continues at 18 liters per minute with the continuous flowing of hydrogen peroxide under the effect of gravitational force and operating conditions (pressure 2 bars and 25°C). The system is operated for 10 minutes before starting the experiment. The air passing through the gas distributor has two primary tasks: first, to stripping the contaminated chloroform from the water according to mass transfer principle as a result of concentration difference for organic pollutant between the air and water. The secondly task is dispersing the polluted water, which causes a difference in the densities between the air and polluted water, creates a driving force for circulation the polluted water through annuals space between the inner (riser) and outer tube (downcomer) for giving the time and surface area needed to complete the stripping, adsorption and oxidation processes. Samples of treated water are taken at a rate of 5 minutes for each sample, equivalent to 12 samples of total treatment time of 60 minutes. An analysis of the concentration of chloroform in these samples is performed using the UV - spectrophotometer (u-1800, spectrophotometer, Hitachi, Japan) at a wavelength of 254 nm. The same steps are repeated, but in different conditions in terms of airflow rates (2-18 L/min), molar ratio for chloroform to the hydrogen peroxide as oxidation agents (1:10, 1:15 and 1:20) and retention period of 5-60 min, respectively to determine the effectiveness of chloroform removal of water.

All experiments were carried out on synthetic polluted water with a pH of 7-7.5. The efficiency of removing chloroform is calculated from the following equation:

$$E_F = [(C_{in} - C_{out}) / C_{in}] * 100 \quad (1)$$

where  $E_F$  represents the efficiency of removal%,  $C_{in}$  and  $C_{out}$  are the initial and final concentrations of chloroform in the solution in mg/L.



▶	Valves	P1	centrifugal pump
R1	regulator	RE	reactor
N2	nitrogen cylinder	C1	compressor
F1	flow meter	T1	hydrogen peroxide tank
T2	wastewater tank	D1	distributor

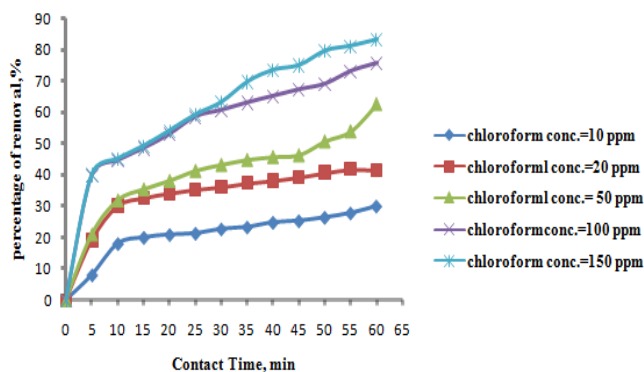
Figure 3. Schematic of the experimental device

### RESULTS AND DISCUSSION

Results include knowledge of the impact of the following five factors in addition to the scenario of the procedure of operation.

1. Effectiveness of the design of a triple synergy system for the processes of stripping, oxidation, and adsorption in one device.
2. Change the initial concentration of the pollutant in the synthetic solution prepared, which input to the process.
3. Effect of change in a molar ratio of chloroform to hydrogen peroxide on oxidation reaction and consequently the efficiency of chloroform removal from water.
4. The extent effect of the change in the airflow rates on circulation time of polluted liquids and the contact time with the packaging filled with the adsorbent article in adsorption process and thus the efficiency of the chloroform removal of water.
5. Change the residence time of contaminated water in the reactor and its effect on the efficiency of removal of chloroform from contaminated water.

Figure 4 displays the effect of the retention period on the removal percentage of chloroform from polluted wastewater. Figure 4 shows an increase in the percentage of removal with increasing the residence time, where the rate sequence of removed chloroform for 60 minutes as follows for 150ppm, 100ppm, 50ppm, 20ppm, and 10ppm were 83.09%, 75.8%, 62.6%, 41.43% and 30% respectively. As well as the resurgent increase in the rate of decomposes of contaminated organic matter in the oxidation process, subsequently the efficiency of removing chloroform is increased whenever increasing its concentration in the feeding solution. The feature of synergy in the work of this system is to start at the same starting point and at the same time moment, which is a different concept of integration in the sense of starting a new stage after the completion of a previous stage. So we do not



**Figure 4.** Influence of residence time on the percentage of removal of chloroform with a various primary concentration of chloroform in an air loop reactor

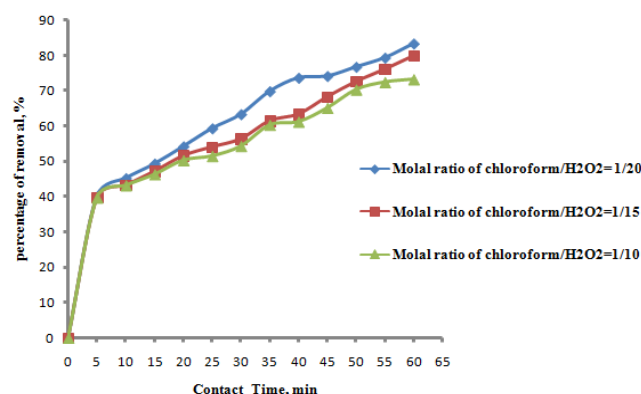
know the effectiveness of each process alone on the percentage of removal of organic pollutant (chloroform). At the moment when the air passes through the distributor to the reactor, which is accompanied by the introduction of a mixture of polluted water and hydrogen peroxide into the reactor, the strong free radicals ( $\text{OH}^\bullet$ ) resulting from the dissolution of hydrogen peroxide begin to attack and disintegrate the organic pollutant, and this may be leading to total disintegration which produces carbon dioxide and water. At the same time as a result of the dispersion of water by the air. It will pass through the packed filled with adsorbent materials (GAC and 5Å molecular sieves in the bed) at the upper end of the inner tube of the loop reactor to initiate a process of adsorption of organic pollutant, which was partially removed in the stripping process, that which synchronize occurrence with the incidence of oxidation and adsorption process. Results showed that the percentage of removal of chloroform under the synergistic effect of the three processes for 150 ppm concentration of chloroform in the contaminated feeding water during the first 10 minutes has a 45% while the removal rate for next ten minutes is 55%. That means the driving forces for the three processes (rate of reaction in oxidation process, rate of mass transfer in stripping and adsorption) decreasing through the second ten minutes of the reaction time this case is repeated for all types of concentrations of the pollutant (chloroform) contained in the feeding stream entering to the internal loop reactor [14-16]. The elimination percentage of chloroform reached approximately 83.3% when the molar ratio of (chloroform/ $\text{H}_2\text{O}_2$ ) = 1/20, as shown in Figure 5. The results showed that access to removal efficiency of 83.3% was associated with a ratio of 1/20 mole chloroform per mole hydrogen peroxide at a 60-minutes contact time. This is logical with increasing the creation of free radicals to certain limits, (resume increase the concentration of hydrogen peroxide may lead to the occurrence of what is known as the scavenger of free radicals, i.e., the return of the re-composition of hydrogen peroxide) with a decrease in the concentration of pollutant in the feed stream will increase the efficiency of the process of oxidation and consequently increases of the efficiency of removal. Figure 5 also shows access to removal efficiency of 73.2 and

79.9% when the initial concentration of the contaminant in the feeding stream is 150 ppm and the air flow rate is 18 liters per minute and the molar ratios of 1/10 and 1/15 chloroform to hydrogen peroxide, respectively.

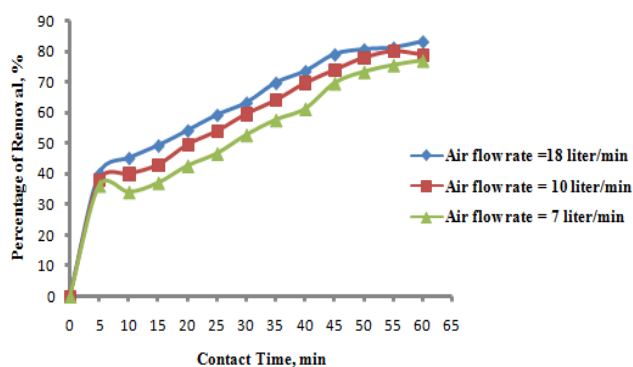
Based on the literature review of the subject of the need to select the dimensions of what is known as the contact time of the empty bed (EBCT) to give the time and space required to complete the process of mass transfer of the pollutant due to the concentration difference of polluted in water and in solids absorbed in the packed bed (containing molecular sieves and activated carbon pellets at the top of the inner tube of the reactor) during the absorption process [17, 18]. Therefore, the dimensions of the bed were chosen as 7.5 cm \* 30 cm.

The choice of suitable design factors has a great impact on the success of the synergy system, the chosen an appropriate flow rates 5-20 liters per minute for the air, with the ratio of the internal tube diameter to outer tube diameter 0.5 for loop reactor will provide an appropriate circulation velocity for the contaminated water and a sufficient time to disengagement the gas and liquid at the top of the reactor and create a dynamic state during the passage of the polluted water through the freight bed with absorbent substance to establish the mass transport for the pollutant mass through the optimal quantity of granular activated carbon with molecular sieves, and gives the suitable opportunity to complete the adsorption process in high efficiency.

Figure 6 shows the extent limited of the effect of the different airflow rate on the removal efficiency for a 60-minute retention period, where the percentage of removal did not increase more than 6%, the percentage of chloroform removal from polluted water ranged from 77% to 83% for all flow rates from 7 to 18 liters /min. This implemented design of the synergy system for three operations (stripping, oxidation and adsorption) has reduced the cost of manufacturing, installation and maintenance of three devices in one device in addition to reduce the cost of the material of construction (Plexiglas) and shorten the period of treatment 60 minutes which means in an economic feasibility that the system which is economically feasible.



**Figure 5.** Impact of residence period on the percentage of removal for the various molar proportion of chloroform to hydrogen peroxide



**Figure 6.** Influence of residence time on the percentage of removal with various air flow rates

## CONCLUSIONS

By implementing the research idea in a practical way, it is possible to conclude the following:

1. The success of the idea of synergy effect for more than a chemical and or physical processes conduct in a single device.
2. The successful design of the synchronization scenario to conduct three processes (stripping, oxidation, and adsorption) in terms of choosing the details of engineering dimensions of the internal air loop reactor.
3. Achieve an 83% percentage of the removal of the organic pollutant (chloroform) from the water with specific operating conditions. The ratio of 1/20 polluted matter to the oxidizing agent and 18 liters per minute is the more active flow rate of air.
4. The use of hydrogen peroxide alone as an oxidizing agent with molar proportion twenty to one mole contaminated organic matter may be an economically feasible method.
5. At the level of the pilot system, the simple cost of materials for manufacturing, erection, maintenance, and space occupied by the perspective of economic feasibility, the system is considered economically feasible.
6. The outputs of the Synergistic system is a less hazardous organic compound in the treated water and safer to be released in the environment.

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Persian Abstract

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چکیده

در این پژوهش، از یک راکتور با جابجایی هوا در حلقه داخلی اصلاح شده برای حذف آلاینده‌های آلی در فاضلاب مصنوعی که در تصفیه کاربرد داشته و به صرفه می باشد، استفاده شد. این راکتور با استفاده از ترکیب (اثر اکسیداسیون، سلب کردن و جذب) اثر سینرژیک طراحی شده است. اعتبار سبک فعلی در آزمایش تصفیه پساب‌های مصنوعی حاوی کلروفرم مورد آزمایش قرار گرفته است. تست آزمایشی در محدوده جریان هوا مختلف (۲۰-۵) (L / min) ، با دوره اقامت متغیر (۵-۶۰ دقیقه) با نسبت مولی‌های مختلف از CHCl<sub>3</sub> به H<sub>2</sub>O<sub>2</sub> یعنی ۱:۱۰، ۱:۱۵ و ۱:۲۰ انجام شد. نتایج نشان داد که بهترین نسبت مولی کلروفرم به پراکسید هیدروژن ۱:۲۰ برای جریان هوا ۱۸ L / min و مدت نگهداری (۶۰ دقیقه) با بالاترین نتایج (۸۳/۳٪) برای حذف کلروفرم از آب پساب آلوده بوده است. این طراحی اهداف تحقیق را با بهره‌وری بالا و بطور ترکیبی از فرایندهای عریان‌سازی، اکسیداسیون و جذب برای حذف کلروفرم آلوده از فاضلاب را بدست آورده است. این کار می‌تواند به بخشی از راه حل مشکلات زیست محیطی آب آلوده قبل از بازیافت، استفاده مجدد یا آزاد شدن به محیط امن ما را مهیا سازد.

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