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Review Article

The Possible Mechanisms of Bacterial Biodegradation of Contaminants in Wastewater

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Abstract

Microorganisms caused a revolution in the treatment of wastewater and achieved promising results to rely on biological treatment ways in wastewater treatment processes. Besides their availability and eco-friendly, they have unique biodegradation characteristics of the complex compounds in wastewater treatment systems. Microorganisms including bacteria have good capabilities to degrade different pollutants in wastewater such as dyes; heavy metals; hydrocarbons; detergents; fertilizers and pesticides by successive enzymatic reactions ending with less toxic compounds. In this review, the possible mechanisms of bacterial biodegradation of pollutants in wastewater could be highlighted. Extensive articles have been published on the effective role of bacteria in the biodegradation pollutants, however there is a lack in the study of biodegradation mechanisms in the literature review.

Keywords: Biodegradation; Mechanisms; Bacteria; Wastewater; Pollutants

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Graphical Abstract

Introduction

The attention of the environment is considered as a major aspect in the sustainable development concept [1,2]. Therefore, the preservation on our environment became a mandatory action need to be addressed clearly. Owing to the development of the world and advanced industries, the demand on the water consumption elevated and consequently the amount of wastewater increased [3]. Therefore, treating wastewater for reuse is a mandatory solution for obtaining clean water could be suitable for reuse in different fields such as irrigation and industry [4,5]. For example, green eco-friendly materials and methodologies have to be involved strongly in the environmental applications [6]. Not only that, effective solutions for water treatment and removal of contaminants need to be developed. As reported that physical and chemical treatment methods have showed their effectiveness in elimination of pollutants from wastewater, however there are still some disadvantages such as formation of sludge and presence of unwanted chemical materials which could harm the surrounding environment and aquatic life [7]. On the other side, biological treatment using microorganisms has proved its outstanding advantage in wastewater treatment and biodegradation of pollutants [8,9]. They provide sustainability to the treatment process as well as they are cost-effective, that's why shedding the light on using microorganisms in the biodegradation of pollutants has to be considered nowadays. Whereas, bacteria are faster in growth and time-saving agents in the biodegradation process in comparison with algae and fungi [10,11]. There is a positive way for depending on biodegradable materials in the environmental applications to be easily biodegraded in the environment and do not cause a type of problem by their accumulation in the environment [12]. In recent years, approaches towards production of biodegradable polymers with controlled life span have been considered by researchers and scientists to overcome the problem of waste accumulation in the environment [13]. Biodegradation has been defined as a decomposition of materials by the action of microorganisms [11]. However, the mechanisms of biodegradation of pollutants by microorganisms are complex and not easily found in literature review. The aim of this review is to summarize possible mechanisms of bacterial biodegradation of pollutants in wastewater treatment. The novelty of this review could be highlighted in gathering the possible information in literature about bacterial biodegradation pathways and mechanisms.

Biodegradation of dyes

In terms of the nature and composition of toxicants that might cause serious biotic risk, industrial dye-contaminated wastewater has been deemed the most complex and harmful [14]. Bacterial species have been shown to be particularly successful in treating wastewater containing reactive dyes. Under optimal environmental conditions, dye biodegradation happens either by adsorption or breakdown in bacterial metabolic pathways [15]. In aerobic and anaerobic circumstances, many bacterial strains are utilized to breakdown dyes. In azo dye, bacteria such as *Pseudomonas luteola, Xanthophilus azovorans, Klebsiella pneumoniae*, and *Clostridium perfringens* are utilized*. E. coli* that has been genetically modified azo reductase activity is enhanced by this strain. *Aeromonas hydrophila* LZMG14 was reported to be capable of degrading 96.8% (200 mg/L) malachite green (MG) from dye industrial effluent under 12 hours. The efficiency of malachite green breakdown was increased by *Aeromonas hydrophila* LZMG14 bio-augmentation in a membrane bioreactor. Under microaerophilic circumstances, Pseudomonas aeruginosa and *Bacillus subtilis* may significantly reduce Allura Red (R-40) dye by 92.13 percent and 88.21 percent, respectively. At 30°C, a *Halomonas* sp. strain was isolated from coastal sediments contaminated by chemical effluent and found to degrade azo dye 90 percent in 24 hours using yeast extract as a carbon source. The results revealed that in increased saline concentrations, the bacterial strain decolorizes various azo dyes. Bacillus stratospheric SCA1007 was used to study the total breakdown of Methyl Orange (sulfonated azo dye). At pH 7 and 35°C temperature under static circumstances *Bacillus stratospheric* SCA1007 gave extensive breakdown of Methyl Orange (150 mg/L) across a wide range of dye concentrations [16]. Various microorganisms, such as fungi, bacteria, yeast, and algae, can decolorize and entirely remove color. Many azo dyes can be mineralized through it. These include the following: *Citrobacter* sp., *Enterobacter* sp., *Aspergillus niger*, *Aeromonas hydrophila*, *Candida krusei*, *Gloeocapsa, Pleurocapsoides*, *Alternaria solani* bacterial decolorization is usually faster than that of fungus, therefore more desirable However, there are a few reports accessible on decolorization caused by gram positive bacteria. The first report of dye decolorization was achieved by the gram-positive *Bacillus stratosphericus* SCA1007 within 12 hours of incubation under optimal culture conditions [17]. For treatment of wastewater contain textile dyes a phenomenon has been developed, begin with a photocatalytic disintegration process that relied on sunlight as a source of energy and progressing through bacterial biodegradation procedure. In a solar collector for the photocatalysis, Solo phenyl Blue azoic dye, and Erionyl Blue and Terasil Blue anthraquinone dye-colored solutions were treated with the Pd/Al 80 Ce 10 Zr 10 catalyst. While the waste dye, resulted from photo catalysis was inoculated for biodegradation. 90.91% for the Solophenyl Blue azoic dye, 87.80% and 87.94%, for the Erionyl Blue and Terasil Blue anthraquinone dyes respectively were degraded after both processes, An Eco toxicity test with Daphnia magna, proved that toxic metabolites were not produced [18]. In a study of the biodegradation of methylene blue (MB) dye by Bacillus Paramycoides bacterial species, it was found that the biodegradation occurred anaerobically by enzymatic reactions. The first step was the decolorization using reductase enzyme for cleavage of the double bond present in methylene blue dye. After the reduction reaction, colorless compounds produced and the blue color of the MB disappears [6]. The biodegradation of reactive brilliant blue KN-R-contaminated wastewater had been studied and found that the Rhodocyclus gelatinosus XL-1 showed over 93% degradation efficacy in anaerobic environment. It was determined that mineralization, hydrolysis, and co-metabolism took place, with peptone serving as the primary substrate. In the co-metabolic process, bacterium utilized dye as a co-substrate, therefore the addition of peptone to the treatment system increased the efficiency of degradation [15].

As the industry based on dyes have been expanding, the release of these dyes into the environment increases. Therefore, the removal of these dyes has become a critical issue that has toxic effect on the human and animal life. Several techniques have been reported in literature that can be used for degradation of dyes in wastewater. Some of these techniques are physical method such as physisorption, filtration, coagulation and flocculation. The other techniques are chemical techniques such as photodegradation, oxidation, electrochemical method and ozonation. All these techniques have some limitations including low dye removal performance, low effectiveness, low effectiveness and high cost. Furthermore, these techniques have significant drawback that prevent their application which is producing high concentration of sludge and cause another severe pollution [19]. Biological techniques have been reported as potential technique for decolorization of different dyes. They can overcome the drawbacks of other traditional techniques. They have some features including high effectiveness, low-cost method and eco-friendly to environment with low sludge production instead of other traditional techniques [20]. In this section, we will discuss biodegradation mechanisms of dyes using bacteria.

Among different types of dyes, azo dye is the main type of dyes and used in most industries. Azo dye consists of cyclic compounds with the ring containing at least two different elements. The azo dye has a characteristic bond which is azo bond (-N=N-) and promotes carcinogenesis. Consequently, the removal of azo dye is a critical issue to avoid its accumulation on the water causing carcinogenesis [21]. These dyes can accumulate in water causing harmful effects to humans and animals through food metabolism. Furthermore, their accumulation on the human body causing inhibit the enzyme that hydrolyze the urea [22].

In general, the biodegradation of azo dyes using bacteria can be performed in various conditions such as anaerobic respiration and aerobic respiration. The bacterial degradation of azo dyes is based on the azo bond cleavage forming aromatic amines. The azo bond is a chromophore of double bond that undergo azo reduction for decolorization. The bacterial degradation of azo dyes under anaerobic conditions based on the generation of energy during bacterial metabolism producing electrons that make azo dye reduction [23]. Reduction reaction of (-N=N-) bond can be performed using various anaerobic mechanisms.

The azo dyes can be degraded by bacteria based on one of the following anaerobic mechanisms: (1) In the first mechanism, the azo bond undergoes reduction in the cytoplasm and membrane in which there is very low concentration of azo reductase. The bacteria produce membrane vesicles that can reduce azo bond in absence of any redox mediators [22]. By inhibition all of these membrane vesicles, there's no decolorization of any dye. This ensures that the membrane and cytoplasm consist of all effective components that facilitate the electron transfer to the azo bond leading to reduction. By alternative inhibition of cell and membrane components, it has been reported that the electron transfer components such as dehydrogenases, cytochromes, and menaquinone [24]. Another literature showed that hydrogen, lactate or formate can act as electron donor using *Sphingomonas* sp. Strain [25]. The flavin reductase (NADH) is a natural component of ribonucleotide reductase that can directly catalyze the reduction of azo dyes and electron transfer. This mechanism is based on cytoplasmic enzymes that have effective role as azo reductase. So, this mechanism is called direct enzymatic anaerobic bacterial degradation [26]. Although, the decolorization of azo bonds under anaerobic bacterial respiration is effective for most dyes. It is non-specific for any types of azo dyes. The researchers have reported that the anaerobic degradation based on the flavin reductase is non-specific. Consequently, the flavin reductase is responsible for its non-specificity of azo reductase [27].

The direct enzymatic bacterial degradation is not effective for decolorization of high polar dyes, large molecular weight or polymeric dyes that cannot enter the cell membrane. Therefore, the azo reduction must be catalyzed using a molecule that act as linkage between intracellular electrons chain and outer membrane azo dyes. The redox mediators are the main electron transporters that enhance the azo reduction of many azo dyes [26].

Biodegradation of heavy metals

Heavy metal contamination is probably the major issue of industrializations. Heavy is an overall aggregate term which applies to metalloids or metallic components that have somewhat high atomic weight and are toxic even at low concentration. Heavy metals are toxins of extraordinary worry as they are widely spread and are non-degradable [28]. Heavy metals can be removed from waste water by using different microorganisms such as algae, fungi, bacteria and plants through a phenomenon known as biosorption. The mechanisms of bio sorption include physical adsorption, ion exchange, complexation, precipitation and transport across the cells while the biosorption capacity of different bio-sorbents depend upon several factors like water pH, temperature, contact time, biomass dosage and initial heavy metal concentration [29]. Most of the bacterial species have great bio sorption ability due to their high surface-to volume ratios as well as active chemisorption sites (teichoic acid) on the cell wall [12]. Various bacterial species have been tested such as *Enterobacter, Bacillus*, and *Flavobacterium*, *Pseudomonas Micrococcus* sp. consortia of cultures are considered metabolically better for the biosorption of metals because mixed culture of bacteria are more stable and appropriate. It was reported that bacterial consortium of *Acinetobacter* sp. has reduced 78% of chromium (Cr) and in order to remove a large quantity of Pb from a synthetic medium Micrococcus luteus was used. Tannery effluent mostly contain Pb, Cr and Cd they are mostly removed by bio sorption through *Bacillus-subtilis*, *B. megaterium*, *Aspergillus-niger* and *Penicillium* sp. while *B. megaterium* recorded the highest Pb reduction [30]. There is electrostatic force of attraction between positively charged cations of metal ions and negatively charged functional groups in capsules or polymers on the cell wall of bacteria. That's why the structure of cell wall plays an important role in the adsorption process of metal ions [31]. Gram-positive bacteria have thick peptidoglycan cell walls therefore they are considered more suitable for biosorption process as compared to Gram negative bacteria. The walls of B. subtilis is composed of peptidoglycan in which carboxylic groups of glutamic acid serves as vital site for metal adsorption. In some other bacteria like B. licheniformis, major binding site are teichoic acid and teichuronic acids. Carbonyl, hydroxyl, amine, sulfonate, carboxyl, amine, thioether, imidazole, phosphodiester, phosphonate and amide are some other important groups in the wall of many bacteria which were used for binding purpose. The dead biomass of B. subtilis is considered to be highly efficient for removal of Cr (III) from aqueous solution. It is previously reported that dead B. subtilis biomass, cheap and reusable bio sorbent used for the removal of trivalent chromium. The major advantage of utilizing dead biomass for wastewater treatment is that the dead organism is not affected by toxic wastes, secondly, they don't require continuous supply of food. Besides that, the dead cells can be stored or used for long period of time at room temperature [32]. It was previously reported that when waste water was treated with *Pseudomonas* sp. and *Bacillus* sp., there were an average reduction of 56% and 44% of Cd from the effluent samples respectively. *Pseudomonas* sp. was able to remove. As with an average reduction of 34%. It also removes Co with an average reduction recorded was 53% While Hg was removed by *Bacillus* sp. with an average reduction of 45%. Both *Bacillus* sp. and *Staphylococcus* sp. removes Cu with an average reduction recorded of 62% and 34% respectively. From this study it could be concluded that bacteria play a very crucial role in the removal of heavy metals from wastewater [32].

Chemoautotrophic bacteria have been attracted the attention of the most of researcher in removal of heavy metals due to its additional activity in generating energy based inorganic compounds or organic compounds such that energy can be generated through transformation of electrons from one compound which is called electron donor to another compound which is called electron acceptor. The bacteria that produce energy based on transformation of electron from organic Substances, are called Chemoorganotrophic Bacteria. In contrast, the bacteria that generate energy by transferring electrons from inorganic substances such as heavy metals, hydrogen sulfide, hydrogen and ammonia, are called Chemolithoautotrophic Bacteria. One of the most common Chemolithoautotrophic Bacteria is Knallgas bacteria. Knallgas bacteria have the potential to generate biofuels and removal of heavy metals from CO_2 metabolism and the oxidation of hydrogen producing water [19,33].

Recently, the researchers have investigated the removal of heavy metal by electrochemical method that consists of two electrodes; the first electrode is the anode that make oxidation reaction and act as electron donor, the second electrode is the cathode that receive the electron and make reduction for the heavy metals that are recovered and accumulated at the cathode leading to removal of heavy metal wastes from water. The electrochemical method is a robust technique for removal of organic and inorganic pollutants. This technique can efficiently remove heavy metal such as Zn, Pb, Cr and Mn using different electrodes such as aluminum and stainless-steel that can be hybridized with other material such as activated carbon [20,34].

The electrochemical removal of heavy metals is based on electrons in reduction of heavy metals which provide fast removal of heavy metals and no secondary toxic products. It is required to supply the reaction with current applied between the two electrodes. The carbon material for electrodes provides cost-effective water treatment under normal conditions [35,36].

In the process of electrochemical reaction, the hydrogen gas is generated at the cathode as result of reduction reaction and the oxygen gas is produced at the anode resultant from oxidation reaction. The hydrogen and oxygen gases can generate clean energy [25,37]. For instance, the electrochemical method was used for removal of copper and nickel as heavy metals from water using cathode of carbon material and titanium as anode deposited by platinum as catalyst. As the current passed through the electrodes that were immersed in wastewater, the removal occurred as the following:

At the anode, the water was oxidized.

$2H_2O$ (aq) O_2 (gas) + $4H^+$ (aq) + $4e^-$

At the cathode, the metal ions were reduced.

Cu^{2+} (aq) + $2e^-$ Cu (s)

Ni^{2+} (aq) + $2e^-$ Ni (s)

The hydrogen gas was produced by oxidation of water

$3H_2O + 3e^-$ $2H_2$ (g) + $3OH^-$

The heavy metals were accumulated in cathode and can be removed [38]. Click or tap here to enter text.

During the processing and engineering of heavy metals, large amount of hydrogen gas is produced in addition to precipitation of heavy metals in water. The electrochemical method can use hydrogen gas as effective electron donor such that hydrogen gas is oxidized at the anode. Furthermore, oxidation of hydrogen gas also produced a flow of current [39]. Click or tap here to enter text.

The H_2 is not directly oxidized and must be provided by noble metal as catalyst. According to the direction of this research, the hydrogen gas can undergo direct oxidation using chemoautotrophic bacteria on a carbon material as bioanode which is called Bio-electrochemical method [40].

Chemoautotrophic bacteria use hydrogen gas as electron donor and oxygen acceptor as electron acceptor associated with fixation of CO_2 through the Calvin Benson Bassham (CBB) cycle. The CBB cycle is a biological mechanism required for bacteria growth based on CO_2 fixation as main source for formation of cellular compounds [41]. Click or tap here to enter text.

The CBB cycle require energy including ATP and NADH for CO_2 fixation. The Chemoautotrophic bacteria supply CBB cycle with energy by oxidation of H_2 forming $2e^-$ and $2H^+$. There are different hydrogenases that act as catalyst for hydrogen oxidation including regulatory hydrogenase (RH), soluble hydrogenase (SH) and membrane-bound hydrogenase (MBH). The regulatory hydrogenase (RH) regulates the sensing of H_2. In general, the Soluble Hydrogenase (SH) and membrane-bound hydrogenase (MBH) are the hydrogenases that oxidize the H_2. The Soluble Hydrogenase (SH) oxidize H_2 to obtain NADH. While, the membrane-bound hydrogenase (MBH) oxidize the H_2 to generate $2e^-$. The NiFe hydrogenase is the signal hydrogenase that regulates the function of membrane-bound hydrogenase (MBH) and regulatory hydrogenase (SH). These hydrogenases act as catalysts for H_2 oxidation producing electrons that delivered to membrane or cytoplasmic carrier of electrons that reduce the metal ions and are recovered on the cathode [41-43]. Click or tap here to enter text.

The use of bacteria for electrochemical removal of heavy metals has some features including recovery of heavy metals with low energy supply in addition to the oxidation of H_2 by bacteria instead of noble metals produce electrons that are delivered to the anode generating electricity and reducing the metal at the anode. In contrast, the bio-electrochemical method has some limitations that may restrict its industrial scale such as selective metal removal and toxicity of some metals to bacteria [44-47]. Click or tap here to enter text..

Biodegradation of hydrocarbons

Petroleum is a billion-dollar industry that did not only make our life a lot easier but brought a unique set of challenges. These challenges cannot be overlooked or undermined for that fact that it has brought so much ease in our life. Petroleum and its derivative hydrocarbons such as high-octane and aromatic hydrocarbons play a vital role in our day-to-day life and they play a vital role in human production and life [48]. Their day-by-day increasing demands both in the life sector and industrial sector is raising concern for their disposal. Since more production lines are coming together to meet the needs more processing waste is being released into the environment through mining, transportation, handling, and usage. Moreover, within the wastewater streams there found tough to degrade halogenated compounds such as polychlorinated biphenyls (PCBs), chlorophenols, chlorotoluenes, chloropropanes, phosphorylated organics, and polynuclear aromatic hydrocarbons (PAHs). The biodegradation process of all these compounds is halted not only due to the toxicity of these compounds but also from the radioactive components which are present in wastewaters. Out of all the derivatives of hydrocarbons, diesel comes out as the major contaminants of soil and water. Diesel pollution not only causes physical and chemical damage to the soil it also imposes a serious threat to the groundwater. Different methods like physical cleaning, chemical treatment, and phytoremediation have been used to deter the physical and economical loss that diesel imposes on the environment [49]. Despite doing physical cleaning, chemical treatment, and all other types of remediation it is still not enough to get this hydrocarbons waste under control. For this, we need to look for a permanent degradation source that could degrade this hydrocarbon waste from the environment and does not get consumed by it and could last ever last [50]. Among these solutions, one major solution is the biodegradation of the hydrocarbons by bacteria which could remediate the environment by breaking down these pollutant petroleum wastes into CO_2 and H_2O without producing any form of secondary pollutants. Biodegradation of hydrocarbons happens by the petroleum-degrading bacteria who take up the molecules of petroleum and break them down into smaller unharmful molecules. No matter how efficient a petroleum degrading bacterium is, the most critical step in the degradation of petroleum is the formation of contact between the microorganism and the substrate. While preparing to make contact and degrade the petroleum molecules petroleum- degrading bacteria can take three different approaches [49]. The molecules of petroleum hydrocarbons are dissolved in the aqueous media by the bacterial cells [51]. Microbial cells can be exposed to the molecules of hydrocarbons for direct uptake [52]. Furthermore, microbial cells interact with pseudo-soluble, quasi-soluble, or encapsulated particles of petroleum for taking up. Among all these strategies, the deciding factor in the breakdown is the hydrophobicity of the bacteria this affects the adhesion of bacterial cells to the petroleum cells which in turn impacts the breakdown. Therefore, a more hydrophobic bacterium would attach more firmly to the petroleum particles and do the efficient breakdown. It is now understood that the addition of surfactants improves the hydrophobicity of bacteria [53]. At the moment, the species of P. aeruginosa is a well-known bio-surfactant producing microbes which increase the hydrophobicity of the bacteria thus helping to attach more firmly to the petroleum molecules for the breakdown. Two bacteria P1 are being an efficient petroleum-degrading bacterium and B2 being bio-surfactant-producing bacteria. These two bacteria were isolated from Huangdao District (Qingdao, Shandong, China) to analyze their petroleum breakdown capabilities. Herein, surface adsorption is the key factor in petroleum degradation [54]. Therefore, in Figure 1 the diesel adsorption performance of the groups P1 and B2 were studied at different times to see what difference that occurred on the bio-surfactant of the breakdown and adsorption of petroleum molecules to the microbial cells.

Figure 1: Surface adsorption of diesel at different times [55].

The two species P1 and B2 bacteria are present in the contaminated water along with the hydrocarbons. When hydrocarbons (here diesel) and the bacteria first make a contact with each other, the diesel is quickly absorbed by the microbial cells which are followed by the sorption-desorption process. This process happens due to the presence of some functional groups like −OH, CO, and N−H these groups help in the adsorption between the petroleum molecules and the microbial cells causing distribution effects. Furthermore, P1 and B2 have a high hydrophobicity which allows them to adsorb more molecules to them and utilize more hydrocarbons for breakdown. Moreover, the B2 bacteria have an emulsifying effect on the hydrocarbon molecules which allows B2 to emulsify the hydrocarbon molecules into tiny particles so that they are more easily accessible to P1 for the breakdown and are readily available in the aqueous media and picked up by P1 bacteria and degraded. P1 has two possible ways to take up the hydrocarbon molecules, first is the bacteria is exposed to large molecules of hydrocarbon for the breakdown and the second way is that P1 takes on the quasi-molecules of the hydrocarbons for the breakdown. In this case, the second approach was utilized for the uptake of hydrocarbons. Finally, the diesel is degraded into simple, unharmful molecules, CO_2 and H_2O [49].

Biodegradation of detergents

In today's modern world the importance of detergents cannot be neglected whether they come in any form of soap or in a powder form. Now-a-days detergents are being used in great quantity in industries as well as household premises [52]. The main cleaning agent in any soap based or a powder-based detergent is a lathering agent which is known as Alkyl Benzene Sulfonates or ABS. With the new technological advancements like the kettle process in the field of making soaps and detergents many of the dangerous chemicals are getting involved in the making of those detergents. Such an addition of these chemical in the making of detergents might seem to work for one direction but they are harming the environment in the other direction. These strong chemicals might work perfectly for the cleaning purpose but they are posing a great threat to our environment when released to the close vicinity of wastewaters. Generally, a considerable amount of degradation happens on their way to streams and rivers but only the easily degradable chemicals are used out by the microorganisms while hard to breakdown chemical gets accumulated and cause a serious problem to the environment. Some of the concerning problems are deprivation of oxygen in the waterways, lack of ability for aquatic life to breed, lowering of the surface tension of the water, thinning of the external mucous layer of fishes which protects them from bacteria, and a considerable damage to the gills of aquatic life. The main chemicals contributing to the toxicity of the detergents are sodium silicate solution and the surfactants which comprising 10-30% of the detergents [49,52]. By looking at the adverse effects of detergents and the chemicals they contain on the environment and the aquatic life it is mandatory to device a method or a mechanism to breakdown these harmful chemicals. A part of this job is done by the bacterial lines which are typically found in wet soil and in the wastewaters or smudges. These bacteria's work to breakdown the harmful chemicals found in the detergents in wastewaters before they could reach to riverbanks or waterways to disturb the aquatic life. The general concept of what makes a detergent stay in the water and pose a threat to the environment is it's amphiphilicity. When a detergent (surfactant) loses its amphiphilicity it breaks down and cannot cause a threat to the environment anymore. The broader concept of degradation of these surfactants is beneficial both ways because it breakdowns the harmful chemical before they could harm the environment and still allowing them to be used. When surfactants come in contact with the microorganism in the wastewaters the microorganism particularly bacteria's see those surfactants as a viable source of energy and an endless supply of carbon for their growth. A bacterium can choose two different paths to breakdown surfactant when it comes in contact (Figure 2), the first mechanism is that the bacteria might work first to detach the hydrophobic end to the hydrophilic end and them attack them oxidatively. The second mechanism is that the bacteria might start to oxidize the alkyl chain from the end whilst still attached to the hydrophile. Whichever strategy is employed by the bacteria would result in the immediate loss of amphiphilicity of the molecule which therefore can no longer behaves as a surfactant. Which mechanism is employed to breakdown the surfactant depends upon the type of the surfactant faced for some surfactants only one route is effective while for some surfactants both ways can work however, for complex surfactants which require a strong metabolic activity to be breakdown, different organism with complementary metabolic capabilities might need to work together to completely breakdown that molecule instead of a single route.

Figure 2: Bacterial attack strategies on surfactants.

Furthermore, two types of strategies can be employed to separate the hydrophilic head from the hydrophobic tale and which strategy is used depends solely upon the overall chemical stability between the two ends. Some surfactants like alkyl sulphates and sulphosuccinates typically share an ester bond between two ends so such kind of surfactants can be easily cleaved through the ester linkage via simple hydrolysis from bacteria. Hydrolysis would give long-chain alcohols and anionic products from the hydrophilic groups. Such reactions are energetically favorable and do not require a co-factor. On the other hand, surfactants like alkane sulfonate share a C-S link between the hydrophilic head and the hydrophobic tail this link cannot be breakdown by a simple hydrolysis instead bacteria would now utilize a complex mechanism using a catalytic monooxygenase enzyme which requires oxygen and a reduced co-factor. Similar mechanism is applied for the surfactants which have ether-linkage between hydrophilic head and the hydrophobic tail. Whether hydrophilic/hydrophobic separation occurred by a simple hydrolysis or by complex monooxygenase enzyme the products that will come out from the hydrophobic end will be the same including fatty acids, alcohols or aldehydes. Since these products are the normal bacterial metabolites and they can be catalyzed by quite easily by the bacteria using β-oxidation pathway to give acetyl-CoA which bacteria can use either for the energy production or biosynthesis of cellular components. The second general strategy that bacteria uses to attack surfactant is the β-oxidation of alkyl chain while it is still attached to the hydrophilic head. But before the β-oxidation of alkyl chain could begin the distal end of the surfactant alkyl chain needs to oxidized by the ω-oxidation to give a carboxyl group at the distal end of the alkyl chain. After the carboxyl group has formed this group can be activated by the co-enzyme A which is the primary requirement for the β-oxidation to be initiated. The ω-oxidation of alkyl chain is achieved through energy dependent monooxygenation reaction which utilizes NADH and oxygen during the process, and this is the same process which is utilized by the bacteria to breakdown alkanes and other hydrocarbons which lack the hydrophilic head. Once the β-oxidation of alkyl chain has started then it can go either towards the completion of β-oxidation of alkyl chain or at least reaching the hydrophilic head. During the β-oxidation of alkyl chain it can cope with a limited amount of branching which may come in the way like the methyl groups at Alpha-positions but not with the dimethyl substituted carbon atoms which occur in quaternary carbons in the alkyl chain. This is because the of β-oxidation of alkyl chain requires energy and β-oxidation mode of attack by bacteria is only seen when the linkage between the hydrophilic end and the hydrophobic end of a surfactant is difficult to break [56].

Biodegradation of fertilizers

It has been in the general understanding that most of the fertilizer producing industries is setup near river banks or oceans. It has been observed that a single fertilizer industry near a river bank could throw off as much as 5.2 tons of nitrogen waste to the wastewater system annually; these numbers are alarming and must require a well-planned strategy to remove these deadly nitrogen-based chemicals from wastewaters before they could reach water bodies to disturb the marine life. Natural water bodies around those heavy industries are the first-hand recipients of this toxic water [57]. When the nitrogen concentration in water bodies rises to 1.9 mg/L then the water is said to be eutrophic this is inhabitable for marine life or for the drinking purposes. Not only that higher concentrations of nitrogen entities in the water bodies give bloom to the algal bodies they thrive on the nitrogen entities for their growth and food and would multiply in great numbers. These algal bodies when grow in great numbers would cover the water surface thus blocking the sunlight and exerting oxygen from the aquatic life [58]. This in turn would decrease the life expectancy of aquatic life from lack of oxygen. When it comes to treating this wastewater before they could reach river banks and pollute the aquatic environment the only method that comes in to the mind is wastewater treatment plants (WWTPs). The WWTPs require a mechanical aeration to provide with enough oxygen to the ammonia oxidizing bacteria (AOB) and nitrogen oxidizing bacteria (NOB) sitting in the wastewaters. It has been estimated that it takes 4.57 grams of oxygen to oxidize per gram of ammonia to nitrite, not only that a large amount of oxygen is produced through mechanical aeration but it also requires a total to 45-70% of the energy which is not feasible for any WWTPs. The mechanical aeration also has the risk of vaporizing the volatile compounds which are useful. Through mechanical aeration the waste activated sludge (WAS) also comes out as a by-product the amount of WAS produced is directly related to the amount of the wastewater that has been treated. It produces 70-1000 kg of WAS by treating 1 million liters of wastewater this surely is not working in the favor of the environment with the increased amount of wastewater that has been treated with the mechanical aeration more of WAS is being produced, to treat this this WAS requires a significant amount of energy, resources and a vast area of land. Therefore, it is a need to find a nexus between the nitrifying, denitrifying bacteria and algae, because algae are the primary oxygen releasing microorganisms with a simpler cell structure and have no roots, stems or leaves. Microalgae can reproduce and grow faster and they are able to double the colony within 24 hrs. they have the ability to grow exponentially within 3.5 hrs. they are corporative with the environment and can live in any harsh or soft environment as long as the source of nutrition is there. Some of the microalgae can even grow on rocks, in soils or with symbiotic relationship with plants. In an aquatic environment these algae act as a micro oxygen producing devices which provide oxygen to other bacteria here nitrifying and denitrifying bacteria and works as a carbon dioxide sink to fix the issue of excess carbon dioxide. Other than the oxygen and carbon dioxide nexus between the bacteria and algae they have plenty of other parameters on which they relate and which makes bacteria-algae nexus system to be used in the wastewater treatment plants (WWTPs) more effectively. In WWTPs, the activated sludge which contain most of the nitrogen-based entities are present along with them there present a whole colony of microalgae which feeds on the nitrogen-based entities for their growth and reproduction and also these present bacteria which take part in the disintegration of nitrogen-based entities mainly fertilizers. The removing of nitrogen from wastewaters requires two types of bacteria nitrifying bacteria which are the autotrophic bacteria, which do not need an organic carbon source to thrive but they require a continuous large amount of oxygen to work this oxygen is provided by the algae. In the nitrification process the electrons are provided by the inorganic nitrogen sources. The process of nitrification happens in two steps, (Eq. 1) in the first step, the ammonia in the wastewater is oxidized to nitrite by the ammonia-oxidizing bacteria (AOB), later the nitrite is oxidized in to nitrate by nitrite-oxidizing bacteria (NOB), and these two steps generate energy which is used by both of these bacteria for assimilation. At this point the nitrification of ammonia has happened now the denitrification of nitrate happens by the denitrification bacteria (DNB) in this step the DNB reduces the nitrate or nitrite to accept electrons which in turn provides energy for the assimilation of organic matter, later to be converted in to un harmful nitrogen gas [59].

Biodegradation of pesticides

Bacterial biological degradation is categorized as aerobic and anaerobic treatments. For aerobic treatment there are basically two steps to degrade pesticides, firstly the ether bond is oxidized and cleaved. Secondly the chloro-catechol is formed by hydroxylation of the chlorophenol, once it had been done then the compound can be easily degraded by bacteria into water and carbon dioxide. The dechlorinated pesticides are mostly digested by aerobic bacteria, while can also be treated in anaerobically circumstances through reductive dehalogenation. In this case the final products are methane and carbon dioxide. Sometimes pretreatments are essential, such as breakdown of complex compounds by photochemical degradation or enzymatic reactions might facilitate their biological digestion [60]. Iprodione mineralized from the genus Micro bacterium, and strain CQH-1 could be a promising candidate for application in the bioremediation of contaminated environments. The bacterial strain CQH-1 capable to mineralize iprodione. Iprodione is a dicarboxamide fungicide which is mostly employed in a greenhouse and field crops to control fungal infections. The degradation of iprodione and 3,5-DCA, with growth of strain CQH-1 were studied simultaneously in MSM. Iprodione and 3,5-DCA were 100 $mg \cdot L^{-1}$ and 30 $mg \cdot L^{-1}$ respectively. In first 16 h Iprodione reached to 41.2 $mg \cdot L^{-1}$ and then completely degraded within 96 h of cultivation. While in the non-inoculated samples within 128 h at pH 7.0 and 30 °C only 39% of iprodione degraded. Strain CQH-1 could also use 3,5-DCA to grow and completely degrade 30 $mg \cdot L^{-1}$ 3,5-DCA within 120 h at pH 7.0 and 30 ° which revealed that both iprodione and 3,5-DCA were used as the sole source of energy and carbon for the growth of bacterial strain CQH-1 [61]. Another, one of the most widely used pesticides for agriculture crop production is Cypermethrin. Pseudomonas, was analyzed to find its biodegradation potential for cypermethrin in aqueous environment. The experimental results showed that under suitable environmental conditions provided in the reactor, Pseudomonas was able to degrade cypermethrin. Complete removal of cypermethrin (20 mg/L) has occurred within 48 hours [62]. Pentachloronitrobenzene (PCNB) is an organo-chlorine pesticide. PCNB is widely spread in the atmosphere and released into soil, water and air. It is highly toxic and carcinogenic substance. As compared to degradation of mono-chlorinated nitro aromatic compounds, bacterial degradation of PCNB is considered a complex process. Certain bacteria have been reported which can mineralize PCNB but no metabolic pathway of bacterial degradation using pure culture of bacteria have been identified so far [63]. Many microorganisms have been identified around the world for their pesticides degradation ability. The pesticides degrading microorganisms provide the possibility to count with new tools to treat wastes and to clean polluted environment. The actual mechanism by which microorganisms degrades the pesticides is complete oxidation of parent compound as a result carbon dioxide and water are formed and provides the energy for their metabolism. While enzymes play crucial role in the degradation of parent compounds. Such as, carbamates are responsible for the greatest number of poisonings in the rural areas. Many bacterial species have been characterized as carbamate degraders. Its degradation occurs mainly through the hydrolysis of the methyl-carbamate linkage by an enzyme called carbofuran hydrolase, which was first described in *Achromobacter* sp. [64].

Conclusion and Future Perspectives

In conclusion, bacteria as a microorganism can biodegrade a variety of pollutants in wastewater systems and this could be considered a source of nutrition and/or a defense mechanism to maintain their viability and reproduction. The mechanisms of bacterial biodegradation may vary according to the type of pollutant and also the species of the bacteria; each organism has its own life technique. Researchers need to focus on the applications of bacteria in wastewater treatment systems while studying the mechanism of action of each bacterial species on a specific pollutant. The mystery behind many bacteria needs to be explored and their adaptation mechanisms against the toxicity of the massive pollutants need to be deeply studied.

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Conflict of Interest

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