Chapter

Adsorption Technique an Alternative Treatment for Polycyclic Aromatic Hydrocarbon (PAHs) and Pharmaceutical Active Compounds (PhACs)

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Abstract

Water is essential to human consumption; however, its pollution is caused by populace activities from both organic and inorganic compounds sources that require serious attention, to provide clean water. Organic contaminants are known as persistent organic pollutants (POP). They are accumulated in the fat tissues of wildlife and human beings and are toxic to their organs. Degradations of POP are very difficult since they are persistent and also termed as semi-volatile, for example, polycyclic aromatic hydrocarbons (PAHs). Apart from POPs, others toxic organic contaminants with subtle ecological effects are the emerging organic contaminants (EOCs), like pharmaceutical actives contaminants (PhACs). They penetrate the aquatic environment and alter the natural quality. To obtain future discharge requirements, new technologies with granular activated carbon were developed using *Oxytenanthera abyssinica* and *Bambusa vulgaris* in remediating PhACs and PAHs. The activated carbon with KCl had removal efficiency of 73.3, 78.1, and 86.2%, which indicated the highest efficiency for PhACs removal, while adsorbent activated with H_3PO_4 gave 63.9, 66.7, and 82.2% for paracetamol, salbutamol, and chlorpheniramine, respectively. Removal efficiency of 42.5–81.2% and 8.9–65.5% ranges of PAHs were obtained for CBV and COA, respectively. The alternative adsorption treatment techniques are detailed in the chapter.

Keywords: wastewater, adsorption technique, organic pollutant, polycyclic aromatic hydrocarbon, pharmaceutical active compounds

1. Introduction

The earth's surface is covered by 70% of the water of which 97.5% are from seas and oceans which are salty for consumption, out of the remaining 2.5% water, 1.73% are in form of glaciers and ice-caps, left only with 0.77% available for freshwater supply. The amount of water available on the earth that can be renewable is only

0.0008% in the rivers and lakes for humans and agricultural use [1]. Fundamentally water is needed by all living creations of God, hence it must be provided in the rest state for their consumption, therefore clean water becomes a critical issue as the world population increases [2]. The populace activities are a factor that causes an increase in pollution from both organic and inorganic compounds sources that require serious attention to ensure clean water that the same growing world needs to consume.

Clean water becomes a critical issue as the world population increases. It has been estimated that by the year 2025, there would be an additional 2.5 billion people on the earth that will live in a region already lacking sufficient clean water [1]. Similarly, scholars have indicated that the recent problems in water treatment originate primarily from the increasing pollution of water by an organic compound that is difficult to decompose biologically because these substances resist the self-purification capabilities of the rivers as well as decomposition in conventional wastewater treatment plants [3, 4]. Further observations state that the conventional mechanical-biological purification is no longer sufficient and must be supplemented by an additional stage of processing [5].

Adsorption is the capacity of the adsorbate to form a bond with the adsorbent [6]. It is also defined as a physical and chemical process in which substances are accumulated at the interface between the faces which may be liquid-liquid, liquid-solid, or gas-liquid [7]. Adsorption differs from absorption in that it is the process by which the surface concentrates fluid molecules by chemical or physical force while absorption is the partial chemical bonds formed between adsorbed species or when the absorbate gets into the channels of the solids [8]. In other words, fluid molecules are taken up by a liquid or solid and distributed throughout the liquid or solid. Adsorbate is the substance that is removed from the wastewater or the amount of contaminant adhering to the surface of the adsorbent, while the adsorbent is the solid phase that accumulates the pollutant. This may be activated carbon or other biosorption materials [7]. For adsorption to take place, the adsorbate must have less free energy on the surface of the adsorbent in solution.

Organic contaminants are occasionally termed persistent organic pollutants (POP), their occurrences in the environment are frequent and possess the ability to move fast across the water and settle from where they are sources. Accumulated in the fat tissues of wildlife and human beings and are very toxic to their organics. Degradations of POP are very difficult since they are persistent and also termed semi-volatile for example PAHs. Apart from POPs other toxic organic contaminants which can create subtle ecological effects are the Emerging Organic Contaminants (EOCs), the extent to which the environment can be adversely affected by EOCs is still under study. One of such is the (PhACs) which are products of synthetic chemicals, natural organic chemicals, or microorganisms not controlled. They possess the ability to penetrate the aquatic environment and alter the natural quality leading to adverse health issues in human and ecological disorders [9, 10].

The Petroleum and Pharmaceutical industries are seen among others as major contributors of organic contaminants because of continuous usage and pollutant from them are emerging and steady in the environment [10].

Produced water and crude oil spills are the major sources of pollutants generated by the petroleum industry. Produced water is the largest by-product of wastewater attributed to the petroleum industry and it is a mixture of salt, organic and inorganic compounds.

Among the organic constituent of crude oil is a group of hydrocarbons called PAHs [11]. These are large groups of organic contaminants, which are characterized by the presence of at least two fused aromatic rings and are seen by the United States Environmental Agency (USEPA) as priority organic pollutants [12]. PAHs are highly lipophilic contaminants that are ubiquitously present in the environment [13] because of their low biodegradation and bioaccumulation in the adipose tissues of organisms and biomagnifications through the food chain, they are considered persistent organic pollutants POPs [14].

The pharmaceutical industries on the other hand have to do with the well-being of living organisms. Their products refer to a group of chemicals used for the diagnosis, treatment, or prevention of health conditions. Most of the chemicals or ingredients used in production can be active, inactive, additive, or preservative. When most of these ingredients are no longer used for the intended purpose and if the pharmaceutical product is designated for discarding, it is then classified as pharmaceutical waste. Active chemicals like paracetamol (acetaminophen), salbutamol, amoxicillin, ibuprofen, chloramphenicol, etc. can be referred to as pharmaceutically active compounds (PhACs), and preservatives such as parabens, e.g., ethyl, propyl, etc. are called excipient [15]. Pharmaceutical wastes are EOCs of concern and are mostly unregulated contaminants that need future regulation [16].

Like any EOCs, they do not need to persist in the environment to cause negative effects because they are continually being released into the environment mainly from manufacturing processes, disposal of unused products, and excreta [17]. At the 2005 Burger AEC programme on EDCs, it was reported that most EOCs can disrupt the endocrine system-a health condition called endocrine disruptors [18]. The WHO defines an endocrine-disrupting substance as an exogenous substance that alters the function of the endocrine system and consequently causes adverse health effects in an organism or its progeny or subpopulations [19].

Petroleum and pharmaceutical Industries have been seen as major generating sources of organic contaminants that create adverse effects on surface water which are the primary source of livelihood. For water to be available in its pure state, identifying and remediating processes of those contaminants is key, if clean water is a necessity [10].

Most research works had employed analytical techniques like gas and liquid chromatography, UV-spectrophotometers and gravimetric, etc. to identify organic contaminants, gas and liquid chromatography with mass spectrophotometer followed by a cleanup method such as solid-phase extraction (SPE) and solid-phase micro-extraction (SPME) [20] are seen as most effective techniques in determinations of organic pollutants in trace amount (or micro-pollutant).

Induced Gas Flotation (IGF) or the Induced Air Flotation cells are usually used as conventional treatment methods by petroleum industries to separate produced water from crude oil with Enviro-cell as the newest technology that uses the principle of gravity with differences in density between the oil and water [20].

The hydrocarbon content in either the produced water or water polluted with crude spills can be classified as free, dispersed, and dissolved oil [21, 22]. The conventional method is seen to be effective in the removal of dispersed oil and grease but cannot be used in the removal of the dissolved hydrocarbon which includes the PAHs. Different literature had reviewed that conventional wastewater treatment plants (WWTPs) are not the best in the removal of PAHs pollutants from wastewater, additional methods that had been researched and are still being researched is the adsorption mechanism. It had been suggested that carbon and membrane filtration with reverse osmosis are very effective in the removal of dissolved and emulsified oils [23, 24]. Many materials in their raw or waste form had been developed or modified into adsorbent in adsorption of pollutants which could be agricultural materials, clay, zeolite, vibratory share enhanced process, etc.

The commonest adsorbent used by most industries for the removal and recovery of inorganic and organic substances from gaseous and liquid streams is activated carbon [25]. Because of its high internal surface area and porosity formed during the carbonization process, the adsorbent is said to have a high adsorption capacity. Similarly, the use of activating agents and heat during carbonization will influence the development of pore structure but its uses are limited to high cost hence the use of agricultural products or materials have been observed to be potential precursors in activated carbon production because of the abundant supply and low cost.

Most of the research conducted lately made use of agricultural product such as adsorbent in the removal of heavy metals from water and wastewater, such agricultural products are coconut shell and rice husk [26, 27], palm kernel shell, and oil palm fruit fiber [28], bamboo [3, 29], maize cob [6]. Other works had been done on the identification and remediation of organic contaminants in petroleum [30–31] and pharmaceutical wastes [32–33] but few works have been done on the use of adsorbents in remediating organic pollutants (PAHs and EOCs).

Since water is the prime necessity of life and very essential for the survival of all living organisms it is imperative to improve the quality of available water. The presence of pharmaceutical residues (PhACs) and PAHs as newly recognized contaminants in aquatic systems is one of the current environmental issues [34]. It should be noted that organic contaminants usually occur in multi-component in aquatic environments. Thus, it is expected that there will be interspecies interaction among these pollutants which will cause chemical reactions that can generate other metabolites compared to when the single contaminant is present [35].

Adsorption method of bioremediation had proven to be the chosen treatment option for PAHs and PhACs and other micro-pollutant in aqueous or any environmental media because it is easier to understand and has obvious advantages of convenience, easy operation, efficiency, effective, and very simple to design as compared to another kind of treatment. Apart from the identified attributes, it does not add harmful degradation metabolites or undesirable by-products [36].

Adsorption is better than any other wastewater treatment method due to its insensitivity to toxic substances and is economically based on types of materials employed as adsorbents [37]. But, the complete use of adsorption processes in purifying water is impeded by the insufficiencies of the commercial adsorbents like activated carbon and synthetic polymer resins, synthetic Nanomaterial. Hence, there is a need to develop a low-cost adsorbent for environmental research. So, the adsorbent of agricultural products is becoming the popular alternative for commercial and synthetic adsorbents due to the hydrophobic-oleophilic potential that is needed for bioremediation processes [38]. With this new trend in mind, this chapter will seek to explain courses of organic pollutants with a special interest in industrial wastewater and adsorption techniques as an alternative treatment.

2. Assessment of production activities that leads to the generation of wastewater in the selected industries

To determine wastewater characteristics, generation disposal processes and assessment of production activities that lead to wastewater generation within the pharmaceutical and petroleum industries were conducted through interviews, observation, and experimental analysis. From the information gathered, most pharmaceutical industries in a country located in West Africa produced more syrups than any other form of drugs because it is cheaper to produce. Production of syrups takes more than 50% of production water and an average of 48,000 L of water per day is being discharged as effluent during the production of syrups. Syrups can be analgesic, antacids, or pain relievers. Effluent discharge may contain codeine phosphate, paracetamol, chlorpheniramine maleate, ephedrine HCl, parabens, etc. which are regarded as active pharmaceutical compounds. PAHs and PCBs can be found within the effluent as a result of chemical metabolites. Most of the pharmaceutical industries around the States visited in that country discharge their effluents through the drains into the surface water.

The petroleum industries visited were located within the Delta area of the country. The industries have two sources of liquid waste which are produced water and water pollutant with crude spills. Averagely about 30 million barrels of produced water are said to be discharged per day into the environment. Most of the oil and gas industries in the Delta region utilize the common treatment technique like the Induced Gas Flotation (IGF) or the Induced Air Flotation called WEMCO with the Enviro-cell as the latest technology of the group. The orthodox separation technique used the standard of gravity with variances in density between oil and water.

The oil and grease in the produced water can be classified as free, dispersed, and dissolved oil [21, 22]. The conventional method is seen to be effective in the removal of dispersed oil and grease and cannot be used in the removal of the dissolved oil and grease which are the PAHS (**Figure 1**).

2.1 Production of local Adsorbent using local Technology

The production of local adsorbent from the natural agricultural material using local Technology is a crucial alternative to commercial absorbent since adsorbent is used in carrying out adsorption which is better than any other wastewater treatment methods due to its insensitivity to toxic substances and economically

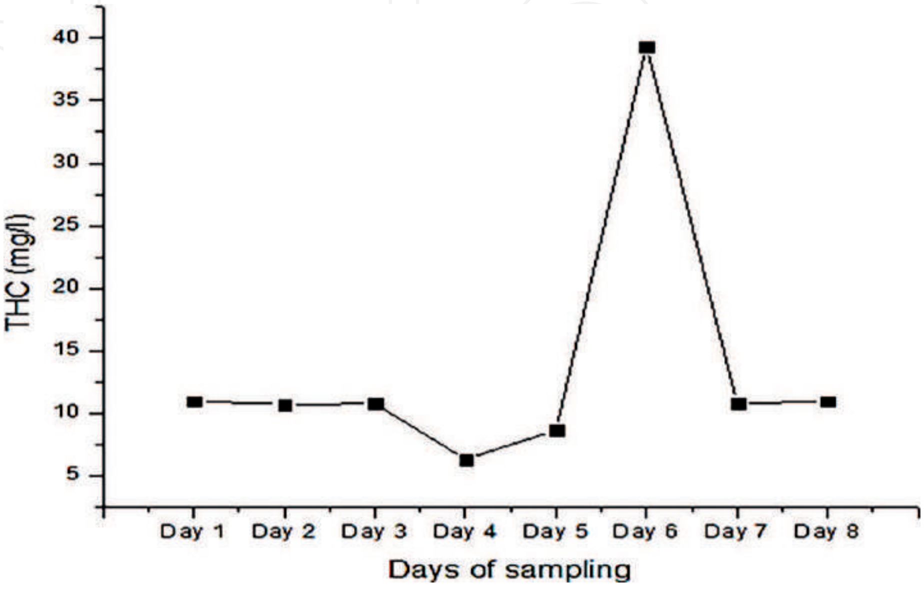


Figure 1.
Concentrations of oil and grease in produced water at different days of sampling.

based on types of materials employed as adsorbents [37]. But, the complete use of adsorption processes in purifying water is impeded by the insufficiencies of the commercial adsorbents like activated carbon and synthetic polymer resins, synthetic Nanomaterial. Hence, there is a need to develop a low-cost adsorbent for environmental research. So the adsorbent of agricultural products is becoming the popular alternative for commercial and synthetic adsorbents due to the hydrophobic-oleophilic potential that is needed for bioremediation processes [38]. The Activated Charcoal which is also known as activated carbon is a kind of carbon treated under heat to be extremely porous as processes very large surface area making room for adsorption or chemical reactions [39]. The activated carbons that are employed were formed from two different species of fresh bamboo culms that were cut at the height of 20 cm from the soil level and were chopped into 20 cm each as the peripheral materials were detached. The chopped bamboo culms were left to dry at the normal ambient temperature of 26-28°C and later cut down to 5 cm. The bamboo species were weighted and the aluminum foil was used to tightly cover in preparation for carbonization, the wrapping with the foil was done to complete deoxygenated processes. It was carbonized at 350°C for 2 hrs in an electric muffle furnace. Carbons were cooled and oven-dried at 105°C for 360 min. The carbonated samples were granulated and sieved to 1.18 m size and stored. Activation was done with Phosphoric acid (H_3PO_4) and Potassium chloride (KCl) as dehydrating agents. 26.25w/w of activator was used in the activation of the carbonated samples. Characterization was done chemically using Point of zero charge (pH pzc) and The Scanning Electron Microscopy (SEM) was used to view the surface structure of the samples at a magnification of 100, 300, 500, 2000, and 5000 times the original size to view the pore space development and reveal other information such as texture (external morphology) and structural orientation see **Figure 2** [10]. The point of zero charge (pH pzc) was used for further determination of pore and adsorption capacity. The point of zero charge is the point where the pH of the net total particle charge is zero. It is important in describing variable charge surface and it indicates the approximation equilibrium time at which the carbon is required to adsorb. Points of zero charge of the adsorbents were determined by measuring 20 ml of 0.01 m Nacl solutions into 9 separate beakers. The pH of each solution was adjusted to between 2 and 10 by adding 0.1 M of HCl or NaOH solution to each of the flasks. The flasks were thereafter placed in a water bath shaker at 25°C. The suspensions were agitated for 30 min and allowed to equilibrate for 48 hrs to ensure equilibrium point (pH pzc) after which the final pH(s) were measured see **Figure 3**. The differences between the initial and final were calculated as:

$$\Delta pH = pH_i - pH_f \tag{1}$$

Where ΔpH = Change in pH, pH_i = Initial pH, and pH_f = Final pH.

The values of changes in pH were then plotted against the initial pH values.

From **Figure 3** above the pH pzc for carbon activated with salt is greater than pH value of the activated with acid, i.e., pH pzc < pHi COA KCl and pH pzc for CBV H3PO4 is lower than that pHi implying that pH > pH pzc This implies that the surfaces of these carbons are positively charged and this arises from the basic site that combines with protons from the medium. These results also confirmed [40, 41]

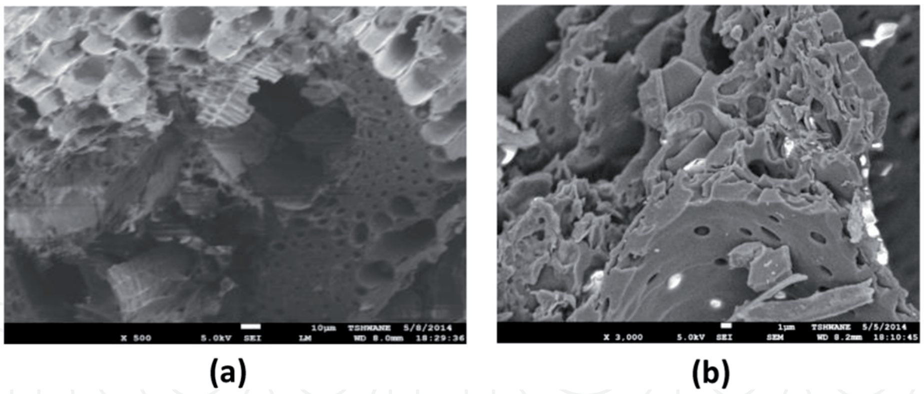


Figure 2.
SEM image of (a) CBV 350°C H_3PO_4 *and (b) COA 350°C KCl at magnification of 2000.*

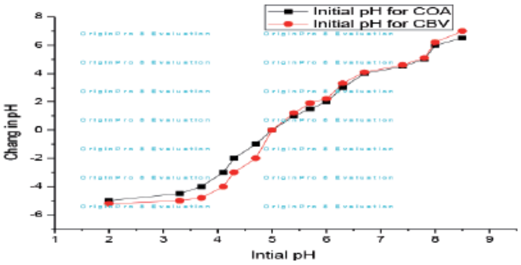


Figure 3.
Potentiometric titration curves (pH pzc) for CBV H_3PO_4 *and COA KCl.*

studies that a positive surface charged adsorbent would strongly attract to acidic compound in any polluted water, while a negative surface charge would strongly attract pollutant in a natural media.

2.2 Adsorption of PAH and PhACs from industrial wastewater

The behavior of Adsorption for PhACs in pharmaceutical effluents and polycyclic aromatic hydrocarbon (PAHs) in petroleum wastewater onto activated carbon produced from bamboo was studied in a batch process. Experiments were done at room temperature and the adsorption efficiency of activated carbon made from bamboo was determined using contact time. Half a liter of Pharmaceutical effluent was poured into conical flasks with a capacity of 600 ml. Selected bamboo activated carbon of two grammes each was weighed into conical flasks to make an adsorbent/solute solution. Solutions were mixed at a stirring speed of 160 rpm to ensure propped contact of the adsorbent and solute in the solution. 6 hrs contact time was used to observe each solution before reaching a dynamic equilibrium. Thereafter, solutions were filtered with filter paper 0.45 μm size. 300 ml filtrate was poured into sampling bottles with a tie cap sealed with aluminum foils and kept at a temperature of 4°C for further analysis of extraction, clean-up, and Vis-UV. For accuracy, all experimental analysis was repeated. Similarly, 200 ml of petroleum wastewater simulated, was poured into different conical flasks of 250 ml capacity. 1 g of each selected bamboo activated carbon was weighed into the conical flasks to form an adsorbent/solute solution. Solutions were mixed at a stirring speed of 160 rpm to ensure propped contact of the adsorbent and solute in solution while observing each solution in equilibrium for 5 hrs contact-time to attain dynamic equilibrium. After 5 hrs of clean up and solutions were filtered with filter paper 0.45 μm and the filtrate of 150 ml was poured into amber bottles with a Teflon cap and kept at a temperature of 4°C for further analysis of and extraction were done before analying with GC-MS. The 5 hrs contact time was informed based on the experiment performed at the terminal station of the oil and gas industry. To obtain accuracy, all experimental analysis was duplicated [10]. The amount of PhACs (qe) and PAHs (qe) adsorbed by bamboo activated carbons can be expressed mathematically as:

$$qe = ((Co - Ce)/M) \times v \tag{2}$$

The percentage removal is evaluated using.

$$\%\,Removal = \left(\left(Co - Ce\right)/M\right) \times 100 \tag{3}$$

Where V is the volume of PAHs and PhACs in solution (L), Co is initial concentrations of PAHs and PhACs ($mg\,L^{-1}$), Ce is equilibrium concentrations of PAHs and PhACs ($mg\,L^{-1}$), M is the mass of the adsorbent (g).

The Spectra in **Figure 4** shows, 16 priority PAHs in Simulated Petroleum wastewater. The efficiency of adsorbent based on contact time in the removal of PAHs from simulated petroleum wastewater by COA KCl and CBV H_3PO_4 are stated in **Figures 5** and **6**. The various contact times used were 30 min, 2 hrs, and 12 hrs, and there were otnotany changes differences in the adsorption rate with time. It was deduced that the percentage removal efficiency of PAHs with time by COA KCl was not consistent. At 30 min of adsorption rate; the percentage removal efficiency was 49.8% of total PAHs, while 39.1% of total PAHs were adsorbed at 2 hrs and about 72.3% of total PAHs were adsorbed at 12 hrs contact time.

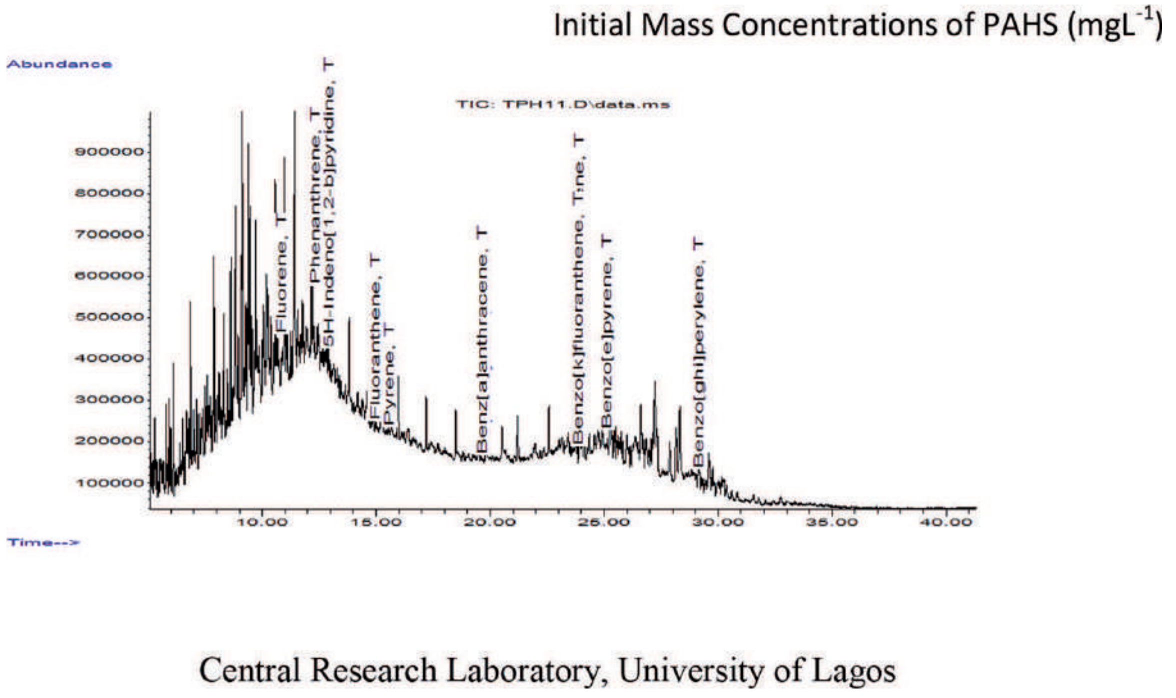


Figure 4.
Spectra of 16 priority PAHs in Simulated Petroleum wastewater.

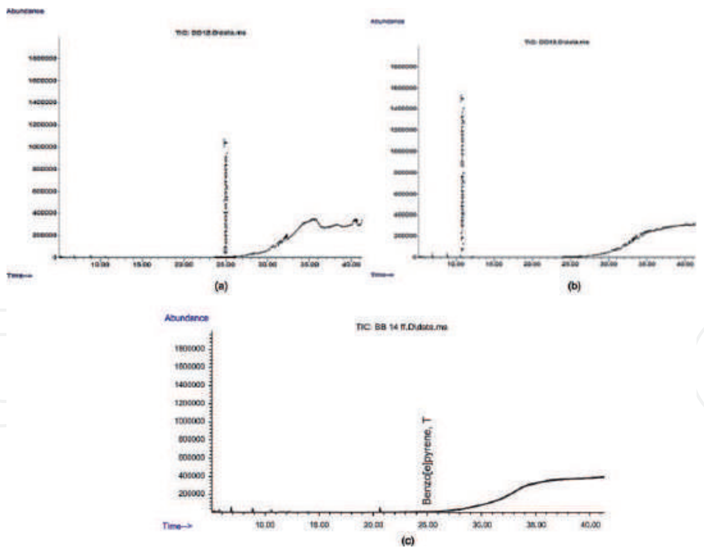


Figure 5.
Effect of contact time on adsorption rate of PAHs by COA KCl at (a) 30 mins, (b)2 hrs and (c) 12 hrs.

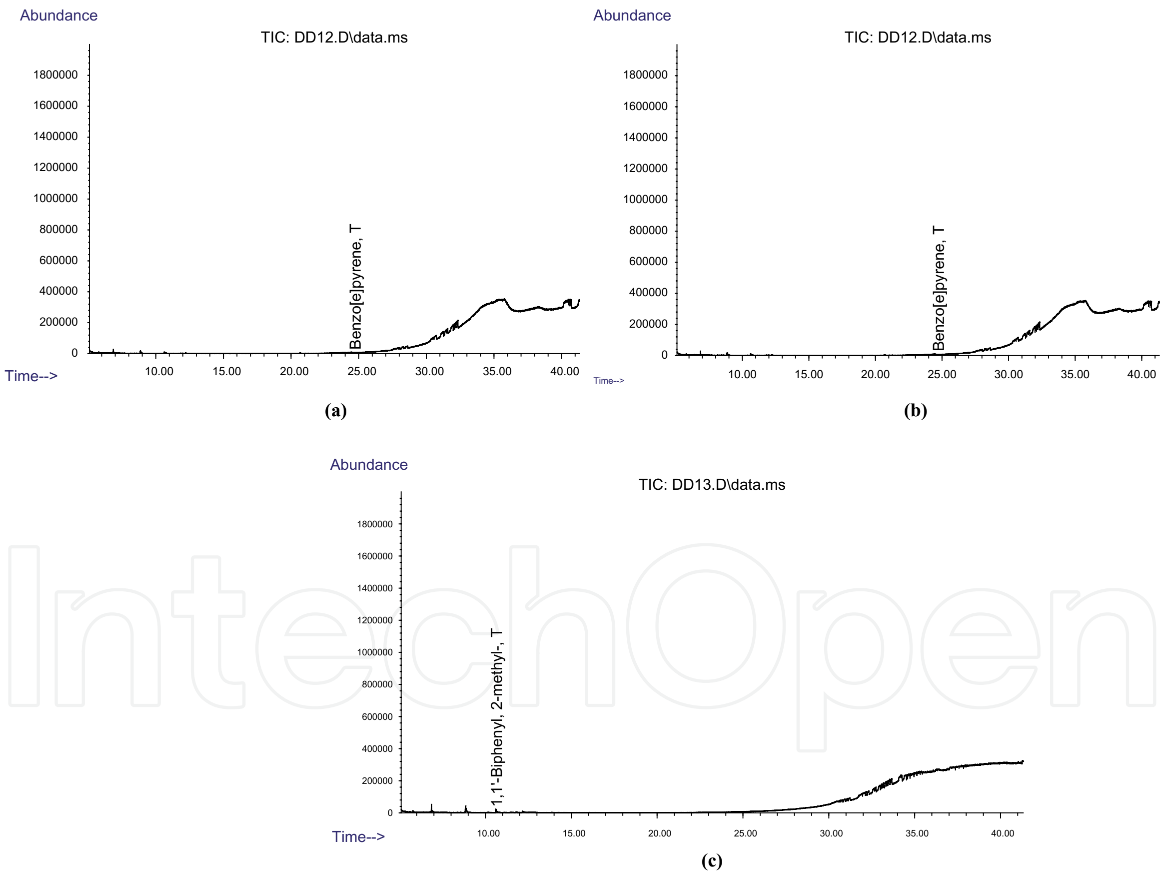
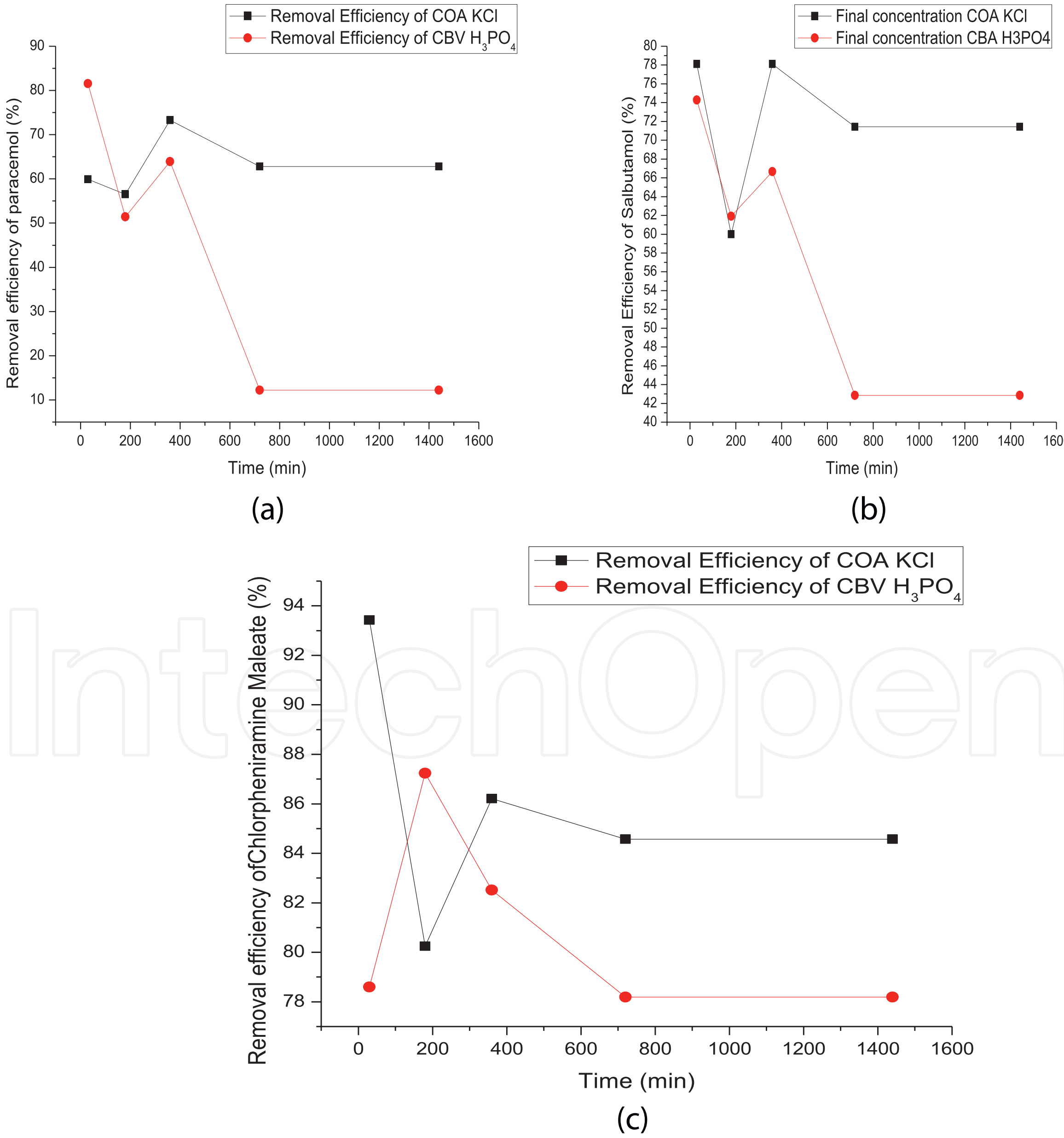


Figure 6.
Effect of contact time on adsorption rate of PAHs by CBVH3PO4 at (a) 30 mins, (b) 2 hrs and (c) 12 hrs.

Also, the adsorption rate of PAHs by CBV H_3PO_4 was seen not to follow the adsorption pattern wherein the adsorption rate increased with time. About 85.1% was adsorbed at 30 min; with an increase in contact time to 2 hrs its shows a reduction in adsorption rate to 25.1% but a further increase in time to 12 hrs increases adsorption efficiency to 87.7% which is the maximal contact time for CBV H_3PO_4 in adsorbing PAHs. It was deduced that adsorption patterns do not follow the norms of adsorption, hence adsorption of PAHs is in two stages. In the first stage, the PAHs were adsorbed easily onto the accessible hydrophobic site within the adsorbent or granular activated carbon matrix for the first 30 min. These may have resulted from the chemical interaction between the PAHs and the adsorbent. The reduction in adsorption rate implies that in the second stage, the adsorption rate may be restricted by the slow movement of PAHs to less available sites associated with the microspores within the adsorbents matrix which could take hours [10].

Figure 7a-c revealed the adsorption trend of PhACs, it was deduced that a slight reduction of adsorption rate was observed before an increase after which equilibrium was observed for COA KCl adsorbent. Similarly, the adsorption trend of CBV H_3PO_4 shows a sharp reduction to a level, and thereafter an increase was seen before an equilibrium point was reached. These observations are similar to [42–45] findings. It can be explained that absorption of PhACs with COA KCl and CBV H_3PO_4 occurred in two different stages. The first stage occurred during the first 30-360mins



(a)

(b)

(c)

Figure 7.
(a-c). Effect of contact time on adsorption rate of PhACs by COA KCl and CBVH_3PO_4 *at 30, 180, 360, 720, and 1440 mins.*

contact time, with a high number of active binding sites on the adsorbent's surfaces. The adsorption rate is rapid in this stage and the points to adsorption are being controlled by diffusion processes of paracetamol, salbutamol, and chlorpheniramine molecules from the bulk phase to the adsorbent surface. The second stage of adsorption is an attachment-controlled process due to a decrease in the number of the active sites available for Paracetamol, salbutamol, and chlorpheniramine. Adsorptions graphs showing the rate and removal efficiency of PhACs by COA KCl and CBV H_3PO_4 at varying contact times of 30, 180, 360, 720, and 1440 min are shown below.

3. Conclusion

The ever-growing human population cannot do without water; hence clean water becomes a critical issue. Therefore, the various conventional ways of treating water have been established by existing researchers, most of which are said to be inadequate in the removal of organic contaminants. This study showed that adsorbents made from Oxytenanthera Abyssinia and Bambusa vulgaris can efficiently adsorb selected PhACs and PAHs in industrial Contaminated Water. *Oxytenanthera abyssinica* (COA 350°C KCl) had a Removal efficiency of (73.3%, 78.1%, and 86.2%) for PhACs while *B. vulgaris* (CBV 350°C H_3PO_4) had (63.9%, 66.7%, and 82.2%) in remediating Pharmaceutical actives contaminants such as paracetamol, salbutamol, and chlorpheniramine, respectively. For polycyclic aromatic hydrocarbons (PAHs) Removal efficiency of COA and CBV ranged from 42.5–81.2% and 8.9–65.5% respectively. The adsorption mechanism of trace organics followed the same pattern though with little differences. For all organic pollutants, adsorption rate is in two stages viz.: optimization and reduction followed by equilibrium. In comparison, COA showed the highest removal efficiency for PhACs and PAHs. The characterization of the adsorbent developed from agricultural materials was also revealed by Scanning Electron Microscopy (SEM) and point of zero charge (pH pzc)

Acknowledgements

The author expresses her heart of gratitude to all organizations and industries that afford her access to their facilities and environment to carry out the study.

Conflict of interest

The author declares no conflict of interest

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Chapter

Study of Change Surface Aerator to Submerged Nonporous Aerator in Biological Pond in an Industrial Wastewater Treatment in Daura Refinery

Omar M. Waheeb, Mohanad Mahmood Salman and Rand Qusay Kadhim

Abstract

Daura refinery, with a capacity of 140,000 barrel per stream day as a refining capacity, wastewater discharged from refining and treatment processing units, polluted water as foul water, drainages, oil spills, blowdown of boilers and cooling towers, and many other polluted water sources, aims to remove pollutants and reject clean water to the river; wastewater treatment system takes place in this treatment process. Wastewater treatment system suffers from many problems and specifically biological stage; at this stage, activated sludge with bacteria, should be supplied with oxygen, aeration system done by surface aerators with four surface fans; these fans suffer from high vibration, loss support, and in consequence, lack in oxygen supply to aerobic bacteria less than 4 ppm. The nonporous aerator is suggested as an oxygen source for the biological pool. The pilot plant builds the aim to study the ability to apply the new aeration system at the biological pool, pilot plant build with 1 cubic meter capacity tank and continuous overflow of wastewater of 10 liters.min^{-1}, air injected with the pressure of (0.5–0.75) bar(g), and airflow of (7.6–9.7) liter.min^{-1} respectively. Oxygen concentration was recorded as (3.4–6.0) ppm; in terms of consumption power, changing the aeration system reduces it to less than 20%.

Keywords: wastewater treatment, submerged aeration, fin bubbles aeration, biological pool, activated sludge

1. Introduction

Industrial wastewater treatment in refineries just receives water infected with a large number of pollutants; these pollutants are hydrocarbons (light oil products – heavy oil products), phenols [1–4], solvents, high turbidity water, saline water, foul water, drainages, and water may be discharged from equipment under maintenance or test [2]. Water with all of these pollutants is treated with a train of processes as follows:

- **API separator:** Hydrocarbon cuts, free oil, and greases can be removed by skimming from the surface of the water [2, 5], oil skimmed from the surface is sent to the tank, settled, and dehydrated, the water is sent back to the API separator; it may contain a low percentage of oil suspension, separated oil pumped to the slop tanks in refinery [6].

- **Clarifiers and flocculation**: Emulsified oil can be removed by using clarifier and flocculation (air flotation), which are attached to a dissolved air floatation system (DAF) [5]; emulsified oil is separated by flocculation and sludge sent to the sludge dehydration and loading system [5, 6].

- **Biological reactor:** Dissolved oil can be removed by using a biological tank reactor (biological digestive pool) [5]; this stage uses the activated sludge [1, 7], which uses aerobic bacteria aiming to break down organic material into carbon dioxide (CO_2) and biomass with aid of oxygen (O_2).

Oxygen supply can be done by surface aeration or direct-contact air injection inside the water (porous or nonporous aeration system). Water overflows from the biological tank to another stage, which contains a secondary clarifier, overflowed water from biological reactor is treated in this clarifier (called secondary clarifier), water is separated as treated water and sludge divided into two portions, portion disposal as sludge and another portion of sludge circulated back to the bioreactor [7, 8]. The aeration tank (Biological Reactor) in an industrial wastewater treatment system needs urea and phosphoric acid, which are added to the biological reactor as a feed to bacteria, but in the municipal system, it is not required due to the high content of urea and phosphoric acid in the feed. Treated water is discharged to the river as clean treated water (**Figure 1**) [6].

- **Aeration system:**

This system is responsible for supplying oxygen into a biological reactor, which gives the bacteria the ability to digest and oxidize wastes (oil and all other undesirable materials) [9–11].

Oxygen concentration can be estimated in a theoretical way as in equation no (1) [6, 12]

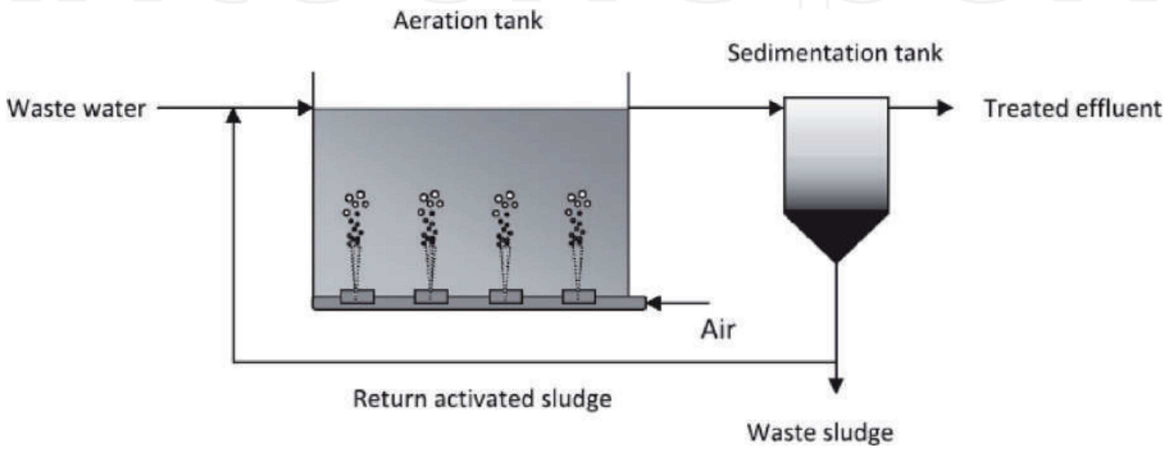

Figure 1.
Activated sludge system.

$$\ln \frac{C_S - C_O}{C_S - C_t} = K_{la} t \tag{1}$$

Where:
C_s: Oxygen concentration at saturation mg.l^{-1}.
C_o: Oxygen at time 0 mg.l^{-1}.
C_t: Oxygen at time minute.
K_{la}: Transfer coefficient.
t: Time in minutes.

There are many types of aeration systems to supply oxygen to the biological pool as follows:

1. **Surface aeration:** This type of aeration is a mechanical-type aerator, which supplies oxygen by introducing air into the water in the (biological reactor), by making turbulence at the surface of the liquid inside the pool with a depth of not more than 3.5 m, types of rotor (blades type, brush type) vertical or horizontal position [11, 13, 14]. A mechanical aerator supplies the biological reactor with a sufficient amount of air (oxygen) and mixes the content, oxygen supply will promote the biological activities and digest wastes, remove carbon dioxide and other undesirable gases released due to the biological activities [15].

2. **Subsurface aeration:** This type of aeration injects air inside the biological reactor pool directly; there are many types of methods as follows:

   - Fine bubble aerator (nonporous diffusers): This type of aeration supplies oxygen to the bioreactor with a small bubble size (fine bubble), with a high rate of oxygen transfer in terms of efficiency, low consumption power [11]; there are many types of these diffusers (such as membrane diffuser, coarse diffuser) [14, 16].

   - Porous diffusers: Classified into four classes: disc diffuser, dome diffuser, tube flexible sheath diffuser, and plate diffuser [11, 17]. These types of diffusers are always made of membrane, ceramic, and plastic [11, 14]; this type of diffusers supply oxygen to the biological reactor at high rate and efficiency [6, 18].

The oxygen transfer rate for each aeration system can be estimated in terms of horsepower as in Eq. (2) [6].

$$hp = \frac{\mathrm{Q} * \mathrm{d} * \mathrm{L}}{24 * \mathrm{q}} \tag{2}$$

Where:
hp.: Horsepower required.
Q: Liquid flow rate million gallons per day (mgd).
d: Density of liquid 8.314 lb.gal^{-1} for water.
L: BOD – biological oxygen demand (PPM).
q: Oxygen transfer rate in lbO_2.hp-h.$^{-1}$

Sludge treatment system: sludge treatment needs a train of processes with the aim of treating sludge as follows:

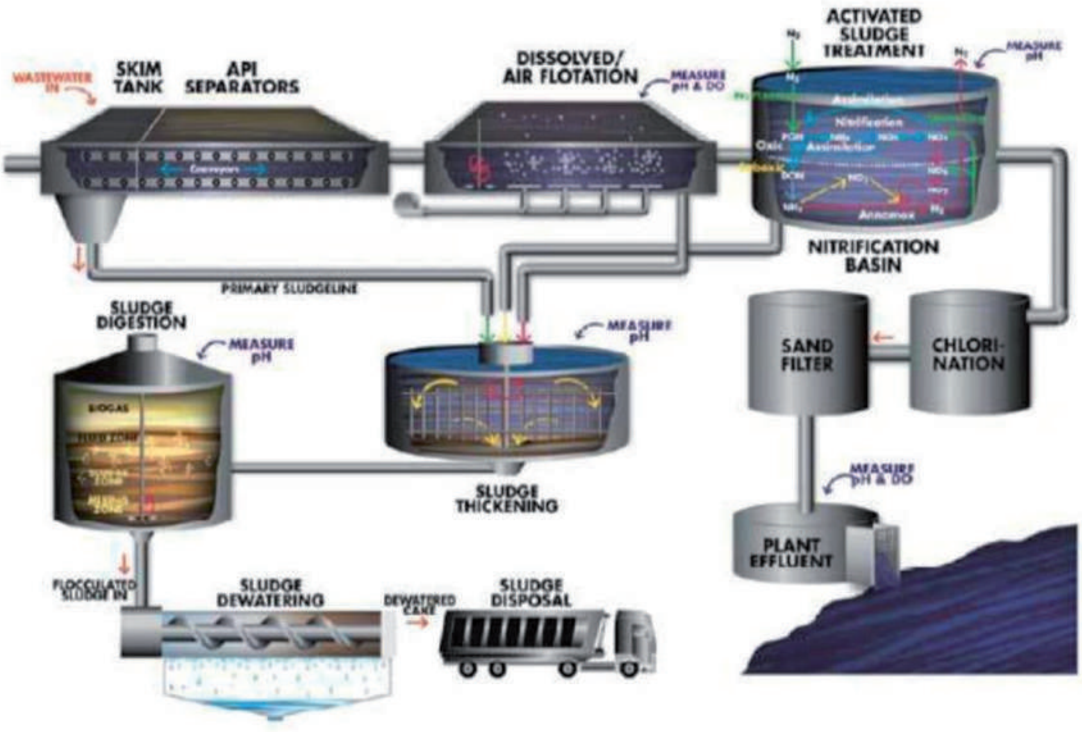

Figure 2.
Wastewater treatment system in general [5].

Sludge decanting separates water from sludge, sludge from decanting system is sent to the incineration system, ash and other nonhydrated sludge send to the rotary drum vacuum filters with the aim to separate the maximum amount of water from sludge, water is separated and sent to the API separator again (**Figure 2**) [5].

1.1 Wastewater treatment in Daura Refinery (DR)

Wastewater treatment system in DR, designed with a capacity of 850 $m^3.h^{-1}$ and operating capacity of 750 $m^3.h^{-1}$, and 1450 $m^3.h^{-1}$ in stormy weather for 2 hours only. Polluted water is received from many sources as follows: sewer water, drainages, foul water out of desalters, saline water from reverse osmosis units (RO), blowdown of boilers, cooling towers, condensate, equipment washing or the hydrostatic test, oil spills, and stormy weather [19].

The wastewater treatment system consists of the following operations:

1. API separator: all the wastewater in the refinery is collected in the header and entered the API separator to separate hydrocarbons from water by stormy water basin, and precipitated sludge at the bottom is removed by gravity separation.

Oil removed from the surface of water is sent to a slop tank in the DR, and collected sludge at the bottom of the API separator is sent to the sludge treatment unit (thickener).

2. Flocculation and flotation: at this stage, de-oiled water out of the API separator passes to the flocculation basin; at this stage, pH is controlled from 7 to 8 by adding sulfuric acid, or adding caustic soda, aluminum, or ferrous basin also contain mixer to homogenize the mixture.

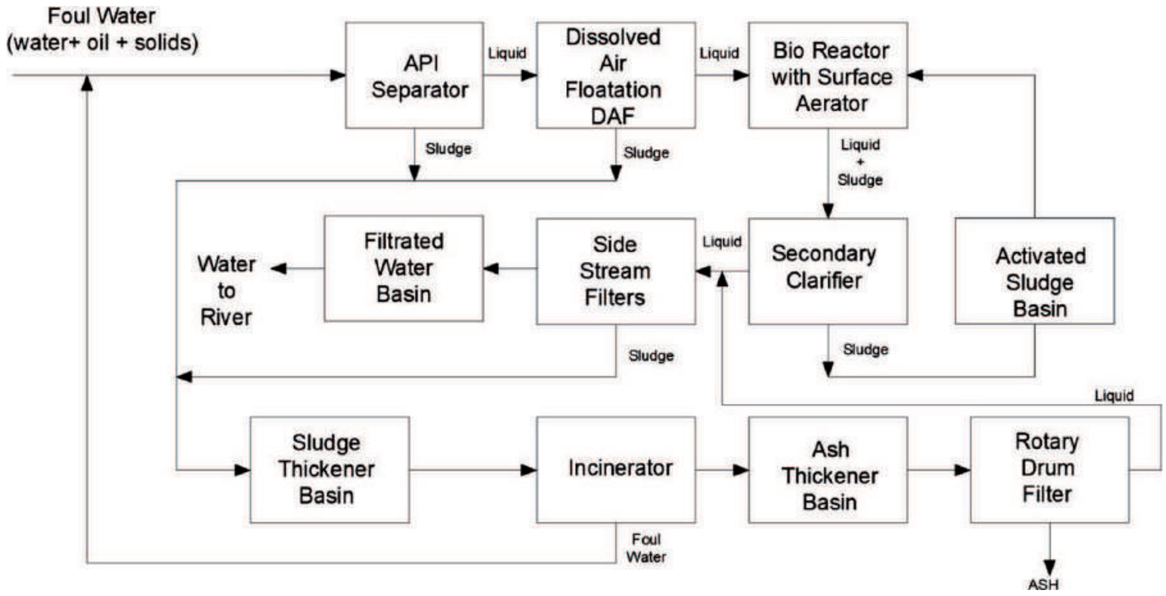

Figure 3.
Wastewater treatment system in Daura Refinery.

3. Bioreactor unit

4. Clarification and filtration

5. Final check basin (filtrated water basin)

6. Sludge treatment unit (sludge thickener, incinerator, ash thickener basin, rotary drum filter) (**Figure 3**).

1.2 Problem

Aeration system installed in biological pond in wastewater treatment in Daura refinery with dimensions of (16,000 X 32,000) mm two pools, type of aeration is surface aeration of mechanical fan aerator fixed at the concrete supports.

Four fans were fixed at the top of the pond, these fans were installed in the middle of each quarter of the pond, Fins of the fan were fiberglass type, fins of each fan were corrupted and replaced with stainless steel fins.

These fins are heavier than fiberglass, and the vibration generated is more than that generated by the original fan.

Stainless steel fan installed in 2004, due to the continuous operation of fans, cracks in concrete foundations of each fan appear; cracks in the foundation as a result of excess vibration, cracks in the foundation as in **Figure 4**.

Cracks in the bearer foundations make run of these fans' type of imagination, due to the risk of failure of the concrete foundations.

Suggested solution:

Maintenance measures to solve vibration problems or fix the bearer foundation, this type of solution does not pass away, and the problem is just raised to the surface. Replace the surface aeration system with another type, such as a submerged aeration system, this system will be a suitable type of aeration in terms of solving the problem and avoiding vibration and foundation failure.

Figure 4.
Surface with corrupted foundation due to the vibration.

1.3 Methodology

The pilot plant was just built to study the performance of air injection non-porous diffuser (aeration system) in an activated sludge tank with a continuous overflow system of wastewater out of a flocculation system with the aim to simulate a biological tank.

The apparatus is just built as in **Figure 5** from the following items:

1. Isocontainer with dimensions of 1X1X1 m with a capacity of 1 m^3.

2. ¾” high-pressure flex rubber hoses ended with connection adapters, six hoses.

3. Foul water flow measurement 0–50 liter.min^{-1} (Nippon – Japan)

4. Pressure gauge 0–6 bar (Wika – Germany).

5. Airflow measurement 0–50 liter.min^{-1} (Yokogawa – Japan).

6. Air distributor with a diameter of 200 mm, 89 holes, 5 concentric circles with a hole diameter of 0.8 mm, ½” female threaded end connection.

7. ½” Polyvinyl chloride pipe SCH-80 (Al Amal Al Sharief)

8. ½” ball valve

9. Air source 0–4 bar (g).

10. Oxygen concentration indicator

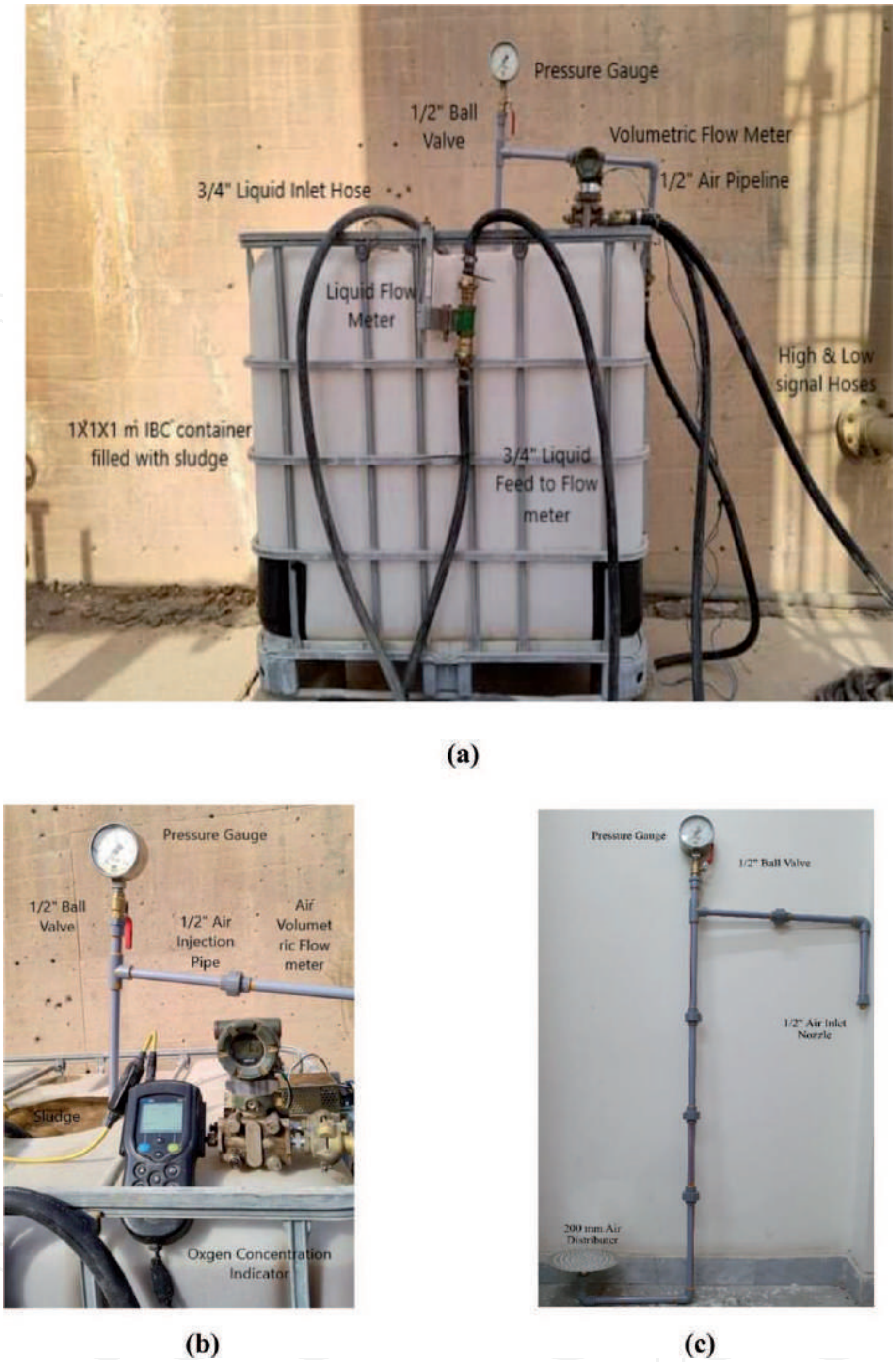

Figure 5.
Test apparatus arrangement: (a) sludge tank. (b) oxygen indicator device, (c) air diffuser.

The procedure of the experiment:

1. All the previous parts are connected as in **Figure 6**.
2. The air valve opened and the air passed to the air distributor inside the sludge tank, the pressure was just set at 0.5 bar(g) with a flow rate measured as 7.5 liter. min^{-1} at 30°C.
3. Oxygen concentration was recorded for each minute.

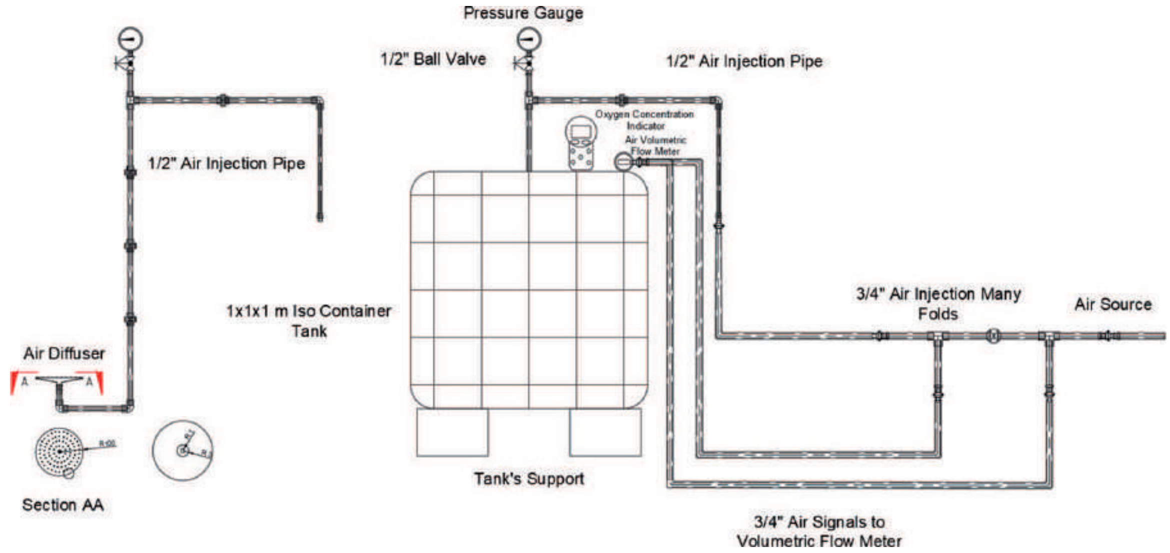

Figure 6.
Apparatus diagram.

4. The second experiment with an air pressure of 0.65 bar(g) and 30°C, i.e., air pressure increased by 0.1 bar(g), and airflow of 8.5 liter.min^{-1} and oxygen concentration was recorded for each minute.

5. The third experiment with an air pressure of 0.75 bar(g) and 30°C, i.e., the air pressure increased by 0.1 bar(g), and airflow of 9.7 liter.min^{-1} and oxygen concentration was recorded for each minute.

6. Foul water inlet to sludge tank just set to 10 liter.min^{-1}, constant at all three experiments.

2. Result and discussion

Air was injected inside the tank through the air diffuser, and the feed of wastewater to be treated, which was pumped into the tank, activated sludge placed in the experiment tank.

The oxygen transfer rate was recorded through the experiment and the oxygen concentration was measured with an oxygen detector.

Oxygen concentration was measured through the first experiment and recorded with 0.45 PPM at the beginning and 3.2 PPM after 33 minutes as in **Figure 7**.

The temperature of the system raised from 26.7°C at the beginning of the experiment to 27.7°C after 33 minutes as in **Figure 7**.

Oxygen concentration was measured through the second experiment, oxygen concentration was recorded at 3.23 PPM 34 minutes from the beginning and 4.46 PPM after 18 minutes from the beginning of the second experiment as in **Figure 8**.

The temperature of the system raised from 27.8°C at the beginning of the experiment to 28°C after 18 minutes as in **Figure 8**.

Oxygen concentration at the last experiment was recorded as 4.8 PPM after 41 minutes from the beginning of the experiment, concentration of oxygen was recorded at the end of the experiment at 6.01 PPM, Temperature increased from 28 to 28.2°C at this experiment.

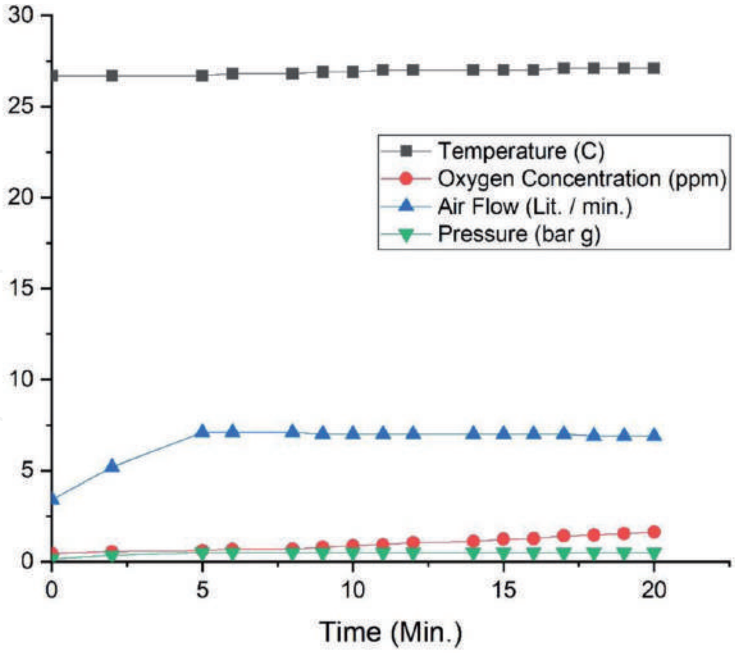

Figure 7.
Concentration of oxygen and temperature of liquid with time at 0.5 bar(g) and air flow of 7.5 L.min^{-1}.

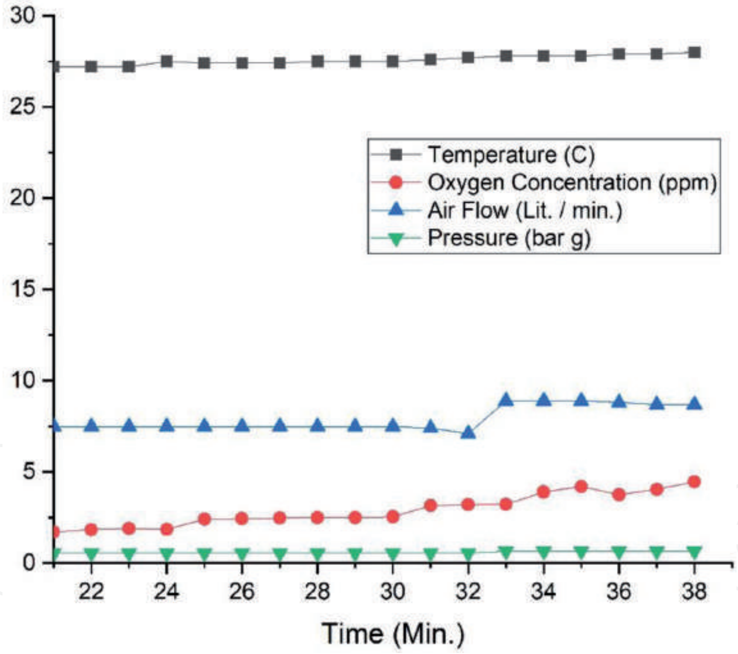

Figure 8.
Concentration of oxygen and temperature of liquid with time at (0.5–0.65) bar (g) and air flow of 8.7 L.min^{-1}.

Increasing the temperature can relate to the biological activities of bacteria due to the digesting of wastes in wastewater [20].

The rate of oxygen (air), supplied with an air diffuser in the experiment tank was high compared with the calculated air required by Eq. (2) [6] and as in **Table 1**.

The amount of air supplied was more than that estimated in the third experiment, because the short path of air from the injection point to the surface leads to air bubbles escaping out of the liquid tank, [21], the pressure of injected air increased with the aim to increase the flow rate of air and reach the required concentration of 6.01 PPM.

Pressure bar (g)	Air flow rate L.min^{-1} (required)	Air flow rate L.min^{-1} (Measured) (Maximum)	Oxygen concentration PPM	Temperature °C of tank
0.5	9.4	7	1.46	27.1
0.55	8.642	7.5	3.23	27.7
0.65	8.428	8.5	4.46	28
0.75	7.940	9.7	6.01	28.2

Table 1.
Final results and estimated amount of air required.

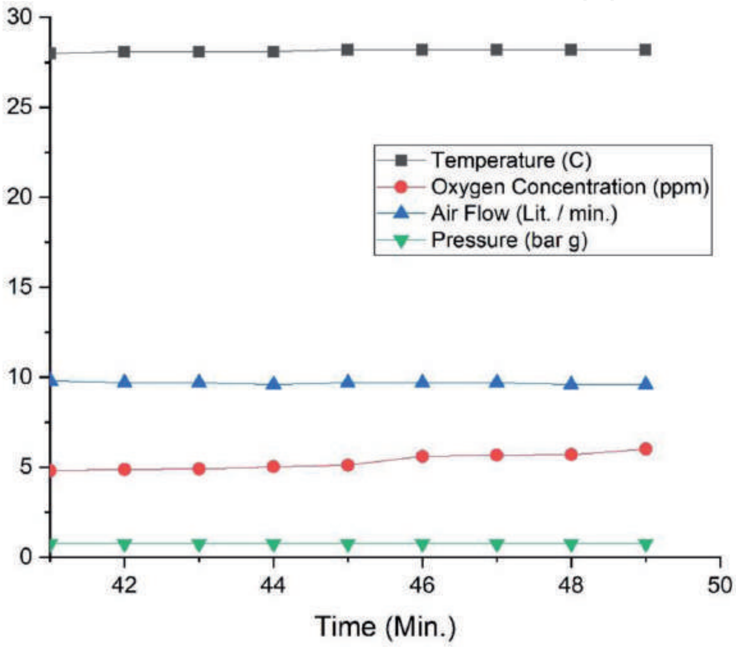

Figure 9.
Concentration of oxygen and temperature of liquid with time at 0.75 bar (g) and air flow of 9.7 L.min^{-1}.

All three experiments were continuous and pressure increased with the aim to increase the flow rate of air, this was when the oxygen concentration did not increase and stopped increasing and sometimes decreased when the temperature of the liquid increased [22], and this was observed very clearly through the experiments data (**Figures 7, 8** and **9**).

New Aeration System Proposed for Biological Reactor of Waste Water Treatment Complex in DR:

The biological reactor in wastewater treatment complex in DR will be changed from mechanical aeration to air direct injection by nonporous diffusers, air distributor applied at 1cubic meter capacity can be applied at the biological reactor.

The power duty and oxygen transfer rate (air flow rate) required can be estimated as in Eq. (2) [6]. power duty with 10% over design is 200 hp. at (BOD 250 PPM as a design condition), the amount of air required to realize 6 PPM oxygen concentration is not less than 587 kg.h^{-1} (454 Nm^3.h^{-1}) at a liquid flow rate of 500 m^3.h^{-1} as a charge to the biological reactor.

The total number of nonporous diffusers required to cover the required amount of air is 604 with a diffuser capacity of 0.9735 kg.h^{-1} (12.532 NL.min^{-1}), which was used in the experiments.

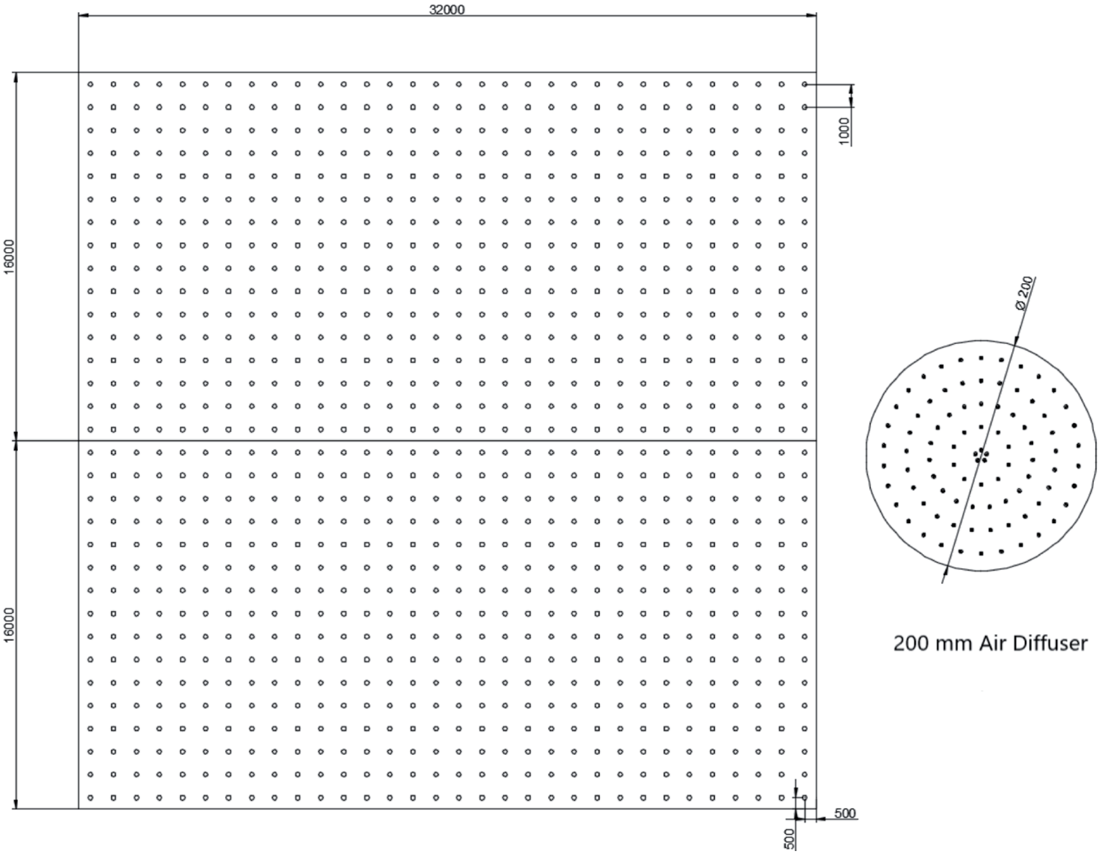

Figure 10.
Arrangement of air diffusers in biological pool.

The number of diffusers will be used more than that calculated according to the capacity of the diffuser, in terms of providing the required amount of oxygen required.

The number of diffusers will be 1024, distributed for two sides of the biological reactor of dimensions 16,000 X 32,000 mm, the distance between each diffuser and the other is 1000 mm, and the distance from the wall is 500 mm as in **Figure 10**.

Installing excess numbers of diffusers can provide well mixing and at the same time avoid the dead zones in the biological reactor; dead zones in the biological reactor activate anaerobic bacteria and in consequence reduce the efficiency of waste digesting [22].

The consumption power through the new proposed system of fine bubbles (diffuser nonporous type) will be reduced from 241.4 hp. in surface aeration to 200 hp, and this is due to the reduction in the amount of air required in the aeration process.

3. Conclusions

1. Oxygen concentration achieved is 6.01 PPM, which is close to the optimum required concentration when 0.9735 kg.h^{-1}of air is injected through a fine bubble diffuser (nonporous type) in a 1 m^3 liquid tank filled with sludge.

2. Biological reactor (the liquid tank) temperature increased with increasing oxygen concentration due to bacteria's biological activities. Even if the temperature rise affects the oxygen concentration in an aqueous solution, airflow must be increased.

3. The type of diffuser used in the experiments can be applied at the biological reactor with an excess aim to supply the oxygen demand, which realizes well mixing, avoids dead zones, and avoids the growth of anaerobic bacteria.

4. Replace the surface aeration system with a direct injection fine bubble diffuser (nonporous diffuser) will reduce consumption power from 241.4 hp. to 200 hp. due to the reduction in air supply, which can be considered more economic and power saving.

Acknowledgements

I would like to thank Mr. Waleed H. Mhaseb Head, division of wastewater treatment for his support and cooperation, and also I would like to thank Miss Aza A. Fiadh, senior instrument engineer for her cooperation.

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Chapter

Electro-Peroxone and Photoelectro-Peroxone Hybrid Approaches: An Emerging Paradigm for Wastewater Treatment

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Abstract

Electrochemical advanced oxidation practices (EAOPs), remarkably, electro-peroxone (EP), photoelectro-peroxone (PEP), and complementary hybrid EP approaches, are emerging technologies on accountability of complete disintegration and elimination of wide spectrum of model pollutants predominantly biodegradable, recalcitrant, and persistent organic pollutants by engendering powerful oxidants in wastewater. A concise mechanism of EP and PEP approaches along with their contribution to free radical formation are scrutinized. Furthermore, this chapter provides a brief review of EP, PEP, and complementary hybrid EP-based EAOPs that have pragmatically treated laboratory-scale low- and high-concentrated distillery biodigester effluent, refractory pharmaceutical, textile, herbicides, micropollutant, organic pollutant, acidic solution, landfill leachates, municipal secondary effluents, hospital, and industries-based wastewater. Afterward, discussion has further extended to quantitatively evaluate energy expenditures in terms of either specific or electrical energy consumptions for EP and PEP practices through their corresponding equations.

Keywords: electro-peroxone, photoelectro-peroxone, wastewater, complementary hybrid EP approaches, energy consumption

1. Introduction

In current scenario, diverse industrial setups have been expanded very rapidly. Consequently, numerous industrial effluents particularly textile, oil, and gas, pharmaceutical, paint, fertilizer, petrochemical, metal, and mining industries have made major contribution to wastewater. These industrial effluents contain toxic dyes, nitrates, 2,4-dichlorophenoxyacetic acid herbicide (2,4-D herbicide), toxic heavy metals, pharmaceutical waste, organic waste, total ammonia nitrogen (TAN), micropollutants, and so on [1]. Wastewater comprising these noxious chemicals is lethal to humans as well as aquatic life. In this frame of reference, several techniques have been exploited for wastewater treatment in the literature explicitly, biological techniques, chemical procedures, and physical methods. Since biological techniques were constrained due to toxic contaminants, long processing time, as well as insufficient degradation of pollutants, that is, perfluorinated compounds is devoid of biological disintegration owing to 533 kJ mol^{-1} energy content required to fracture C—F bond [2, 3], and physical adsorption is a nondestructive method, which could not oxidize pollutants entirely, solely accountable for shifting pollutants from one phase to another as well as pricey method for a powerful adsorbent, which cannot regenerate [4], and chemical methods, which increase cost as well as generate toxic sludge [5].

Over the last few decades, diverse advanced oxidation processes, namely peroxone, ozonation, and electro-oxidation, have been carried out for wastewater treatment through hydroxyl-free radical ($H\dot{O}$) production [6, 7]. Peroxone technique is a blend of hydrogen peroxides (H_2O_2) and ozone (O_3), and on this account several free radicals are produced, which oxidize waste organic compound present in water, but requirement of hydrogen peroxide enhances its cost as well as its storage and transport problem [8]. Furthermore, peroxone has shortcomings of low oxygen ozone conversion rate and been suppressed under neutral and acidic environments [9]. Likewise, ozonation is highly resourceful practice for treatment of large bio-recalcitrant-based wastewater; such type of waste usually required high quantity of energy to decay and has the ability to resist microbes; being an oxidizing agent, a large number of intermediates are generated by ozone, which initiated chain reaction and hence degraded waste. On the contrary, ozone reacts with naturally occurring bromide ions in water to form carcinogenic bromates as side products [10] and has less oxidation potential of 2.07 as well as inadequacy of degrading ozone refractory compounds [11]. Although electro-oxidation process has been provoked in treatment of refractory compounds [12] and micropollutants-based wastewater, nevertheless it has a drawback of more energy consumption (3–5 V) during electrolysis [13]. Additionally, electrochemical-based electrocoagulation techniques are where current is passed across wastewater solution containing electrodes, and metallic ions released from dissolution of anode result in coagulation *via* counter ions in corresponding solution and suspended waste particle made cluster at bottom, it has drawback of electrode encapsulation *via* oxide layer, and hence, it was not a continuous technique [14].

To overcome these dilemmas of traditional advanced oxidation techniques, researchers have been devising various electrochemical advanced oxidation practices notably, electro-Fenton, photoelectro-Fenton, electro-peroxone, and photoelectro-peroxone for wastewater treatment. Nonetheless, homogeneous electro-Fenton and photoelectro-Fenton techniques catalyzed degradation of persistent organic pollutants only under acidic media, and its alternative heterogeneous techniques could conduct full mineralization of same pollutants under neutral pH [15]. In this circumstance, hybrid electro-peroxone (EP) and photoelectro-peroxone (PEP) have been accredited for wastewater treatment under alkaline, neutral, acidic pH, posed good disintegration, and mineralization rates [16–18]. As a matter of fact, EAOPs are hybrid approaches, which have been constructed by integrating two or more practices for enhanced $\dot{O}H$ formation to accelerate abatement of pollutants in wastewater [19]. As a matter of fact, $\dot{O}H$ species is the second strongest oxidant with 2.8 V oxidation potential usually prompting nonselective attacks on C—H bond to oxidize and mineralize pollutants very swiftly as demonstrated through Eq. (6) [20]. Additionally, $\dot{O}H$ could randomly demolish refractory pollutants when existing satisfactorily in water and exploited admirable degradation rate of 10^8 to 10^{10} M^{-1} s^{-1} [21].

Similarly, electro-peroxone is basically hybrid of two elementary approaches, which includes ozonation and electrolysis. In this context, all these techniques were taken into an account to mitigate their drawbacks and develop a novel method named electro-peroxone by putting all together [22]. Solely, oxygen was injected into ozone generator, which interleaved its inlet sparged effluent within cathode at electrolytic cell, where oxygen reduction *via* two electrons at cathode was main culprit of *in situ* hydrogen peroxide generation founded on Eq. (1). Electrochemically formed H_2O_2 subsequently catalyzed transformation of ozone into $\dot{O}H$ by means of peroxone reaction as discussed *via* Eq. (2). Henceforth, electrochemical formation of H_2O_2 and peroxone reactions are the two key reactions of hybrid electro-peroxone approach [23]. Other reactions could have taken place *via* EP process as elaborated with Eqs. (3)–(5) [24, 25]. Major gratification of EP technique is to produce low sludge, comparatively cost-effective, manageable, and continuous production of H_2O_2, alleviate energy intake owing to good rate flow within the system, which promotes mass transfer and convection [26].

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2 \tag{1}$$

$$H_2O_2 + O_3 \longrightarrow \dot{O}H + \dot{O}_2{}^- + H^+ + O_2 \tag{2}$$

$$2H_2O_2 + 2O_3 \longrightarrow \dot{O}H + H_2O + H\dot{O}_{2^-} + 3O_2 \tag{3}$$

$$2O_3 + OH^- \longrightarrow \dot{O}H + \dot{O}_{2^-} + 2O_2 \tag{4}$$

$$H_2O + O_3 + e^- \longrightarrow \dot{O}H + O_{2^-} + OH^- \tag{5}$$

$$R + \dot{O}H \longrightarrow CO_2 + H_2O_2 \tag{6}$$

Even though EP is an expedient approach, its rate of degradation of pollutants usually diminishes with acidity of solution; these acids further make complex with ions, thereby preventing their oxidation. Furthermore, much quantity of O_3 is consumed during EP process [27]. Therefore, existing techniques were modified by incorporating UV light as energy source into electro-peroxone to devise hybrid PEP approach. Photo-electro-peroxone is fundamentally hybrid of three elementary approaches, which include ozonation, electrolysis, and photolysis; these methodologies were coupled to endorse full abatement of pollutants by $\dot{O}H$ formation, which could be proceeded either through Eq. (7) or through (8) *via* PEP approach [28]. This process is expedience with elegant performance even at acidic media where photosynthesized electron within conduction band of a semiconductor bismuth oxychloride (BiOCl) interacts with ozone to yield ozone-free radicals ($\dot{O}_3{}^-$) based on Eqs. (10) and (11); afterward, $\dot{O}_3{}^-$ subsequently will take H^+ and then finally convert into $\dot{O}H$ as discussed in Eqs. (12) and (13) [2, 29]. Moreover, activation of ozone and H_2O_2 is being abetted by PEP. Likewise, PEP technique has demonstrated 98% efficiency for decontamination of total organic carbon (TOC) from wastewater with specific energy consumption of 0.66 kWh $(gTOC_{removed})^{-1}$, while same amount of pollutants could be refined *via* UV/O_3 and electro-peroxone with specific energy consumption of 3.56 and 1.07 kWh $(gTOC_{removed})^{-1}$ sequentially, *via* low reaction rate. That is way photoelectro-peroxone and electro-peroxone are privileged over conventional hybrid advanced oxidation techniques such as UV-integrated electrolysis (UV/electrolysis) and ozone (UV/O_3) for wastewater treatment [30].

$$H_2O + O_3 + h\nu \longrightarrow 2\dot{O}H + O_2 \tag{7}$$

$$H_2O_2 + h\nu \xrightarrow{\qquad} 2\dot{O}H \tag{8}$$

$$O_3 + h\nu \xrightarrow{\qquad} O + O_2 \tag{9}$$

$$BiOCl + h\nu \xrightarrow{\qquad} BiOCl - h^+ + BiOCl - e^- \tag{10}$$

$$O_3 + BiOCl - e^- \xrightarrow{\qquad} \dot{O}_{3^-} \tag{11}$$

$$H^+ + \dot{O}_{3^-} \xrightarrow{\qquad} H\dot{O}_3 \tag{12}$$

$$H\dot{O}_3 \xrightarrow{\qquad} H\dot{O} + O_2 \tag{13}$$

This chapter study aimed to theoretically probe environmentally friendly, cost-effective, comparatively less energy consuming, no secondary toxic side product instigating, and highly versatile novel techniques for wastewater treatment. In this context, recently EAOPs-based hybrid EP and PEP approaches have been discussed for wastewater treatment. Photo-electroperoxone and EP have vividly treated distillery biodigester effluent [31], refractory pharmaceutical [32], hospital [33], ballast water [34], herbicides [18], micropollutants [35], organic pollutant [30], acidic [2], landfill leachates [36], industrial [37], and municipal secondary effluents [26]-based wastewater. Degradation rate of pollutants could be written in terms of rate law to demonstrate chemical kinetic of pollutants during wastewater treatment by electro-peroxone approach. When uniform current is provided to reactor, $H\dot{O}$ formation rate also turns out to be constant and $k\left[H\dot{O}\right]$ in Eq. (14) becomes equal to k_{app} based on Eq. (15) pseudo-first-order rate constant. Here, $\frac{-d[P]}{dt}$ is rate of disintegration of pollutants in solution; while [P], [$H\dot{O}$], k, and k_{app} denote concentration of pollutants and hydroxyl-free radicals in wastewater, absolute rate constant, and apparent rate constant, respectively [38, 39].

$$\text{Rate} = \frac{-d[P]}{dt} = k[P]\left[H\dot{O}\right] \tag{14}$$

$$\text{Rate} = \frac{-d[P]}{dt} = k_{app}[P] \tag{15}$$

2. Setup devised for electro-peroxone (EP) and photoelectro-peroxone (PEP)

Experimental setup has been devised for degradation of pollutants in wastewater through EP and PEP approaches, which is illustrated in **Figure 1**. Wastewater treatment was processed in air-proof semi-batch reactor [40]. One-liter wastewater was incorporated inside the reactor, and pairs of electrodes, that is, cathode and anode 1 cm apart, were interleaved in the middle of the reactor. Quartz jacket-enclosed UV lamp was perpendicularly immersed in reactor for UV photolysis during PEP process. Bubble diffuser and magnet stirrer bar were placed to diffuse mixture of ozone and O_2 gases in aqueous solution and to mix content inside the reactor. Electrolytic operations such as EP and PEP were performed under galvanostatic conditions *via* direct current power supply in the presence of supporting electrolyte [36]. Additionally, constant temperature was maintained *via* water flow around reactor chamber. Ozone generator was operated to attain ozone and oxygen mixture from inlet oxygen supplied through oxygen cylinder. It was connected to ozone meter to estimate ozone concentration within reactor's inlet and outlet channels, which subsequently attached with gas flow

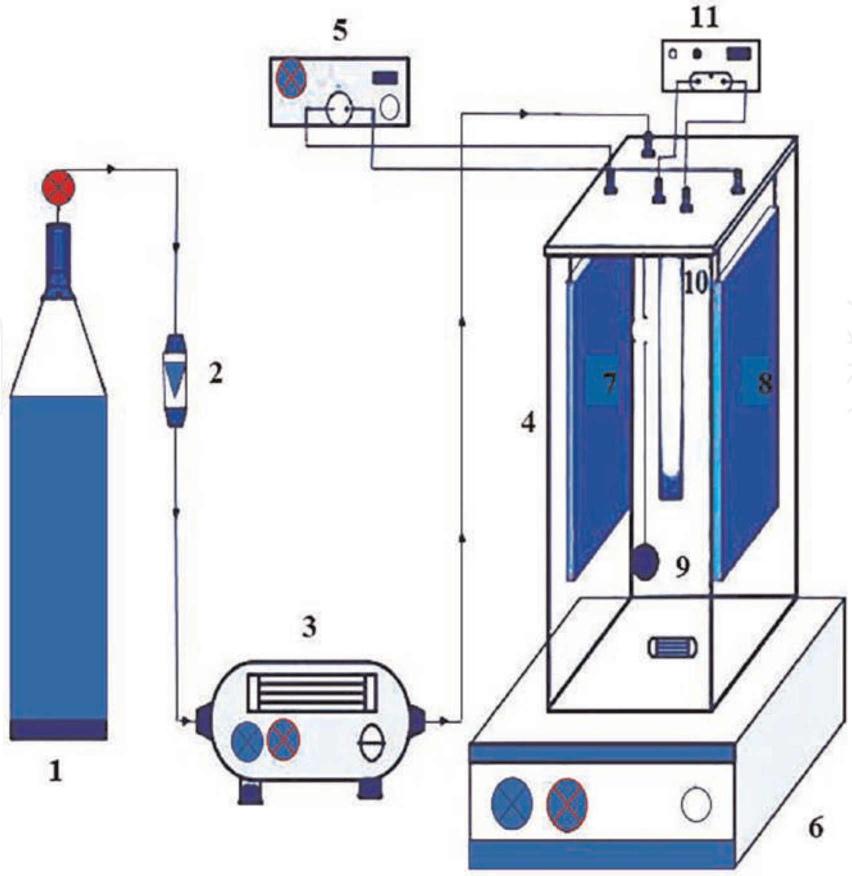

Figure 1.
Schematic illustration of reactor devised for electro-peroxone and photoelectro-peroxone for wastewater treatment image reproduced from ref. [18]. ***1****-oxygen cylinder,* ***2****-rotameter,* ***3****-ozone generator,* ***4****-reactor,* ***5****-power supply,* ***6****-stirrer,* ***7****-anode,* ***8****-cathode,* ***9****-fine bubble diffuser,* ***10****-UV-lamp,* ***11****-UV source.*

meter [40]. Desired quantity of ozone was incorporated inside reactor by modifying flow rate of inlet ozone gas.

3. Electro-peroxone approaches for diverse wastewater treatment

In the literature, a wide spectrum of wastewater applications such as textile, pharmaceutical, biodigester effluents, refractory compounds, and real wastewater treatments have been successfully conducted by researchers as demonstrated by **Table 1**.

Textile industries are producing huge volume of wastewater nearly 30–50 cm^3 water volume $ton^{-1}{}_{dyes}$. Subsequently, dyestuff effluents (10–20 mg L^{-1}) have been discharged into sewages and rivers [49, 50]. Treatment of textile wastewater is inappropriate through biological treatment meanwhile it culprits toxic secondary by products at the end, alternatively several oxidants have been reported which were being restricted on accountability of structural intricacy of dyestuffs. Consequently, textile wastewater treatment is prompted by EAOPs. [51–53]. Anionic dye Acid Orange 7 ($C_6H_{11}N_2NaO_4S$) containing wastewater (500 mg L^{-1}) has been fully decontaminated with 90% and 99% exclusion of TOC and chemical oxygen demand (COD), respectively, within 90 minutes through EP approach carried out in cylindrical reactor [54]. Likewise, Acid Orange 7 was pulverized in a cylindrical baffled reactor to boost exchange among reactants and well-organized electrode arrangement by EP approach. Acid Orange 7 (500 mg L^{-1}) mineralization cleared out 92% TOC and 99% COD were

Category of wastewater	Anode	Cathode	Standard reaction conditions	References
Secondary effluent from coal industry	Dimension-ally stable anode (DSA)	Natural air diffusion electrode	pH: 4, current: 200 mA, electrolyte: 0.3 M Na_2SO_4, treatment time: 3 h, inlet ozone dose: 6 mg min^{-1}, flow rate: 100 mL min^{-1}	[37]
BDE of rice grains	Al	Polytetrafluoroethylene (PTFE)	pH: 6, current: 0.032 mA m^{-2}, electrolyte: 0.15 M Na_2SO_4, treatment time: 50 min, inlet ozone dose: 135 mg L^{-1}, flow rate: 70 L min^{-1}	[31]
Hospital wastewater	Pt sheet	Activated carbon fiber	pH: 9, current: 400 mA, electrolyte: 0.05 M Na_2SO_4, inlet ozone dose: 5 g h^{-1}, flow rate: 1 L min^{-1}	[33]
Ballast water	Perforated DSA	PTFE and carbon black-modified graphite felt (GF)	pH: 7, current: 50 mA, aeration rate: 50 mL min^{-1}, temperature: 25°C, *E. coli*: 10^6–10^7 CFU mL^{-1}, flow rate: 7 mL min^{-1}	[34]
Refractory OMPs	Mixed oxides of ruthenium and iridium (RuO_2/IrO_2) coated Ti plate	Stainless steel plate	Current: 60 mA, treatment time: 15 min, inlet ozone dose: 7 mg L^{-1}, concentration of model pollutant: 150 μg L^{-1}, flow rate: 0.15 L min^{-1}	[35]
LEV	Pt mesh	Carbon fiber composite	pH: 6.8, current: 140 mA, electrolyte: 0.05 mol L^{-1} Na_2SO_4, treatment time: 15 min, inlet ozone dose: 47 mg L^{-1}, temperature: 25°C, flow rate: 0.08 mg L^{-1}	[41]
TC and disinfections	Perforated dimension stable anode	Carbon black and PTFE-modified GF	pH: 7, current: 50 mA, electrolyte: 0.05 M Na_2SO_4, aeration rate: 50 mL min^{-1}, E coli: 1000 CFU mL^{-1}, concentration of model pollutant: 700 μg L^{-1}, flow rate: 35 mL min^{-1}	[26]
Multiple FQs	Pt plate	Fe-modified carbonized MOF	pH: 4.2, current: 210 mA, treatment time: 10 min, inlet ozone dose: 40.2 mg L^{-1}, temperature: 25°C, concentration of model pollutant: 20 mg L^{-1}, flow rate: 50 mL min^{-1}	[42]
Carbamazepine	Carbon rod	CeO_x/GF	pH:5, current: 0.05 mA, electrolyte: 0.05 Na_2SO_4 mol L^{-1}, treatment time: 60 min, ozone output: 50 mg h^{-1}, temperature: 25°C, concentration of model pollutant: 10 mg L^{-1}, flow rate: 0.5 L min^{-1}	[43]
Antibiotics and biocides	Pt	Carbon-PTFE	Phosphate buffer: 50 mM, current: 35 mA, electrolyte: Na_2SO_4 50 mM, inlet ozone dose: 4.5 mg L^{-1}, temperature: 15°C, concentration of model pollutant: 10 μg L^{-1}, flow rate: 0.35 L min^{-1} for each	[44]

Category of wastewater	**Anode**	**Cathode**	**Standard reaction conditions**	**References**
Acid orange 7	Graphite (4 cm^2)	Graphite (4 cm^2)	pH:7.7, current: 0.5 A, anode to cathode ratio: 6: 6, electrolyte: 0.1 M Na_2SO_4, treatment time: 10 min, temperature: 25°C, concentration of model pollutant: 500 mg L^{-1}, ozone flow rate: 8.5 L min^{-1}	[45]
AR14	Pt sheet	Carbon-PTFE (XC-72 carbon powder)	pH:10, current: 0.7 A, electrolyte: 0.1 M Na_2SO_4, treatment time: 30 min, temperature: 25°C, concentration of model pollutant: 400 mg L^{-1}, flow rate: 0.25 L min^{-1}	[46]
AV19	Ti|IrSnSb-oxide plate	3D GDE	pH: 3, current density: 20 mA cm^{-2}, electrolyte: 0.05 M Na_2SO_4, inlet ozone dose: 14.5 mg L^{-1}, temperature: 25°C, concentration of model pollutant: 40 mg TOC L^{-1}, electrolyte flow rate: 2 L min^{-1}, pressure exerted at GDE: 3 psi	[47]
CV	Pt rod	Stainless steel wool	pH: 9, current: 0.1 A, electrolyte: 100 mg L^{-1} NaCl, inlet ozone dose: 2 mg L^{-1}, temperature: 22°C, concentration of model pollutant: 50 mg L^{-1}, peroxide: 15 mmol L^{-1}	[48]

Table 1.
Diverse EP approaches are exemplified for diverse wastewater treatment under standard reaction conditions.

declined within 90 minutes at pH 7.7 with large electrode surface area ratio (6:6) by which degradation was considerably enhanced [45]. Similarly, Acid red 14 (AR 14) wastewater (400 mg L^{-1}) has been disintegrated in Ep-based Box-Behnken experimental setup. Full disintegration of AR 14 was accomplished, and 69% COD exclusion was achieved within 60 minutes at 10 pH [46]. Another attempt has been made on decomposition of crystal violet (CV) with K_{app} of 2.69×10^{-2} and 2.87×10^{2} min^{-1}, for 100 and 200 mg L^{-1} CV in wastewater, respectively. About 98% CV was eliminated at pH range of 7–9 within 5 minutes through combination of electrolysis/peroxone/H_2O_2, and corresponding treated wastewater was manifested no toxicity for microbes. Electro-peroxone approaches were provoked decolorization at alkaline media [48]. A novel approach has been made to smash Acid Violet 19 (AV19) in a lab-scale filter-press-based plant employing 3-D gas diffusion electrode as a cathode to attain better oxygen reduction reaction *via* EP. This led to 60% mineralization and 100% decolorization, at 3 psi pressure that was employed to gas diffusion electrode with acidic pH medium (3). It was demonstrated that AV19 disintegration was consequence of *in situ* generated peroxide coupled with ozonation as well as an anodic oxidation [47].

Recurring detection of personal care and pharmaceutical compounds in water has increased health heedfulness and environmental considerations [55, 56]. Wastewater treatment plant could not completely eliminate antibiotics through traditional activated sludge and sedimentation techniques; as a result, these have been monitored in secondary wastewater effluents in certain quantity [56–58]. In contrast to traditional ozonation practices, ozone recalcitrant micropollutants notably chloramphenicol, ibuprofen, and clofibric acid have been effectively pulverized and accelerated degradation kinetics through triggering $H\dot{O}$ production by means of EP approach [59, 60]. Numerous advanced oxidation techniques have been launched to smash bio-recalcitrant paracetamol (PCT). EP approach has exhibited good efficiency in full disintegration of PCT with rate constant of 0.1662 min^{-1} [32]. Levetiracetam (LEV) removal was a bit challenging owing to polar structures, which was not susceptible to ozone degradation [61]. Extremely water-soluble antiepileptic drug LEV has been manifested pseudo-first-order degradation kinetics *via* EP approach by means of promoted synergy between O_3 and H_2O_2 for actively electrochemical generation of $H\dot{O}$ and led to withdrawn of 53.4% LEV at 15 minutes from wastewater [41]. Numerous antibiotics notably ciprofloxacin, norfloxacin, ofloxacin, and trimethoprim have been degraded with EP and tracked pseudo-first-order kinetics. Outcomes revealed that EP technique effectively eradicates antibiotics and ozone inert biocides within short time and lessen energy consumption than that of ozonation process [44]. Similarly, tetracycline (TC) and microbes were smashed into organic acids and after mineralization totally excluded from wastewater by EP approach [44]. Highly stable polyacrylonitrile-based carbon fiber cathode was designed for mineralization of phenol, where oxidation promoted transformation of pyridinic-N of polyacrylamide into pyridonic-N through EP, which endorsed cathode for oxygen reduction reaction. Major gratification of this procedure was 30-fold recyclability of fabricated cathode as well as cathodic potentials declined energy expenditure from 91.5% (simple cathode) to 48.2% (current cathode) for H_2O_2 formation [62]. Electro-peroxone approach was conducted by fabricating iron-modified carbonized metal organic framework (MOF)-based cathode for treatment of biostatic drugs such as fluoroquinolones (FQs); these were selectively 99% decomposed by O_3 and the rest of its ozone-reluctant transformed intermediates and side products were removed by $H\dot{O}$. Moreover, $H\dot{O}$ was also liable to overall TOC removal, and its formation was promoted by surface functionalities of MOF-based cathode through synergic effect of adsorption and activation [42]. Aforementioned hybrid EP approaches have been successfully applied for the treatment of synthetic wastewater.

Real wastewater in contrast to synthetic wastewater is more complex, having abundant organic micropollutants with varieties of molecular structures accompanying physicochemical properties [63, 64]. Biochemical oxygen demands (BODs)/COD ratio has been commenced for probation of biodegradability prospects and wastewater encompassing 0.4 or its onward ratio has manifested good biodegradability as well as decline in bio-toxicity [65]. Electro-peroxone approach was carried out for processing of reverse osmosis concentrate obtained from industrial coal wastewater. As a result, 92% decolorization, 89% UV_{254}, and 71.2% TOC have been eradicated within 6 hours [37]. After treatment, 91.3% color reduction and 99.9% COD elimination were detected in distillery biodigester effluents (BDE) through EP approach, and low cost of 1 m^3 BDE/2$ and less sludge formation are major gratification of this approach [31]. Chloramphenicol and clofibric acid such as ozone obstinate micropollutants in surface water have been oxidized by EP system and subsequently resulting in hypochlorous and hypobromous acids, which are the main culprit of engendering chlorinated and brominated derived byproducts were efficiently quenched by electrochemically produced H_2O_2 in surface water [35]. Several antibiotics conspicuously ciprofloxacin, norfloxacin, ofloxacin, and trimethoprim have been eliminated from secondary wastewater effluents through EP [44]. Electro-peroxone practice was also employed to process municipal secondary effluents with negligible disinfection side products as well as 65% COD and 44% BOD were declined [26]. Diverse 89 pharmaceutical compounds were examined in terms of organic micropollutants (OMPs) exclusively existing in a real wastewater to evaluate their ozone reactivities and physiochemical properties by means of quantitative structure activity relationship (QSAR) for the sake of kinetic assessment. Pharmaceutical compounds having partial charge moieties, and branched, electrophiles, and lowest unoccupied molecular orbital energies were categorized as ozone-resistant compounds with ozone rate constant (k_{O3}) $< 10^2\ M^{-1}\ s^{-1}$ and were degraded by sole EP. Conversely, ozone reactive pharmaceuticals accompanying with nucleophilic species, highly occupied molecular orbital energies, and conformation contingent charge descriptors were deemed to be ozone reactive with rate constant greater than $10^2\ M^{-1}\ s^{-1}$ would be rapidly eradicated by EP and ozonation [66]. Additionally, ultrasound coupled EP system and virgin EP has been applied for textile industry effluent at 5.8 pH. 93% and 99% decolorization have been accomplished through virgin EP and the integrated ultrasound EP process within 60 minutes after treatment [67]. Similarly, real pesticide wastewater has been treated *via* 3D/EP system with elimination of 97.5% TOC and 95.1% COD up to 500 and 300 minutes sequentially; consequently, long reaction time contributes to more cost although 3-D/EP is more cost effective to that of 2-D EP. Moreover, 30 minutes later BODs/COD ratio has been incremented from 0.049 to 0.571 [68].

In context of acidic wastewater treatment, few attempts have been made to mend EP process. Tannic acid has been oxidatively smashed by EP approach in two phases firstly tannic acid pulverized *via* O_3 and $H\dot{O}$, which were accountable for carboxylic acid like intermediates. Consequently, more intermediate formation lowered pH of wastewater, and thereby $H\dot{O}$ was also declined. Somehow it has been overcome *via* increasing inlet ozone as well as adjusting current and unlike ozonation more than 10% efficacy has been achieved *via* EP [69]. Electrode-separated compartmental-based EP approach was carried out to eliminate para-aminobenzoic acid (PABA) from wastewater solution. As a result, 63.6%–89.5% PABA has been abolished by contribution of cathodic and anodic side reactions, respectively, at 10 minutes as well as incremented pseudo-first-order reaction kinetics and $H\dot{O}$ formation [70].

3.1 Miscellaneous electrode texture-based electro-peroxone approaches for wastewater treatment

Carbon nanotubes (CNTs) have exhibited brilliant adsorption to pollutants, and this tendency along with adsorption kinetic was further enhanced in terms of electrosorption by employing them as electrodes [71]. Furthermore, CNTs have been demonstrated good electrochemical oxidation of pollutants, good chemical stability, electrical conductivity, and noteworthy mechanical strength during electrolysis [72] and photolysis [73]. Advanced oxidation approach has been integrated with adsorption to construct hybrid system for actively pulverization of pollutant in wastewater [74, 75]. Pharmaceutical compounds, particularly diclofenac sodium (DS), were completely fragmented by carbon nanotubes-polytetrafluoroethylene (CNTs-PTFE) electrode over five consecutives cycles exploiting pseudo-second-order kinetics. Where negatively charge diclofenac sodium was exhibited electro-sorption to CNTs-PTFE anode afterward, adsorption phenomena switched this anode into cathode and corresponding adsorbed pollutants were subsequently disintegrated by EP approach within 10 minutes and 99% TOC were eliminated after 1 hour [76]. Likewise, copper ferrite-modified carbon nanotubes ($CuFe_2O_4$/CNTs) were used as catalysts having brilliant recyclability to decomposed fluconazole (FLC) wastewater through EP. Catalyst has adsorbed FLC on its sphere and enhanced FLC mass transfer to electrode surface and thereby eliminated 89% FLC and integrated adsorption-EP technique has contributed 10% efficiency to virgin EP approach [77].

Similarly, carbon nitride-multiwall carbon nanotubes-based nanocomposite (n-C_3N_3/MWCNT) catalyst has actively smashed sodium oxalate in wastewater by endorsing adsorption of pollutant and accelerating electron transfer, which trigger O_3 and O_2 electro reduction [78]; consequently, H_2O_2 and $\dot{O}_3^-$ were generated, which has further enhanced $H\dot{O}$ formation [79]. On account of large surface area, activated carbons are good in elimination of micropollutants (MPs); on the contrary, MPs saturated activated carbons having high affinity for adsorbates pose a major challenge in regeneration of electrode, which was overwhelmed by oxidation of MPs through ozonation process [80] but some sorts of MPs were inert toward ozonation reaction [64]. In this frame, EP coupled with ozonation to exclude diverse MPs, namely trimethoprim, ciprofloxacin, perfluorooctanoic acid, carbamazepine, diclofenac, and benzotriazole from wastewater and efficiently pulverized MPs from ozone. Afterward, ozone-resistant MPs were disintegrated *via* EP with simultaneous regeneration of powdered activated carbons (PAC). In contrast to virgin PAC, all MPs have been exploited more than 100% efficacy for PAC regeneration except diclofenac and perfluorooctanoic acid (PFOA) [81].

Electro-peroxone approaches have been well organized at alkaline and neutral pH; on the contrary, its progress was constrained at acidic pH, which bounds rate constant of H_2O_2 as of 9.6×10^6 to 0.01 M^{-1} s^{-1} for 11 to 3 pH, respectively. Hence, reaction between ozone and deprotonated peroxide has no more yielded reactive oxygen species [22]. Manganese carbon nitride-carbon nanotubes (C_3N_4-Mn/CNT) composite catalyst overcomes drawbacks of disintegrating pollutants in strongly acidic solution *via* EP reaction. Moreover, C_3N_4-Mn/CNT heterogeneous catalyst has been accelerated peroxone reaction between H_2O_2 and O_3, and decomposed oxalic acid within 30 minutes at pH 3 for up to 5 cycles [82]. Additionally, C_3N_4-Mn/CNT-integrated EP system has been evaluated for disintegration efficiency of oxalic acids at a wide range of pH, Outcomes reveal that 57.1- and 2.6-fold increments have been achieved in integrated system, at 3 and 9 pH as compared with virgin EP [82].

Traditional EP approaches were mostly carried out by commencing 2-D electrode system, which have been demonstrated low mass transfer; therefore, to boost electrode performances for additional optimization of conducted treatment were suggested for forthcoming generation [78, 83]. Reticulated enamel carbon, graphite felt, polytetrafluoroethylene, and carbon felt-based cathodic materials were manifested O_2 reduction for H_2O_2 formation [84]. Unlike conventional 2D-electrode in EP approach, 3D-electrode system could considerably promote the electrochemical efficiency of reactor owing to large surface area, which boosted H_2O_2 formation [85]. TiO_2-loaded granular-activated carbon (TiO_2-GAC) as a 3D electrode in EP system was applied for decomposition of diuron, which is a phenyl urea herbicide wastewater, hybrid 3-D/EP system was demonstrated two times more pseudo-first-order disintegration rate (effectiveness) than those of sole EP system. Diurons were adsorbed by TiO_2-GAC and later polarized to synthesize microelectrodes, which yields $\dot{O}H$. Moreover, TiO_2-GAC has considerably enhanced H_2O_2 formation in a corresponding solution [68]. Being a 3-D activated carbon system, carbon felt (CF) has been shown elegant electrolytic proficiency, good mechanical stability, and cost effective [86]. N-doped-reduced graphene oxides (N-rGOs) supported carbon as well-designed cathode was demonstrated to improve oxygen reduction feedback for H_2O_2 generation, better conductivity, boosted electrocatalysis, and electron transfer rate [87, 88]. Diuron was completely smashed at 9 pH within 15 minutes through EP approach using versatile N-rGO/CF-based cathode electrode. Furthermore, N-rGO/CF exploited good efficiency in H_2O_2 formation and lessen energy expenditures for 10 cycles continuously to that of sole CF cathode. This system has led to processed real pesticide wastewater having COD of 3680 mg L^{-1} after processing till 360 minutes, and COD was declined to 47.7 mg L^{-1}. Moreover, BOD/COD ratio of 0.4 and 0.04 has been obtained for processed and unprocessed real pesticide wastewater, respectively [88]. Another attempt was made in which a filter-press flow cell integrated with three-dimensional air diffusion electrode-based lab scale plant was devised to disintegrate levofloxacin and 63% mineralization accomplished at 3 pH [89]. Likewise, GF was modified with cerium oxides (CeOx) to well-designed cathode, and H_2O_2 exhibited chemisorption with CeOx; consequently, it will prompt reaction with O_3 as compared with bulk H_2O_2. Consequently, CeOx/GF-EP system has been manifested 69.4% TOC exclusion in disintegration of carbamazepine within 60 minutes at pH range of 5–9 with upright fivefold recyclability. In contrast to traditional EP, this strategy is perquisite for degradation of refractory organic pollutants under acidic media by proficiently activating ozone, upgraded surface hydrophilicity, and lessen energy expenditure for electro-generation of H_2O_2 [43].

A novel hybrid approach comprising three electrodes in EP system for oxalate-containing wastewater has been developed. After elaboration of reaction mechanism, it was suggested that all reactions in combination subsidizes $H\dot{O}$ formation in EP. In contrast to two electrode systems, three electrodes system could be comparatively privilege in providing precise control and purifying salt-rich wastewater [79].

3.2 Complementary hybrid electro-peroxone approaches for wastewater treatment

To proficiently mineralize and eliminate a wide range of biodegradable contaminants along with refractory pollutants from wastewater by low electrical energy requirement in cost effective and easy ways, some conventional approaches conspicuously biological treatment, ultrasound, electrocoagulation, and low-pressure filtration were coupled with electro-peroxone to devise novel complementary hybrid electro-peroxone system [67, 90, 91]. In this circumstance, synergy overcome constrained individual approaches that have low efficiency independently and accelerated attenuation of wastewater in terms of complementary hybrid electro-peroxone system.

Bio-electroperoxone (Bio-EP) approach has been devised for a two-way treatment of pharmaceutical wastewater, where microbes biodegrade some compounds at electrically bound biofilm reactor (EBBR), and the rest of all compounds that did not undergo biological oxidation was pulverized *via* EP approach. Integrated Bio-EP has been eliminated 89% TOC, 84% suspended solids, 99.99% deactivated microbes, and 92.20% decolorized wastewater [39]. Another attempt was made to pulverize recalcitrant contaminants particularly methylene blue. In this system, self-sustained energy achieved from microbial fuel cell-based cathode by Bio-EP process was supplied and 83% methylene blue has been eliminated within 30 minutes by exploiting pseudo-first-order kinetics with 2.05 h^{-1} rate constant during pulverization [90].

Hydroxyl-free radicals could be synthesized by fracturing bubbles cavitation in aqueous medium through ultrasound (US) based on Eq. (16) [92]. Moreover, US also splits up ozone and peroxide based on Eqs. (17) and (18) [93, 94]. Integrated US/EP approach was applied to fragmentize acid orange 7 at pH 7, which has manifested 88% mineralization, 99% decolorization, and 85% COD elimination with pseudo-first-order kinetics [67].

$$H_2O +)) \rightarrow H\dot{O} + \dot{H} \tag{16}$$

$$H_2O_2 +))) \rightarrow H\dot{O} + H\dot{O} \tag{17}$$

$$O_3 +))) \rightarrow O_2 + O \tag{18}$$

Shale gas fracturing flowback water (SGFFW) was processed with electroperoxone-integrated electrocoagulation (EC/EP) or ECP approach and led to 82.5% COD exclusion up to 90 minutes, with 29.9% average current effectiveness. In ECP technique, coagulant hydroxyl-aluminum at anode eliminates colloids and suspended items [95] as well as catalyzed $H\dot{O}$ formation by reaction with O_3 to breakdown pollutants *via* EP at cathode [96]. Likewise, peroxi-coagulation was integrated with EP; thereby, high efficiency with less reaction time was obtained than that of virgin EP with full decolorization, and 92.2% UV_{254} and 72.2% TOC were eliminated [37].

Low-pressure filtration was coupled with EP approach to design hybrid electro-peroxone filtration (EPF) system, which was continuously eliminated 64.87% ibuprofen (IBU) at less filtration pressure (0.8 kPa) within 8 seconds in its very low concentration of 1 mg L^{-1}. IBU elimination efficacy was comparatively three times than that of individual efficiencies achieved from electrochemical filtration and ozone filtration. In contrast to sole EP, EPF was promoted mass transfer of $H\dot{O}$ and O_3 owing to membrane permeation drift [91].

Downflow bubble column electrochemical reactor (DBCER) has led to incremented mass transfer and contact area owing to energetically liquid inflow, and small bubble formation takes place to cause commotion as well as did not let out electrochemically synthesized *in situ* oxygen *via* Eq. (19) rather it was dispersed within cell [97, 98]. As a matter of fact, under large current density and low pH, $H\dot{O}$ production would favor based on Eq. (20), which subsequently subsidizes oxidation at electrode surface *via* Eq. (21) [99]. DBCER with boron-doped diamond (BDD) electrode system has also been prerequisites for *in situ* formation of O_2, O_3, and H_2O_2 to accomplish EP process with 75% TOC exclusion at pH 3 phenol smashed by ozone and 65% TOC with drawn at pH 7 phenol pulverized by H_2O_2 within 6 hours [98].

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{19}$$

$$BDD + H_2O \rightarrow BDD(H\dot{O}) + H^+ + e^- \tag{20}$$

$$BDD(H\dot{O}) + R \rightarrow BDD + CO_2 + H_2O + H^+ + e^- \tag{21}$$

4. Photoelectro-peroxone practices for wastewater treatment and their comparison with EP

Simple ozonation, photolysis, and electrolysis mechanisms were integrated to fashion novel hybrid PEP approach for wastewater treatment to overcome shortcoming of low mineralization rate during EP at acidic pH and dwindle corresponding electrical energy consumption. Henceforth, PEP and EP approaches have been contributed to synergistic effect, which has been quantitatively determined through enhancement factor calculated by Eqs. (22) and (23) [55].

$$\text{Enhancement} = \frac{(k_{PEP})}{(k_O) + (k_{UV}) + (k_E)} \tag{22}$$

$$\text{Enhancement} = \frac{(k_{EP})}{(k_O) + (k_E)} \tag{23}$$

Where k_{EP}, k_{PEP}, k_O, k_{UV}, and k_E denote rate constants during pollutant disintegration for EP, PEP, ozonation, photolysis, and electrolysis, respectively. Enhancement factors along with degradation rate constants have been comparatively incremented during PEP approaches than those of EP for same wastewater treatment (e.g., **Table 2**).

Organic pollutants containing plentiful wastewater have been magnificently treated by PEP. In this framework, derivatives of benzene particularly nitrobenzene, chlorobenzene, and benzaldehyde containing wastewater were processed through electro-peroxone and photoelectro-peroxone approaches. Although both approaches have been drawn out 98% TOC, PEP exhibited good degradation kinetics, and consumed less energy than that of EP and other advanced oxidation processes, which have been exploited slow degradation kinetics and used up high energy [30]. Similarly, 1,4-dioxane, a major contributor to refractory organic pollutant, is exclusively found in industrial wastewater and landfill leachates and was disintegrated with 33 times proficient pseudo-first-order rate constant *via* PEP as compared with UV photolysis, ozone, and electrolysis. Photoelectro-peroxone approach has discharged 98% TOC after 1,4-dioxane mineralization in wastewater solution. Solely 37% TOC was drawn out *via* EP owing to reliant on pH, which gradually lower consequently interfere with $\dot{O}H^-$ due to resulting intermediates of 1,4-dioxane decomposition notably, carboxylic acid [100]. Furthermore, 4-nitrophenol comprising wastewater has been processed by PEP technique along inserting BDD electrode as an anode that accelerates numerous free radical creations on its sphere and other conventional electrochemical-based advanced oxidation processes. As a result, all mineralized TOC was excluded from wastewater solution in 45 minutes *via* PEP [40]. Likewise, TOC elimination was taken into an account for

Category of wastewater	Conducted approach	Anode	Cathode	Apparent degradation rate constant K_{app}	Enhancement factor	Ref.
Nitrobenzene	PEP	12 cm^2 platinum sheet	40 cm^2 carbon-PTFE	93.0^{a}	5.8	[30]
—	EP	—	—	86.7^{a}	5.5	[30]
Chlorobenzene	PEP	—	—	212^{a}	8.4	[30]
—	EP	—	—	164^{a}	6.7	[30]
Benzaldehyde	PEP	—	—	112^{a}	4.7	[30]
—	EP	—	—	98.0^{a}	4.1	[30]
1,4-Dioxane	PEP	Platinum/titanium (Pt/Ti)	Carbon-PTFE	2.237^{b}	33.4	[100]
—	EP	—	—	1.749^{b}	28.2	[100]
Nitrophenol	PEP	50 cm^2 carbon belt	50 cm^2 BDD	0.145^{c}	13.2	[40]
—	EP	—	—	0.074^{c}	6.7	[40]
2,4-D herbicide	PEP	Titanium	Graphene	0.0009^{d}	**ND**	[18]
MY	ZVI/PEP	Platinum	Graphite felt	0.1926^{e}	1.54	[101]
Reactive Yellow F3R	PEP	Ti/TiO_3	Graphite	1.176^{e}	1.38	[102]
—	EP	—	—	0.834^{e}	1.28	[102]
PFOA	PEP	rGO/BiOClfilm-based photoanode	Graphite	17.5^{f}	4.73	[2]
CBZ	EP	Carbon rod	CeOx/GF	2×10^{-2g}	3.12	[43]
Organic contaminant	Bio-EP	Nematic liquid crystal display electrode	Pt coated titanium	0.0177^{g}	**ND**	[39]
Methylene blue	Bio-EP	Activated carbon granules	XC-72 carbon black	0.237^{g}	**ND**	[90]

rGO/BiOCl = reduced graphene oxide/bismuth oxy-chloride, ***ND*** *= not determined,* ***b*** *=* $K_{app} \times 10^3\ s^{-1}$*,* ***a*** *=* $K_{app} \times 10^2\ min^{-1}$*,* ***c*** *=* $K_{app}^{NP}\ min^{-1}$*,* ***d*** *=* $(min)^{-1}$ *reaction rate constant* (K_{obs})*,* ***e*** *=* h^{-1}*,* ***f*** *=* $K_{app} \times 10^4\ min^{-1}$*,* ***g*** *=* min^{-1}*.*

Table 2.
Comparison between PEP and EP techniques has been demonstrated on basis of enhancement factors along with degradation rate constants for wastewater treatment.

mineralization degree of 4-chlorophenol, benzotriazole, metanil yellow (MY), TC, and carmoisine with 85, 84.2, 65.6, 62.4, and 60.2% TOC removal, respectively. It could be considered that pollutants or compounds with high carbon content were deemed to have low TOC removal owing to compacted structure [101]. Additionally, PFOA was hardly smashed by advanced oxidation techniques and $H\dot{O}$ is also somewhat inactive for PFOA [103, 104]. Therefore, PFOA has been 56.1% decomposed by PEP within 3 hours manifesting pseudo-first order kinetics [2].

Similarly, PEP approaches have been eliminated herbicides at both alkaline and neutral pH. In this context, 2,4-D herbicide was entirely degraded within 25 minutes and its degradation kinetics has exploited first-order reaction rate by PEP approach having rate constant of about 2.5-folds higher than the rate constant of EP. Furthermore, 58.9% TOC has been wiped out during 2,4 D mineralization at pH of 7 from wastewater solution. On contrary to stainless steel and graphite felt, cathodic-activated carbon has promoted reaction rate by engendering H_2O_2 [28]. Likewise, another attempt has been made to boost 2,4-D herbicide disintegration through UV-assisted PEP. Complete fragmentation of 2,4-D herbicide in solution (58 mg L^{-1}) was obtained at 5.6 pH in 112 minutes along with its 91% elimination; moreover, 76% TOC has been withdrawn during 2,4-D herbicide mineralization after 2 hours. Low pH and 85% COD along with trapping assessment revealed that both species $\dot{O}H$ and $\dot{O}_2{}^-$ have contributed to wastewater treatment [18]; hence, approximately at slightly acidic pH reaction could be proceeded between H^+ ions and $\dot{O}_3{}^-$ to produce reaction active species ($H\dot{O}^-$) *via* Eq. (24) [105].

$$2\dot{O}_{3^-} + H^+ \rightarrow H\dot{O}_2 \rightarrow H\dot{O}^- + O_2 \tag{24}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{25}$$

Furthermore, PEP-based some attempts have been made in textile wastewater treatment. In this circumstance, MY dye containing wastewater has been processed by incorporating zero-valent iron (ZVI) as a nano-catalyst in the solution, which was further followed by PEP process and accelerated wastewater treatment. This hybrid PEP/ZVI approach has successfully decolorized wastewater solution (50 mg L^{-1}) at acidic pH 3 within 25 minutes, as acidic media promotes H_2O_2 electrolytically based on Eq. (25) [101]. Moreover, reactive yellow F3R (RY F3R) wastewater was pulverized by PEP manifesting first-order kinetics and 97.66% decolorization and 84.64% TOC has been excluded with 14 and 1.4 times more degradation rate constant as compared with photolysis and EP sequentially.

Moreover, real textile wastewater also has been treated by PEP effectively by withdrawing TOC [102] and decolorization rate could be promoted by incorporating transition metals that in turn produce Fenton reagent. Fe^{+2} triggers ozone activation and hydroxyl-free radical formation as discussed in Eqs. (26) and (27) [28, 106].

$$Fe^{+2} + O_3 \rightarrow FeO^{+2} + O_2 \tag{26}$$

$$FeO^{+2} + H_2O \rightarrow 2H\dot{O} + Fe^{+3} + OH^- \tag{27}$$

$$COD_{exclusion\%} = \frac{C_f - C_0}{C_0} \times 100 \tag{28}$$

In addition, COD parameter was applied to analyze pollutant concentration in landfill leachate and lower the pollutant concentration, and lesser oxidant would be acquired; hence, lower COD exclusion would be attained. Percentage of COD exclusion could be calculated by Eq. (28) where C_0 and C_f denote quantity of COD that has been consumed by leachate before and after its treatment [107]. In this frame, 83% COD exclusion has been achieved at 5.6 pH through PEP [36].

5. Energy expenditures for electro-peroxone, complementary hybrid EP, and photoelectro-peroxone approaches

Some amount of energy has required to perform electrochemical oxidation of wastewater. In this framework, specific energy is mandatory to disintegrate pollutants in innumerable wastewater treatment. Therefore, Eqs. (29) and (30) have been proposed to estimate energy supplied during EP, PEP, and complementary hybrid EP approaches [94].

$$\mathrm{SEC_{EP}} = \frac{\mathrm{U \times I \times t + r \times CO_3}}{\mathrm{(TOC_0 – TOC_t) \times V}} \tag{29}$$

$$\mathrm{SEC_{PEP}} = \frac{\mathrm{P_{UV} \times t + U \times I \times t + r \times CO_3}}{\mathrm{(TOC_0 – TOC_t) \times V}} \tag{30}$$

$$\mathrm{SER_{PEP}} = \frac{\mathrm{UIT \times U_{photolysis} \times rCO_3}}{\mathrm{(COD_0 – COD_t) \times V}} \tag{31}$$

$$\mathrm{SEC_{EP}} = \frac{\mathrm{U \times I \times t + r \times CO_3}}{\mathrm{([PCT]_0 - [PCT]_t) \times V}} \tag{32}$$

$$\text{Energy consumption} = \frac{\mathrm{U \times I \times t}}{\mathrm{V}} \tag{33}$$

$$\mathrm{EC} = \frac{\mathrm{U \times I \times t}}{\mathrm{V \times \Delta\left(TOC_{exp}\right)}} \tag{34}$$

$$\mathrm{EC} = \frac{\left(\mathrm{V \times I} + \text{ozone generator energy}\right) \times \mathrm{t} \times 1000}{\mathrm{C_{dye\ removal}} \times \text{cell volume}} \tag{35}$$

$$\mathrm{SEC_{EP}} = \frac{\mathrm{U \times I \times t + C \times Q \times t \times R}}{\mathrm{(C_0 – C_t)V}} \tag{36}$$

$$\mathrm{EEC} = \frac{\mathrm{U \times I \times t + Q_{gas} \times a \times CO_3}}{\mathrm{V}} \times 10^{-3} \tag{37}$$

$$\mathrm{EEC} = \frac{\mathrm{1000 \times U \times I \times t + Q_{gas} \times a \times CO_3}}{\mathrm{(TOC_0 - TOC_t)\ V}} \tag{38}$$

Where $\mathrm{SEC_{EP}}$ and $\mathrm{SEC_{PEP}}$ are the specific energy consumptions for EP and PEP sequentially measured in kWh $(\mathrm{gTOC_{removed}})^{-1}$, and $\mathrm{SER_{PEP}}$ is the specific energy consumption or electrical energy requirement measured in kWh $(\mathrm{gCOD_{removed}})^{-1}$. U is an average cell voltage (V), I denotes current (A), t represents reaction time (h), r symbolizes energy requirements for ozone formation (kWh $(\mathrm{kgO_3})^{-1}$), $\mathrm{C_{O3}}$ designates ozone quantity consumed during EP and PEP approaches, $\mathrm{TOC_0}$ and $\mathrm{TOC_t}$ indicate total organic carbon in the solution at 0 time and any time t (mg $\mathrm{L^{-1}}$), $\mathrm{[PCT]_0}$ and $\mathrm{[PCT]_t}$ symbolize concentrations of unprocessed and processed paracetamol (PCT), respectively, V shows solution volume (L), $\mathrm{P_{UV}}$ denotes power of UV lamp (W) [108], $\Delta(\mathrm{TOC_{exp}})$ represents change in the concentration of TOC [89], $(\mathrm{C_0} - \mathrm{C_t})$ is the concentration of LEV in untreated and treated wastewater sequentially, R denotes energy expenditure for ozone formation, C symbolizes concentration of inlet ozone, Q indicates flow rate of gaseous ozone [41], a represents energy attained for ozone formation, $\mathrm{Q_{gas}}$ designates feed gas volume, and $\mathrm{C_{O3}}$ reveals feed gas comprising ozone concentration [26].

Total organic carbon was effectively discarded from wastewater during mineralization of benzene derivatives through $\mathrm{SEC_{EP}}$ and $\mathrm{SEC_{PEP}}$, of 1.07 and 0.66 kWh $(\mathrm{gTOC_{removed}})^{-1}$ respectively [30]. Similarly, $\mathrm{SEC_{EP}}$ and $\mathrm{SEC_{PEP}}$ of 0.22 and 0.30 kWh $(\mathrm{gTOC_{removed}})^{-1}$ have been achieved by removing TOC from 1,4-dioxane containing wastewater sequentially [100]. Nitrophenol decomposition has been expended SEC_{EP} and SEC_{PEP}, of 7.5 and 4.1 kWh $(gTOC_{removed})^{-1}$, respectively, for entire elimination of TOC. In addition to PEP, BDD electrode dramatically enhanced reaction kinetic; therefore, deducted energy requirement [40] SER_{PEP} of 1.5 kWh $(gCOD_{removed})^{-1}$ has been consumed in landfill leachate treatment using Eq. (31) [36]. Entire PCT breakdown *via* EP has expended SEC_{EP} of 0.1164 kWh $(gPCT_{removed})^{-1}$ based on Eq. (32) [32]. 1.676 and 22.86 kWh m^{-3} energy have been expended during hybrid bio-EP and solely EP, respectively, calculated through Eq. (33) [39]. Electrolytic energy consumption (EC) of 0.27 kWh $(gTOC_{removed})^{-1}$ was obtained *via* Eq. (34) during levofloxacin mineralization employing 3-D perforated electrode by EP [89]. 37.7% and 41.1% COD have been excluded via EP and 3-D TiO_2/GAC system within 90 minutes by exhausting electrical energy of 0.1 and 0.08 kWh $(gCOD_{removed})^{-1}$, respectively [68]. Additionally, 39.2% and 43.6% COD have been eliminated from real pesticide wastewater with energy expenditures of 0.088 and 0.079 kWh $(gCOD_{removed})^{-1}$ *via* CF-EP and N-rGOs/CF-EP system sequentially [88]. Eq. (35) was taken into an account; afterward, 53 kWh kg^{-1} (kg denote weight of removed dye) energy has been estimated during Acid Orange 7 disintegration with 99% COD exclusion during EP in cylindrical reactor [54]. To diminish SEC, another attempt was made in which Acid Orange 7 was entirely pulverized (99% $COD_{removal}$) through EP with EC of 8 kWh kg^{-1} founded on Eq. (35) [45]. AV19 dye has been 60% mineralized with energy expenditure of 0.085 kWh $(gTOC_{removed})^{-1}$ by laboratory-scale EP plant equipped with 3-D electrode based on Eq. (34) [47]. Similarly, LEV drug was smashed through EP approach with SEC_{EP} of 0.326 kWh $(gLEV_{removed})^{-1}$ on the basis of Eq. (36) [41]. Electrical energy consumption (EEC) of 0.47 kWh m^{-3} has been calculated through Eq. (37) in decontamination of municipal wastewater and TC disintegration *via* EP approach [26]. In the same way, IBU elimination through EPF system used up 0.16 kWh m^{-3} energy [91]. Sequential EEC of 1136.8 and 828.4 kWh $(kg_{TOC})^{-1}$ have been achieved for virgin EP and hybrid peroxi-coagulation/EP system founded on Eq. (38) [37]. Likewise, 99.9% COD exclusion has been achieved during treatment of BDE of rice grains through EP approach *via* EEC of 3.8 kWh m^{-3} [31].

Overall, PEP dwindled almost 45% specific energy consumption than that of EP approaches for a same category of wastewater under unchanged reaction conditions; nevertheless, some exceptions may be commenced conspicuously in degradation of 1,4-dioxone. Complementary hybrid EP approaches have foremost expedience of comparatively reducing energy expenditures to that of a virgin EP as well as enhanced abatement of pollutants in wastewater treatment. In this milieu, bio-electroperoxone system offered much indulgence by in taking very low energy. In contrast to conventional 2-D electrodes, latest 3-D electrodes-based EP approaches have been manifested less energy consumption.

6. Conclusions

High-operating cost-advanced oxidation processes on accountability of derisory performance to wastewater treatment have been exploited sundry shortcomings, which urge necessity for EAOPs-based alternative techniques. In this framework, to exaggerate traditional 2-D EP system has been transformed into 3-D EP by modification in electrode texture as a result, more peroxide formation was catalyzed by large electrode surface area as well as considerably SEC were also dwindled. Notwithstanding PEP approaches were established to overcome dilemma of existing EP techniques under harsh conditions, where UV accelerated further prevailing hydroxyl-free radicals and synergistic effect of individual mechanisms involved in PEP have been substantially boosted enhancement factor along with degradation kinetics of pollutants in wastewater thereby diminishing energy expenditures in the form of SEC_{PEP}. Additionally, to improve some conventional methods more conspicuously filtration, electrocoagulation and biological treatments were coupled with EP to devise novel complementary hybrid EP-based EAOPs, which have demonstrated pragmatic mineralization effectiveness and declined required electrical energy consumption.

Over the last decade, EAOPs in wake of nonselective oxidation and prohibition of secondary products have been acquainted for wastewater treatment. Henceforth, EAOPs more conspicuously novel complementary hybrid EP and PEP approaches could be more economical option for wide spectrum of synthetic and real wastewater treatment along with reducing energy expenditures, which could be fruitful from laboratory to large scale.

Conflict of interest

The authors declare no conflict of interest.

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Chapter

Impact of the Spreading of Sludge from Wastewater Treatment Plants on the Transfer and Bio-Availability of Trace Metal Elements in the Soil-Plant System

Najla Lassoued and Bilal Essaid

Abstract

The spreading of sludge from sewage treatment plants increased the production of durum wheat and rapeseed. Their richness in nitrogen, phosphorus, and potassium gives them a beneficial effect on crops. However, the application of the sludge can induce increases in the concentration of metals in plant tissues. This increase can generate disturbances at the level of the cell and organelles, such as mitochondria and chloroplasts, which can be altered. Repeated applications of the sludge on the same site tend to increase the accumulation of heavy metals in the soil, so that an cause toxicities for soil microorganisms, animals, and humans, via the food chain. However, it is important to specify that these nuisances mainly concerned industrial sludge, but the use of this sludge is strictly prohibited. In addition, the high doses used in our field experiments are significantly higher than those authorized in agricultural practice. Finally, the risk assessment by calculating both the level of consumer exposure and the number of years for soil saturation shows that the use of urban sludge is safe, especially in the short and medium-term. Nevertheless, the quality of the sludge to be spread must be constantly monitored.

Keywords: sludge, trace metal elements, wheat, rapeseed, soil–plant system

1. Introduction

The constant increase in the production of sludge from wastewater treatment plants presents a major environmental problem. Compared to traditional means such as landfill or incineration, agricultural sludge spreading appears to be the most cost-effective option for sludge disposal [1]. The use of sludge in agriculture appears among the most sustainable environmental solutions in their disposal. In fact, sludge potential fertilizer and the high cost of mineral fertilizers promote sludge use in agriculture. Nevertheless, their metallic trace elements content (ETM) presents a real disadvantage in their use. Actually, metallic elements retained by the sludge during wastewater treatment can cause high metallic charges accumulation in soil [2]. Metals can be found in the form of sulphites, oxides, hydroxides, silicates, phosphates, carbonates and insoluble salts. They can also be adsorbed or associated with the organic matter of the sludge. The amount of metals in the sludge depends on the origin of the wastewater and the treatments it has undergone [3, 4]. It is, therefore, necessary to try to understand the mechanisms and factors involved in the transfer of these elements into the soil and their effects on the plant following the addition of sludge. The behavior of heavy metals in soils and their absorption by plants depend on the quality of the sludge, the nature of the metal, the physico-chemical properties of the soils and the plant species. Plants differ in their ability to absorb and accumulate metals [2, 3]. From the perspective of an agricultural recovery of sludge, we have tried to contribute to the study of the impact of sludge on the transfer of metallic trace elements in the sludge-soil–plant system. Therefore, a field experiment was carried out in Oued Souhil (Tunisia). In this context, we propose to study the effect of two types of urban and industrial sludge on the distribution and compartmentalization of metallic trace elements in the different organs of two species (durum wheat and rapeseed) chosen according to their absorption capacity.

2. Materials and methods

The experimental protocol was installed in the field to the Agricultural Experiment Station of Oued Souhil - Nabeul, situated about 60 kilometers from Tunis and belonging to the National Institute for Research in Rural Engineering Water and Forest.

The urban mud used in this study is taken from the wastewater treatment plant in Korba with a treatment system at low load activated sludge followed by maturation. Sludge from this station underwent a stabilization in aerobic followed by drying on beds. The dry sludge is removed from the drying bed.

The industrial mud is provided from wastewater treatment plant Bou Argoub which hosts two big companies, the Tunisian beverage manufacturing company (SFBT) specialized in the food industry, and Assad company specialized in the electrical industry. Sludge from this station underwent a stabilization in aerobic followed by drying on beds. This sludge is loaded with heavy metals especially lead and chromium.

The plant materials that were used in this experiment are the rapeseed (*Brassica napus*), which is an annual plant with yellow flowers of the family Brassicaceae and durum wheat (*Triticum turgidum*) that can be defined as a species of wheat characterized by its hard and glassy kernel. Rapeseed was chosen for its ability to accumulate metals and also because it is one of the three main sources of edible vegetable oil with sunflower and olive.

Experimentation was carried out on two juxtaposed plots reserved for each crop (wheat or rapeseed). For each type of sludge, four doses (5, 25, 50 and 100 t ha^{-1}) were used. Results were compared to a control soil without any treatment.

Sludges were manually dug into the soil. Before utilization, the sludge was analyzed.

The soil was analyzed before the application of sludge and after the harvest. Sampling was conducted between the lines using an auger at four depths (0–10, 10–20, 20–40 and 40–60 cm).

In the laboratory, soil samples were dried in open air and sieved to 2 mm or 0.2 mm depending on the type of analysis required. The main measured parameters were particle size, total calcium, conductivity, carbon, organic matter, total nitrogen and heavy metals concentration. For the particle size, we used the method of the International pipette Robinson, which is essentially based on the destruction of organic matter in the soil using H2O2 and the dispersion of clays by sodium hexametaphosphate. Clays and silts are measured in the suspension of land following the decay time that depends on particle diameter (NF X 31–107). The settling velocity was measured by the formula of Stokes. The Mud and soil samples were analyzed by XRF (X-Ray Fluorescence) and ICP-AES (Inductive Coupled Plasma Atomic Emission Spectrometry Activa–Horiba Jobin Yvon Spectrometer) in the Geosciences and environment Department of National School of Mines in Saint Etienne. The Soil pH was measured by using a 1:2 soil to water ratio. Plant samples were washed with tap water and rinsed three times with distilled water, then separated into leaves, stems and roots, dried at 40°C to constant weight, crushed and sieved at 2 mm. Moreover, the digestion of plant samples was performed using nitric concentrated acid, according to [5–8]. The plant extracts were analyzed by ICP-AES.

The sowings were performed with 50 seeds m^{2-1} for rapeseed and 350 $seedsm^{2-1}$ for wheat. The rapeseed harvest was performed after the formation of slices. We weighed the aerial part and the root. The same work was done to wheat. The samples were subsequently dried and crushed ore to determine the mix of metals in different parts of the plant. The different parts of the plant were dried at 80°C to constant weight and then crushed to a fine powder using a porcelain mortar to prevent metal contamination. Digestion is done at high temperature (70°C) with aqua regia. For histological analysis, preparing the samples carefully for transmission microscopy was essential for obtaining reliable results. Therefore, samples were set at 4°C with a solution of 20.5% glutaraldehyde, pH was maintained at 7.4 with a solution of sodium cacodylate (0.1 M). The samples were then washed with sodium cacodylate buffer (0.1 M) and post-fixed in a solution of 1% osmium tetroxide in veronal buffered (0.1 M) [9]. After several washes in distilled water, the samples were dehydrated with a graded ethanol series of increasing concentrations going from 30 to 100%. The final inclusions were made from a mixture of resin [10]. Only the sections with interference colors are gray or silver, that is to say (thickness of 600 to 900A° (1A° = 0.1 nm)) were collected and deposited on a copper grid with 3 mm diameter. The ultrathin sections were mixed using an alcoholic solution of uranyl acetate and 7 by 1% lead citrate [11]. On top of that, observations were made using a Hitatchi H800 electron microscope.

The data were subjected to analysis of variance. The comparison of means at 5% level of significance was performed by the Newman–Keuls test using the Statistica 7 software.

The amount of heavy metal in sludge is not a good indicator for metal availability for *T. turgidum* plant uptake; accumulation factors were calculated based on metal availability and its uptake by a particular plant. A calculation of biological concentration factor (BCF) was as in Eq. 1, biological accumulation factor (BAF) as in Eq. 2, and transfer factor (TF) as equation

BCF = Metal content (mg kg^{-1}) in root/metal content (mg kg^{-1}) in sludge (1)

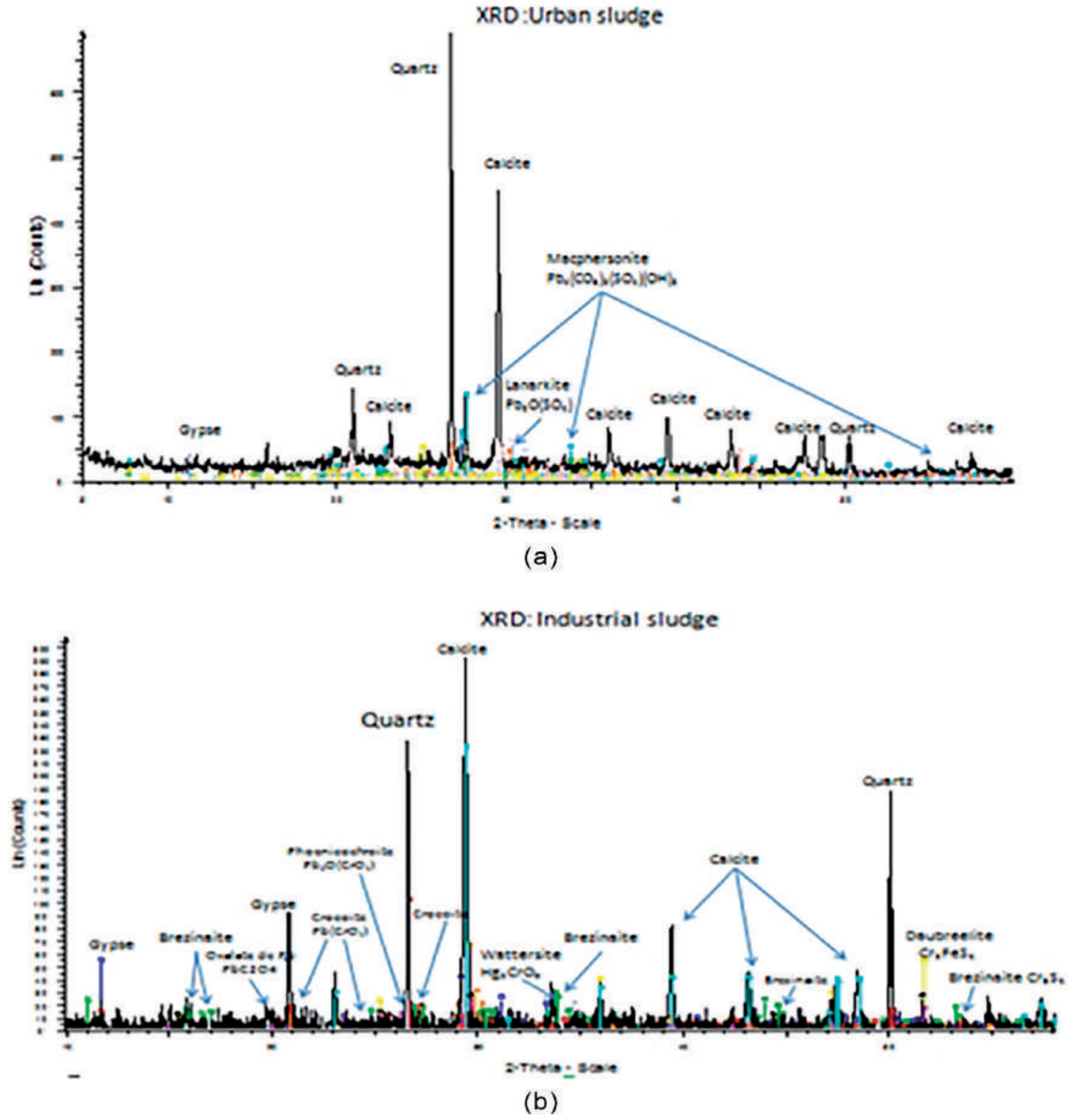
BAF = Mean metal content (mg kg^{-1}) in shoot (root+straw+spike)/metal content (mg kg^{-1}) in sludge (2)

TF = Mean metal Content (mg kg^{-1}) in shoot (root+straw+spike) /metal content (mg kg^{-1}) in root (3)

3. Results and discussion

XRD analyzes have shown that industrial sludge has high levels of chromium and lead. These elements mainly exist as Daubreelite Cr_2FeS_4, Brezininaite Cr_3S_4, Wattersite Hg_5CrO_6, Crocoite PbC_2O_4, Pheonicochroite Pb_2O (CrO_4) and lead oxalate PbC_2O_4. As for urban sludge, we note the absence of chromium and the presence of lead in the form of Macphersonite Pb_4 $(CO_3)_2(SO_4)$ and Lanarkite Pb_2O (SO_4).

The results of the XRD spectrum (**Figure 1**) were confirmed by those obtained by the chemical and mineralogical analysis (SEM) shown in **Table 1**. Thus, industrial sludge from BouArgoub has very high levels of chromium, lead and cadmium. These contents are higher than the limit values of the Tunisian standard NT-106, which is not the case of urban sludge of Korba. Both types of sludge are rich in organic matter and nutrients, especially nitrogen and phosphorus.



(a)

(b)

Figure 1.
XRD spectrum of sludge from urban (a) and industrial (b) wastewater treatment plants.

Contents	Industrial sludge	Urban sludge	Tunisian standard
pH	6.3	6.7	<6
MO %	57.9	66.6	50–70%
N %	4.3	5.2	3–9%
C %	31.9	39.0	ND
C/N	7.5	7.4	5–12
Fe_2O_3%	1.02	1.88	ND
MnO %	0.03	0.02	<1%
MgO %	0.8	1.22	ND
CaO %	8.51	13.4	ND
P_2O_5%	2.18	3.24	4–5%
Cd mg kg^{-1}	11	3	20
Co mg kg^{-1}	18	28	ND
Cu mg kg^{-1}	68	158	1000
Fe mg kg^{-1}	8300	10,700	ND
Mn mg kg^{-1}	81	152	ND
Ni mg kg^{-1}	49	78	200
Pb mg kg^{-1}	577	63	800
Zn mg kg^{-1}	360	440	2000
Cr mg kg^{-1}	8030	155	500

***ND:** not defined/Source ADEME.*

Table 1.
Chemical contents (mg kg^{-1}) of industrial sewage sludge, urban sewage sludge and Tunisian standard values [12].

According to [13–18] sludge is a good source of nutrients for plant growth, it can improve the physical properties of the soil. Vlamis et al. [19, 20] reported that sludge can replace mineral fertilization. Phosphorus in sludge is as effective as phosphorus in fertilizers in increasing the extractable phosphorus in the soil to the level required for crop growth. Likewise, calcium carbonate in sludge increases soil pH more effectively than agricultural lime.

Our results made it possible to highlight the action of the sludge on the behavior of the plant in qualitative and quantitative terms. During the first year of experimentation, the productions obtained were generally higher than those obtained on the control plots. A dose-effect was very clear. The dose of 100 t ha^{-1} records the highest production whatever the crop. Similar results are obtained by other authors. A clear improving action of sludge on English Ray Grass production [21–23]. Zaier et al. [24] showed that the sludge significantly stimulates the biomass production of B. napus. Similar results have been demonstrated by [25] who showed that the biomass production of durum wheat was significantly improved by 18% with the addition of 40 t ha^{-1} of sewage sludge. Pasqualone et al. [26] found positive effects of increasing sludge doses on durum wheat productivity, 12 kg ha^{-1} of sludge was demonstrated to can effectively replace mineral fertilization. Boudjabi et al. [27] found a significant increase in the number of tillers, ears and kernels per ear of barley in amended soils. This has been linked to an improvement in the physical and chemical properties of soils. This beneficial effect has been observed on several crops such as wheat, sorghum, maize, chili peppers, barley and potatoes [21, 28–31].

For the two types of sludge, the results of the second application show a positive effect on rapeseed production at the doses of 5 t ha^{-1} and 25 t ha^{-1}. However, in this second application, industrial sludge causes an increase in the concentration of metals in the soil, especially chromium, cadmium and lead. The cumulative application of industrial sludge generates an excessive accumulation of heavy metals [32, 33] which could be harmful to soil fertility, affecting the ecosystem and human health [34]. Marchiol et al. [35] observed that *B. napus* grown on multi-contaminated soil was tolerant to heavy metals. They concluded that this species could eventually be used successfully in polluted soils without its growth being affected and that heavy metal extraction can be maintained at a satisfactory level. In our case, the tolerance index of this plant exceeds 1 for all treatments but during the second year for the dose of 100 t ha^{-1}, industrial sludge gave lower indices than urban sludge. Nonetheless, the cumulative application of urban sludge increases the production of rapeseed regardless of the dose.

During the experimentation, the plants presented a normal appearance but some rapeseed leaves cultivated in plots having received 200 t ha^{-1} of industrial sludge show spots of necrosis and a purplish color. In the literature, these symptoms are described as due to phosphate deficiency. Soil rich in iron or zinc can reduce the absorption capacity of phosphate ions, which could occur as a result of adding sludge to the soil [36]. In this context, [37] have also shown that the presence of high levels of lead can cause the formation of precipitate of lead phosphates, which cannot be assimilated by plants and consequently a phosphorus deficiency can occur. For rapeseed, we have seen a delay in germination in certain plots following a cumulative effect of industrial sludge. Also, germination appeared to be inhibited by the presence of urban sludge. Laboratory experiments confirmed this effect, but showed that germination was not permanently inhibited, but simply delayed. The latency period is dose-dependent, so it increases depending to the amount of sludge added. A similar effect was induced by heavy metals (Cu, Ni, Zn) in aqueous solution [38]. Also, germination is positively correlated with the degree of stability of the sludge and the organic matter contents [39]. The observed delay of germination was restored after one month and the development cycle resumed normally.

A study by [40] showed that sludge causes the late maturity of wheat. This was not the case in our experimentation where the wheat development cycle was not disrupted. An increase in crop yield resulted in an increase in the number of seed in our study. We also mentioned that urban sludge increases the oil yield of rapeseed after the 1st spreading. Similarly, [41] has shown that urban sludge considerably increases the productivity of sunflower oil. The use of urban sludge as a fertilizer has been considered for years given its richness in organic matter and nutrients [41, 42]. However, sludge contains phytotoxic metals which can cause certain problems at high levels [43]. The response of plants to these metals varies considerably from one species to another [44–46] and the results obtained are disparate. Other factors including edaphic can intervene. In our work, we have shown that whatever the site of culture (control, contaminated, heavily contaminated), wheat has a lower concentration of heavy metals than rapeseed. However, these differences are minimal on the control site and are accentuated with the addition of sludge, especially in the presence of industrial sludge. This finding is not the same for the seed since, on the control site, the wheat seems to concentrate more heavy metals than rapeseed, but this is only due to the high zinc contents of wheat seeds. If we disregard the zinc, we find the same result. In fact, Brassicaceae are generally considered to be metal accumulators that can tolerate high concentrations [47] unlike cereals [48]. However, the accumulating power of rapeseed remains low to consider phytoremediation [49]. It is important to note that both rapeseed and durum wheat were able to survive on a site treated with sludge loaded with heavy metals. This capacity may be due both to the existence of tolerance strategies in the plant making the assimilation of metal limited and also to the strong metal bonds in the sludge and the soil rich in matter organic. Most heavy metals can also be stored and detoxified in root tissues with minimal translocation to leaves whose cells are sensitive to phytotoxic effects [50–54].

Actually, the extent of metal contamination depends both on the concentration of the metal in the environment and on the intrinsic factors of the metal. The concentrations of the main tracemetalic elements are represented in **Figure 2**. In the control environments and those treated by urban sludge, the Zn contents are higher than the other metals while cadmium was the least abundant. The concentrations founded were as following: Zn > > Cr > Cu > Ni > Pb > Co > Cd. For the environments treated by industrial sludge, the amounts of trace elements were completely different, reflecting an increase in chromium and lead amounts. The concentrations founded in these environments were as following: Cr > > Zn > > Pb > Cu > Ni > Co > Cd.

The presence of metals in the soil can influence the uptake of essential nutrients for plant growth [55, 56]. The essential divalent cations such as Ca^{2+}, Mn^{2+}, Zn^{2+}, Mg^{2+} compete with toxic metals such as Cd. Therefore, the increase in the contents of these elements can reduce the absorption of metals such as Cd [57–59]. However, in our experimentation, for the rapeseed, we noted a synergy between a non-essential metal Cd and a trace element Zn. Also, the increase of Cd absorption decreases the absorption of iron and manganese by the root (**Figure 3**). These observations are explained by competitions between these different cations for surface complexation sites in the root and for the unspecific carriers of major cations or trace elements. Other works have shown that treatment with cadmium can cause deficiencies in iron, copper and manganese [57, 60].

For wheat, the absorption of iron, manganese and zinc increases according to the doses (**Figure 4**) of the sludge and probably plays a non-negligible beneficial role on the Phyto availability of non-essential elements such as cadmium, an

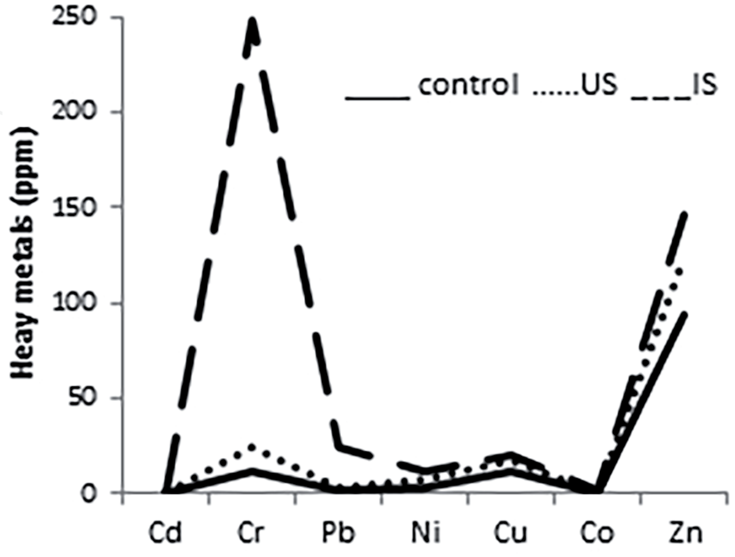


Figure 2.
Effect of metal on some of metal trace element concentrations in the plant.

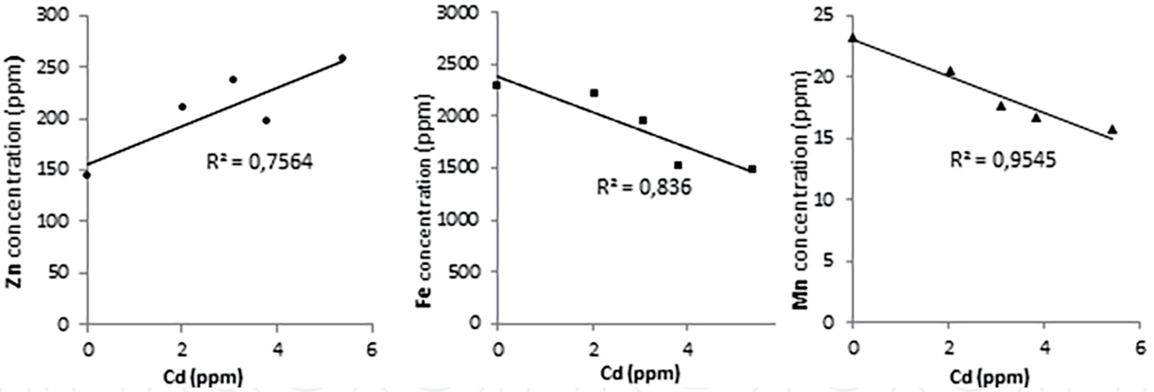


Figure 3.
Influence of cadmium on the absorption of zinc, iron and manganese in rapeseed roots.

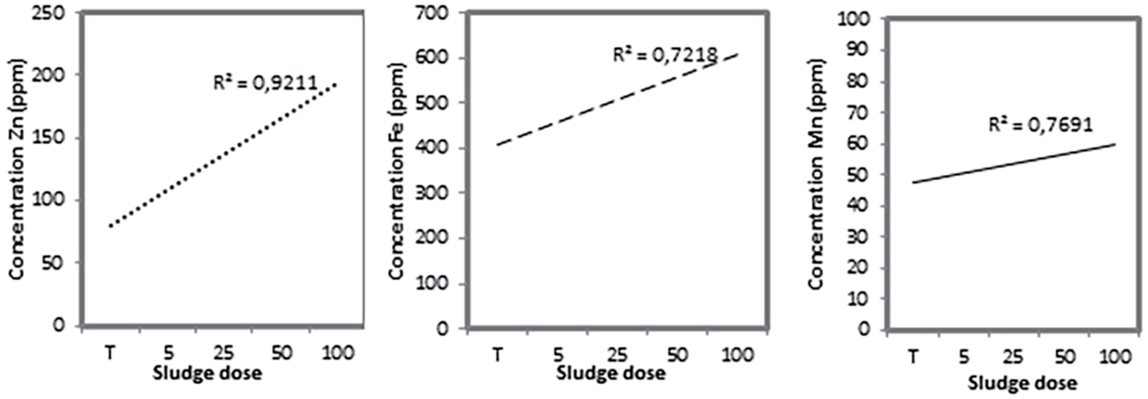


Figure 4.
Effect of industrial sludge on the absorption of zinc, iron and manganese in the roots of durum wheat.

antagonistic effect could have taken place, which could explain the negligible Cd contents found in wheat [61].

Sludge application causes a high accumulation of metallic trace elements in the soil, these metallic elements are then driven to the roots and finally to the aerial part. The addition of industrial sludge causes a significant contamination of the soil and the roots by heavy metals while the degree of contamination at the level of the aerial part is lower as shown in **Figure 5**. For urban sludge, the accumulation of heavy metals is high but much less than that of industrial sludge. The comparison between contaminated and uncontaminated environments shows that the more the environment is polluted with ETM (Trace Metal Elements), the higher the contents of these elements in the plant.

The difference in behavior between aerial organs and roots with respect to heavy metals is reflected in the ultrastructure. From a cytological point of view, the number of cells in apoptosis is higher in the roots. This suggests the existence of much more effective bio protection modalities in the root. The high doses of the sludge cause ultrastructural changes in the roots, but the nucleus retains its integrity and the chromatin is evenly distributed. As for the cytosol, it has a contracted appearance with grouping of ribosomes into polysomes. Mitochondria change their shape and have swollen ridges (**Figure 6**).

Fragmentation of the vacuole into many small vacuoles is also observed (**Figure 6**). The plasma membranes appear damaged. The best-known strategy is to interfere with the entry of heavy metals into root cells by trapping them in the apoplasm where

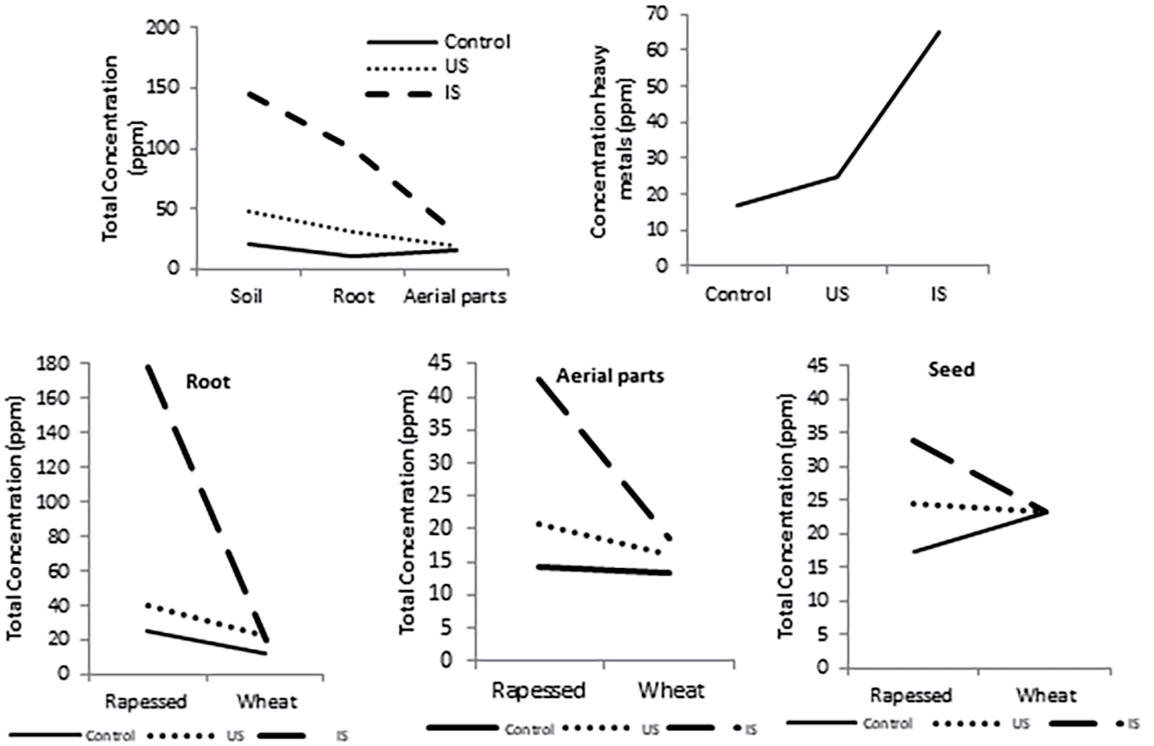


Figure 5.
Accumulation of metallic trace elements in the soil spread by sludges and in the different parts of the plant.

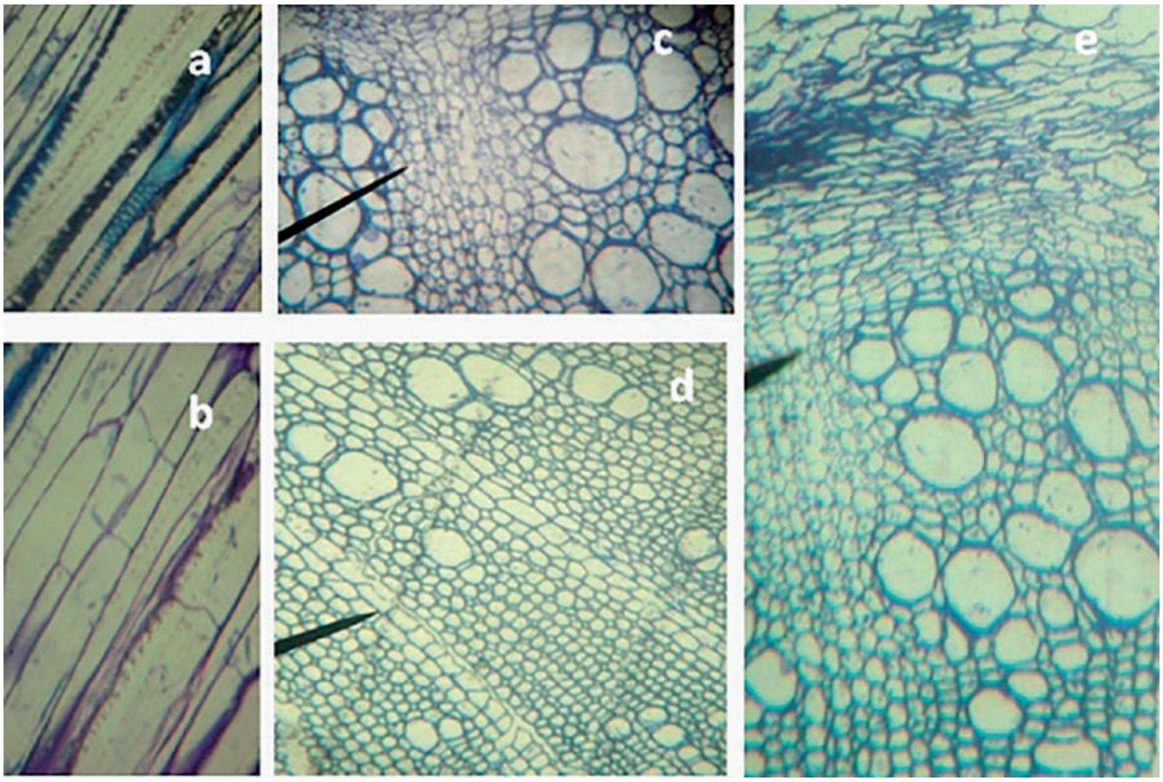


Figure 6.
*(a) central cylinder of control roots in longitudinal section (Gr * 40). (b) central cylinder of a control root in cross section (c) Cross section of a root treated with 100 t ha^{-1} BU (Gr * 40). (d, e) Central cylinder of a root of treatment 100BI (Gr * 40). Cp: Parenchymal cell; X: xylem; RL: Woody rays; CC: central cylinder; P: periderm.*

they associate with organic acids [62] or anionic groups in cell walls [63]. Once inside the plant, most heavy metals are held in deep cells, where they are detoxified by complexing with amino acids, organic acids or peptides and or they are sequestered in vacuoles [51]. This greatly limits translocation to aerial organs, thus protecting the leaf tissues, and in particular the metabolites of photosynthetic cells against possible damage. Another defense mechanism generally adopted by plants exposed to heavy metals is the improvement of cellular antioxidant systems which would limit oxidative stress [52, 53].

The export of metals to the aerial part is accompanied by physiological disturbances. A decrease in chlorophyll could be induced by excess zinc and cadmium [64]. Our results confirm this fact as shown in **Figure 7**. Likewise, a decrease in the level of carotenoids can be linked to an excess of cadmium [65] or to an excess of copper [66].

Metals alter electron transport and inhibit the activity of Calvin cycle enzymes [67]. High doses of industrial sludge also weaken photosynthetic activity [68, 69] and cause a gradual decrease in photochemical quenching (qp) [70, 71] accompanied by a significant increase in non-photochemical quenching (NPQ).

Chromium directly inhibits one of the key enzymes in chlorophyll biosynthesis NADPH [72]. Likewise, several metals such as Cd, Pb, Cu, Zn, and Ni can replace Mg in chlorophylls, resulting in inactive molecules [73–75]. In the leaf, excess metals can also induce changes in membrane stiffness, permeability and stability [76]. At the cellular level, rearrangements were observed (**Figures 8** and **9**). The damage produced at mitochondria and chloroplasts is more severe than that of the nucleus.

In the leaves of plants cultivated in the presence of high doses of industrial sludge loaded with metals, the number of chloroplasts has decreased. Similar results have been reported by [77]. Other structural damage is also frequently observed such as swelling of chloroplasts, rupture of the envelope, deformation of thylakoids. The thylakoid membranes lose their parallel arrangement, the grana become disorganized and the thylakoid surface is reduced. These ultra-structural changes are accompanied by an increase in the degree of membrane lipid peroxidation, appreciated by the production of malondialdehyde. We have also observed an enlargement of the mitochondria, the disintegration of the membranes, the disappearance of the ridges and a clear vacuolation. The intensity of toxicity actually varies from cell to cell.

The attenuation of toxicity could be due, for example, to the retention of metals on the cell wall [78] or their sequestration in the vacuole [79] or their storage in inactivated on specific proteins, amino amines or peptides.

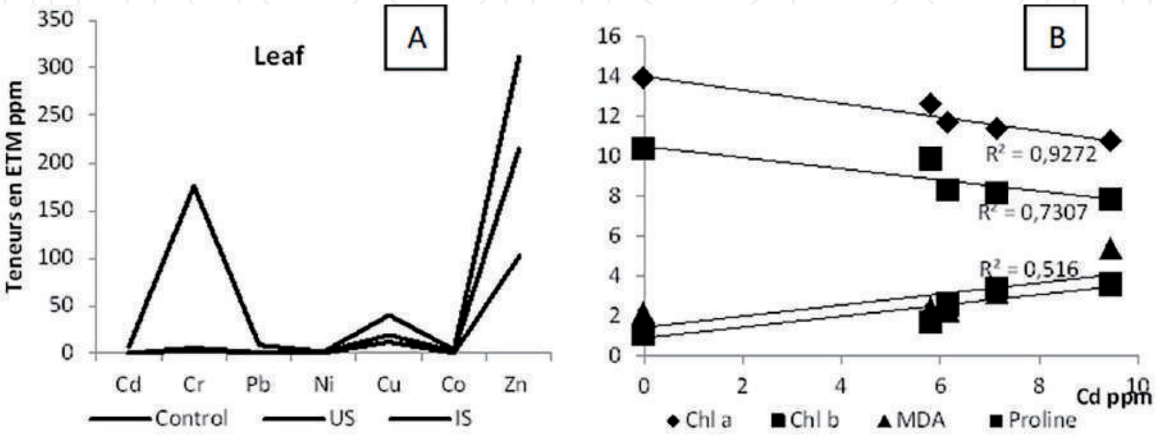


Figure 7.
(a) Variation of heavy metals in the leaf as a function of treatment. (b): Effect of cadmium on the biosynthesis of chlorophyll, proline, and MDA in the leaves of rapeseed.

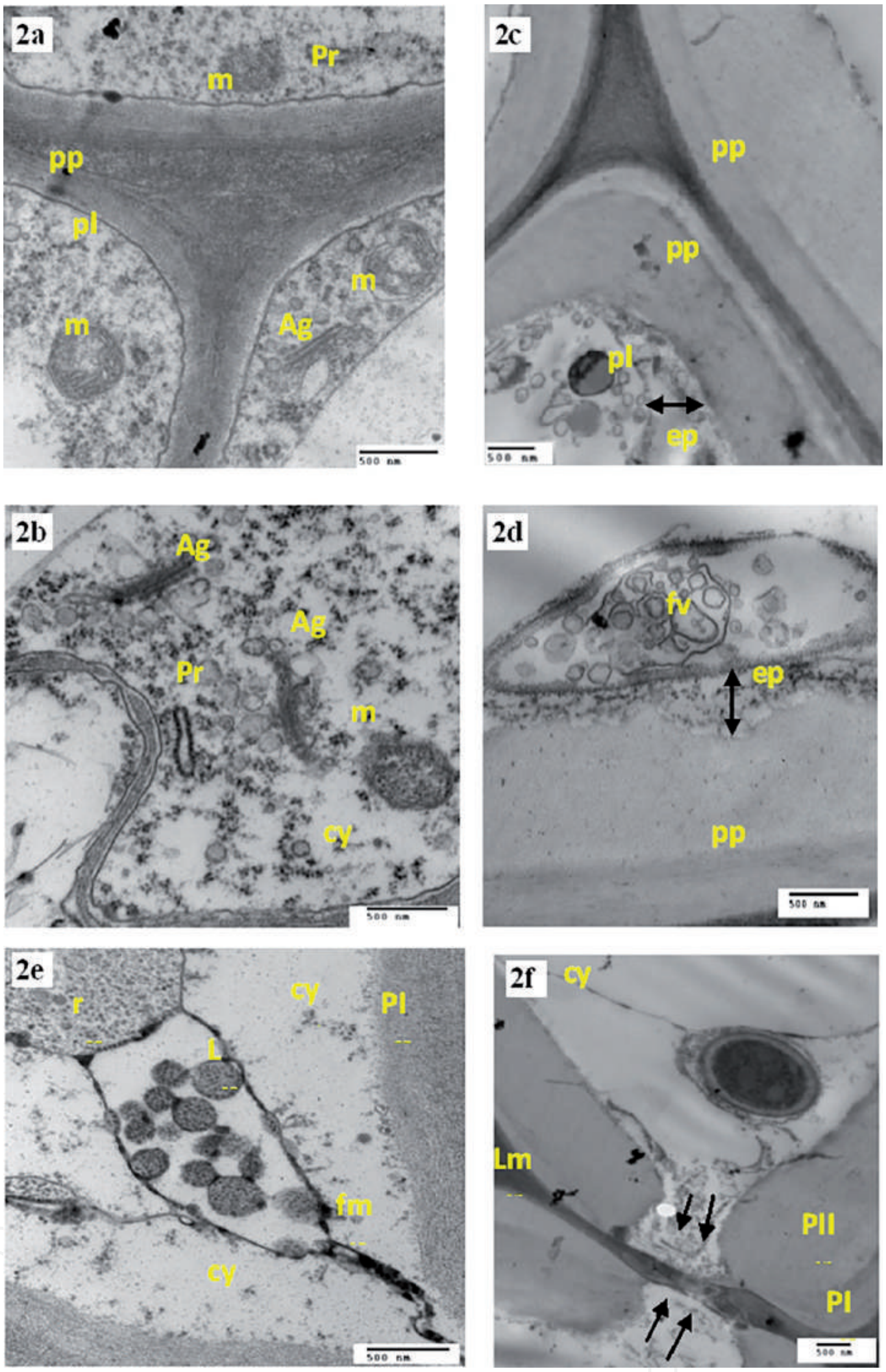


Figure 8.
Observation under a transmission electron microscope of cross sections of root cortical cells of a control plant (2a and 2b) and of a plant treated with 100 t ha^{-1} industrial sludge (2c to 2f). 2 a: Plasmalemma (pl) of a cortical cell of a control root 2 b: Cell organelles of a control root with homogeneous distribution of ribosomes (r). 2 c: Retraction of the cytoplasm with detachment of the plasmalemma and formation of a periplasmic space (ep). 2 d-e: Vesicular formations (vf) and membrane formations (fm). 2 f: Degradation of the primary (PI) and secondary (PII) wall. Pp.: Pectocellulosic wall, m: Mitochondria Ag: Golgie apparatus, cy: Cytoplasm, pr: Polyribosome.

The study of the risks of ETM (Trace Metal Elements) associated with the spreading of sludge requires not only knowledge of the total metal content, but also of the metal content in the various compartments that make up the soil. Nevertheless, assessing the total stock of an element is a good approach to study the degree and extent of soil contamination by a metallic element. Our results have shown that in

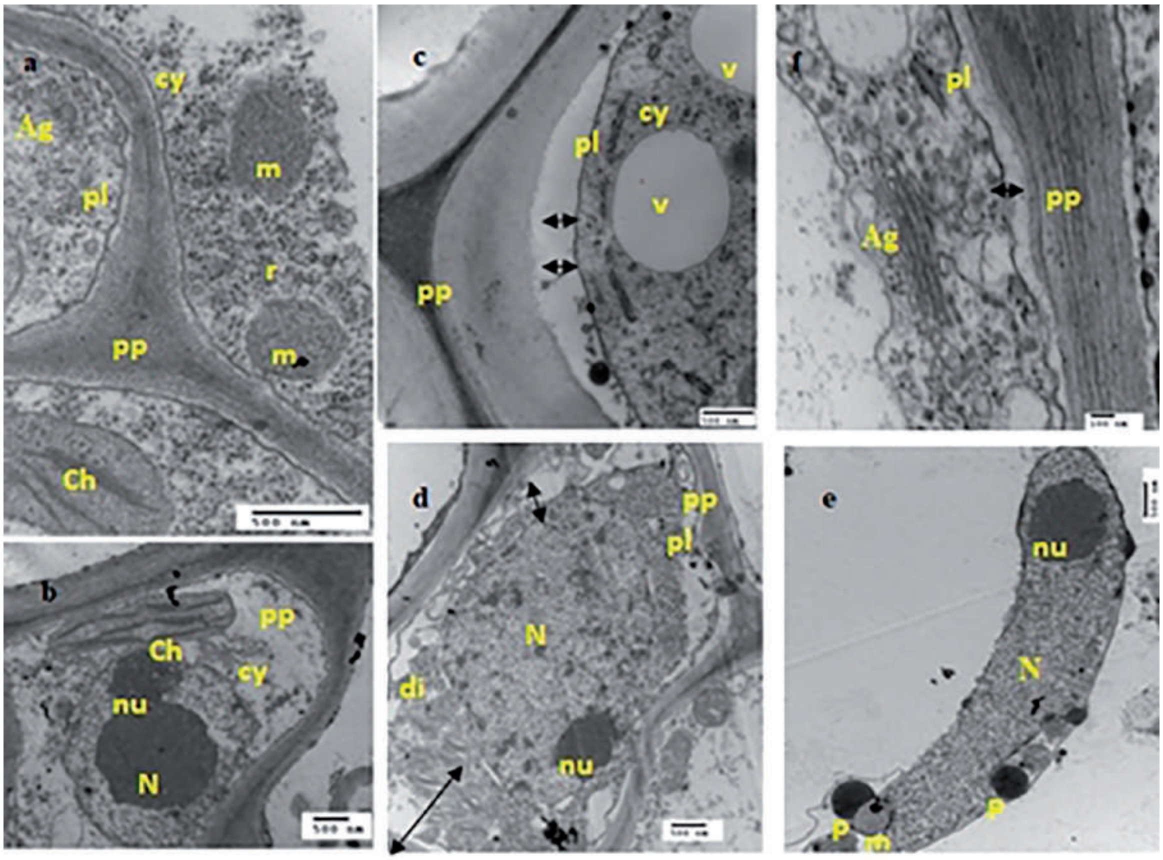


Figure 9.
Observation under a transmission electron microscope of the cortical zone of a rapeseed stem from the control treatment (a and b) (a: General appearance of the cell and b: Appearance of the nucleus (N) and after a contribution of 100 t ha^{-1} BI (c, d and e) (c: Detachment of the plasma membrane (pl) and formation of periplasmic space; d: Irregularly shaped nucleus divided into small nucleoli (nu); e: Vesicle surrounded by a single membrane and containing certain cellular organelles (nucleus, mitochondria and peroxisome (p) and in the presence of 100 t ha^{-1} BU (f) with pairing of Golgian saccules forming a dictyosome (Ag) and releasing Golgian vesicles giving rise to lysosomes. (di): Cytoplasmic digitation.

general, heavy metals are preferentially localized in the surface horizon and this for different media (**Figure 10**). However, on the control medium, the difference in accumulation between the 3 horizons is minimal and the contents are more or less comparable. The more the environment is polluted, the greater the difference in accumulation between the horizons. In fact, the level of accumulation of heavy metals depending on the pollution of the environment is much greater at the surface horizon than for the underlying horizons.

The second addition of sludge increases the ETM (Trace Metal Elements) content in the soil of the two crops. The surface layer (0-10 cm) appears the richest in cadmium, chromium and lead. After the second harvest, the cultivated wheat soil has higher ETM (Trace Metal Elements) contents than those of the rapeseed plots (**Figure 11**). This is due to the low extracting power of wheat compared to rapeseed. In a study on Brassica napus, [80] reported that in the presence of sewage sludge the extraction of heavy metals by this species increases significantly due to its hyperaccumulation power, but its use in phytoremediation is a very long process.

To assess the risk associated with heavy metals in the case of spreading waste products (sludge, compost, wastewater, etc.), one of the most widely used methods is to prevent the accumulation of trace elements in the soil [81, 82]. Only the soil and sludge contents, as well as the quantities of sludge added are taken into account.

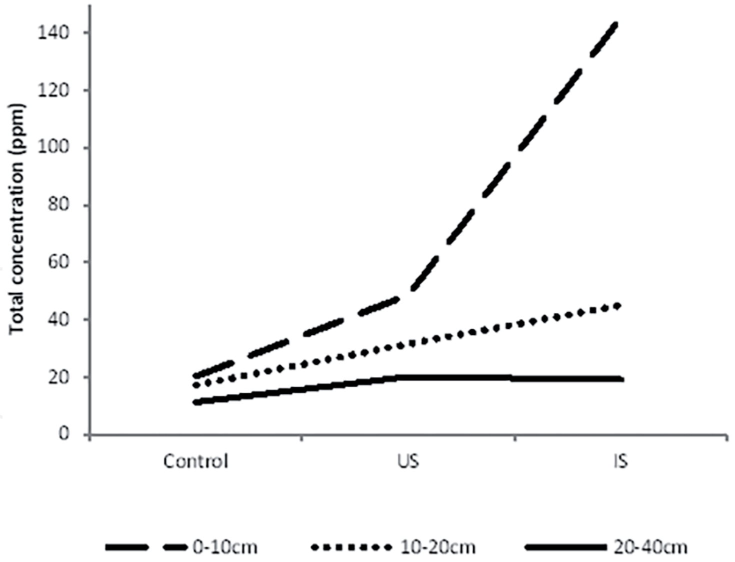


Figure 10.
Accumulation of heavy metals in the different horizons of the soil.4.

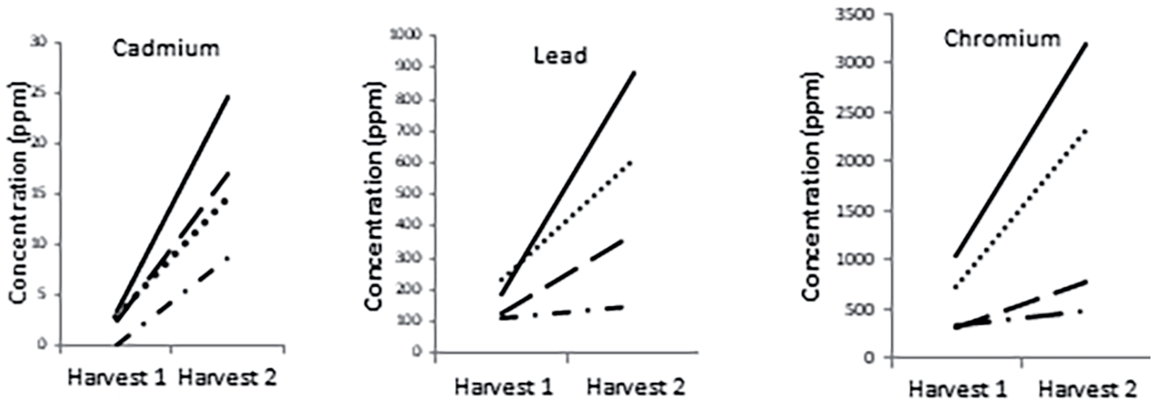


Figure 11.
Comparison of heavy metals in the different horizons of the soil (between 0 and 10 cm and 10 and 20 cm) after the first and second harvest.

Taking into account all our data, we tried to make a balance in order to assess the risk of saturation of the soil by heavy metals provided by the different types of sludge in the case of our experiment. The results obtained are shown in **Table 2**. It emerges from this table that for all the heavy metals, the soil reaches saturation much more quickly with the input of industrial sludge than for urban sludge and this is easily explained by the respective quality of sludge. For urban sludge, the probable duration of saturation varies between 361 and more than 160,000 years depending on the sequence: Cd >> > Ni > Pb > Cr > > Cu > Zn. This is in favor of the use of urban sludge given that the risk of soil contamination is low, in particular for toxic metals (Cadmium, Chromium and Lead) and that the elements which arrive first at the thresholds are copper and zinc which are trace elements essential to the plant. The problem arises differently with the spreading of industrial sludge highly loaded with heavy metals. Indeed, in this case the risk of contamination is present since the saturation time drops to very low levels for toxic heavy metals to reach less than 10 years for cadmium and chromium and 30 years for lead. The sequence found is: Ni > Cu > Zn > Pb > Cd > Cr.

	Cd	**Cu**	**Cr**	**Ni**	**Pb**	**Zn**
Heavy metals soil standard (ppm)	3	140	150	75	150	300
Wheat and rapeseed soil (ppm)	**0,66**	**28,03**	**27,84**	**6,35**	**19,06**	**56,84**
Average annual contribution per BU of 5 t ha $^{-1}$ year^{-1} (g ha^{-1} year^{-1})	**0.05**	**998**	**439,25**	**92,75**	**295,5**	**2425,25**
Increase due to sludge	**1.38 10–5**	**0,277**	**0,122**	**0,026**	**0,082**	**0,674**
Number of years before saturation for Urban sludge	**168,480**	**404**	**1001**	**2640**	**1597**	**361**
Average annual contribution per Industrial Sludge 5 t Ha^{-1}(g ha^{-1} year^{-1})	**909,5**	**766**	**63,380**	**312,5**	**15,075**	**3800,75**
Increase due to sludge	**0,253**	**0,213**	**17,606**	**0,087**	**4188**	**1056**
Number of years before saturation for Industrial Sludge	**10**	**526**	**7**	**789**	**31**	**230**

Table 2.
Assessment of the risk of soil saturation by heavy metals provided by the different types of sludge.

Once in the soil, some of these metals persist due to their immobile nature and the risk of crossing plants is low. Their in-depth migration is unlikely. On the other hand, the most mobile elements can transfer through the soil to the aquifer or be absorbed by the plant. Besides the intrinsic criteria of metals, their bioavailability and their transfer are more or less modified, in particular by edaphic factors such as pH, temperature and organic matter contents, hence the need to take into account all factors for success of a spreading project.

The decontamination of polluted soils can be considered but remains a rather long process requiring a lot of time [80] calculated that more than 1000 years would be needed to clean up a contaminated site. These results have been confirmed by [83]. Likewise, [84] studying the phytoextraction of *Brassica juncea* on a site multi-contaminated mainly by Zn, Cu and Pb showed that the time required for decontamination is between a minimum of 1150 years and a maximum of 360,000 years.

When metals migrate through plants and the food chain is involved, account must be taken of the amounts of the metals that can be transferred to consumers. As *B. napus* is an edible oil crop [85], we were concerned with the quality of the seeds and the oil extracted in terms of its fatty acid composition.

An increase in the levels of metallic trace elements was indeed mentioned at seed level during the second campaign. We also detected a decrease in the oil content with the addition of industrial sludge. The composition of total lipids in fatty acids shows an increase in the percentage of oleic acid (C18: 1) at the expense of linoleic (C18: 2) and linolenic (C18: 3) acids under the effect of heavy metals provided by industrial sludge while no difference is recorded with urban sludge regardless of the dose. No significant difference in heavy metal content was observed with the contribution of different doses of urban sludge, even after two years of spraying. On the other hand, we detected increases in most of the heavy metals, in particular for the high doses of industrial sludge.

The cadmium contents increase significantly with the contribution of 100 t ha^{-1}, it reaches 25 ppb following the cumulative contribution. For lead and chromium, the increase is especially visible at the 100 t ha^{-1} dose. These increases become more important during the second year. For nickel, the levels are higher compared to the control from the addition of 50 t ha^{-1} of industrial sludge for the two spreading operations. For wheat, the composition of the seeds in metallic trace elements is little or not affected by the contribution of sludge. The observed increases concerned only a few metals and for the excessive doses of industrial sludge. In order to assess the health risk linked to heavy metals via the consumption of products amended with sewage sludge, we tried to theoretically determine the daily exposure of consumers of these products to heavy metals (EJE) and to compare it with tolerable toxicological doses (TDI). The TDI is defined as the amount of contaminants that can be ingested daily without adverse health effects [86, 87]. The harmful potential of a product is the greater the lower the TDI value. In our calculations, we considered the seeds of wheat and rapeseed oil that are suitable for human consumption.

The daily exposure dose attributable to the consumption of these EJE products is calculated according to the formula [88]:

$$\text{EJE } (\mu\text{g kg}^{-1}\text{day}^{-1}) = [\text{Cproduct}] \text{ x Qty of product} \tag{1}$$

With: [C product]: Concentration of the metal in wheat grains or rapeseed oil; Product qty.: consumption of the product at the 95th percentile (g person^{-1} day^{-1}) which is equal to 382 g day^{-1} for adult person weighing 60 kg for wheat [88] and 25 g day $^{-1}$ for rapeseed oil [87]. For the trace and zero contents, we assimilated them to the detection limits of the dosing device.

The intake of sludge in its two forms has no effect on the theoretical exposure to Cd of high consumers of wheat, which is estimated at 3.8 μg person^{-1} day^{-1} for all the treatments (**Table 3**). These values are clearly lower than the TDI which is 60 μg person^{-1} day^{-1}. The problem arises differently for Pb where the dose of sludge (urban and industrial) influences by increasing the level of exposure of consumers but the values obtained are all below the TDI (216 μg person^{-1} day^{-1}). It should be noted that the higher the dose, the closer one gets to the TDI. For Ni, the intake of both types of sludge increases consumer exposure to this element but without a net dose effect. In addition, the values obtained remain below the TDI (720 μg person^{-1} day^{-1}). Exposure to Cr is increased with the addition of industrial sludge. Nevertheless, the comparison with the TDI could not be made because the available TDI is fixed for Cr III and Cr IV while our data relate to total Cr.

The hazard quotient (QD) is defined by the ratio between the calculated EJE and the corresponding TDI, according to the formula of [89] i.e. QD = EJE/DJT If the hazard quotient is greater than 1, the occurrence of Adverse effects related to toxicants are potentially possible. Otherwise, the risk can be considered as theoretically non-existent. All the ratios calculated for wheat seed are less than 1, however it is important to note that the high doses, especially of industrial sludge, increase the QD which rapidly approaches 1 for Ni and in particular Pb. It is probable that ‘it is the same for Cr. Thus, it is imperative to note that whatever the quality of the sludge, the spreading must be done at suitable doses and must be controlled. For rapeseed oil, the estimated daily exposure is extremely low since the values are infinitely low and are much lower than the respective TDI. It should be noted that for Cd and Pb, the 100 t ha^{-1} BI increase EJE. From a metals point of view, the addition of sludge, especially urban sludge and at low doses, does not generate a health risk, however, it should not be forgotten that the metals can be introduced by other products which must be taken into account in the process risk assessment hence the need to monitor these situations.

		Estimated exposure µg person^{-1} day^{-1}				EJE/DJT			
wheat seed		**Cd**	**Pb**	**Cr**	**Ni**	**Cd**	**Pb**	**Cr**	**Ni**
	Control	3,8	19,1	525,3	261,7	0,064	0,088	—	0,363
	5BU	3,8	19,1	540,5	355,3	0,064	0,088	—	0,493
	25BU	3,8	19,1	498,5	395,4	0,064	0,088	—	0,549
	50BU	3,8	143,3	548,2	336,2	0,064	0,663	—	0,467
	100BU	3,8	191,0	531,0	269,3	0,064	0,884	—	0,374
	5BI	3,8	19,1	624,6	382,0	0,064	0,088	—	0,531
	25BI	3,8	59,2	618,8	368,6	0,064	0,274	—	0,512
	50BI	3,8	210,1	601,7	389,6	0,064	0,973	—	0,541
	100BI	3,8	194,8	685,7	475,6	0,064	0,902	—	0,661
Rapeseed oil	Control	0,003	0,005	0,0002	0,014	4,3E-05	2,52E-05	—	1,98E-05
	5BU	0,003	0,005	0,0001	0,016	4,3E-05	2,44E-05	—	2,27E-05
	25BU	0,003	0,006	0,0002	0,016	4,3E-05	2,60E-05	—	2,20E-05
	50BU	0,003	0,005	0,0002	0,016	4,3E-05	2,44E-05	—	2,22E-05
	100BU	0,003	0,005	0,0002	0,017	4,3E-05	2,52E-05	—	2,31E-05
	5BI	0,003	0,005	0,0002	0,014	4,5E-05	2,44E-05	—	1,91E-05
	25BI	0,005	0,006	0,0002	0,014	7,9E-05	2,60E-05	—	1,89E-05
	50BI	0,016	0,006	0,0003	0,017	2,6E-04	2,83E-05	—	2,38E-05
	100BI	0,055	0,014	0,0008	0,016	9,2E-04	6,61E-05	—	2,22E-05

Table 3.
Estimated exposure and calculated mean Hazard quotient.

4. Conclusion

The spreading of sludge from wastewater treatment plants increased the production of durum wheat and rapeseed. Their richness in nitrogen, phosphorus and potassium gives them a beneficial effect on crops. However, the application of sludge can induce increases in the concentration of metals in plant tissues. This increase can generate disturbances at the level of the cell and organelles like mitochondria and chloroplasts which can be altered. Repeated applications of sludge at the same site tend to increase the accumulation of heavy metals in the soil which can cause toxicities to soil microorganisms, animals and humans, via the food chain. However, it is important to note that these harmful effects mainly concerned industrial sludge, but the use of this sludge is strictly prohibited. In addition, the high doses used in our field experiments are clearly higher than those authorized in agricultural practice. Finally, the risk assessment by calculating both the level of exposure for the consumer and the number of years for a soil to be saturated shows that the use of urban sludge is safe, particularly in the short and medium term. Nevertheless, the quality of the sludge to be spread must be constantly checked. Other metallic trace elements such as mercury, boron brought in by the sludge must be taken into account.

Acknowledgements

This work was supported by National Institute for Rural Engineering research, Water and Forestry, Tunis and Ecole Nationale Supérieure des Mines de Saint Etienne, France.

Conflict of interest

The authors of chapiter submitted for publication, we confirm that the results presented in this paper are real and original. The authors declare that they have no competing interests. The opinions expressed in this article are those of the authors and do not necessarily represent any agency determination or policy.

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