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Bioleaching for Nanoparticle Production as a Solution for Environmental Pollution

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Abstract

Environmental pollution of heavy metals and plastics has been a great challenge of the last century. E-wastes increase heavy metals and plastics concentration in the environment. These toxic substances are a threat to organisms. So their removal from the environment seems necessary. There are different disposal methods like landfilling and incineration, which cause a great deal of damage to the environment. On the other hand, the need for precious metals recovery like gold and silver from e-waste makes recycling necessary. Nevertheless, these methods are generally expensive. So applying a new alternative is required. The purpose of this paper is to introduce bioleaching as an alternative to conventional disposal and recycling methods. This method is used to remove the heavy and toxic metals in order to produce metallic nanoparticles. Then the application of nanoparticles in wastewater treatment and microplastics degradation is mentioned. The conversion of insoluble metals to soluble ones by microorganisms is called bioleaching. Bacteria like *Chromobacterium violaceum*, *Pseudomonas* species, *Sulfobacillus thermosulfidooxidans*, and *Acidiphilium acidophilum* bioleach gold, silver, nickel, and copper of electronic wastes. There are different fungi like *Aspergillus niger*, *Penicillium simplicissimum*, *Aspergillus fumigatus*, and *Aspergillus flavus* that generate organic acid to leach out copper, lead, nickel, and aluminum. *Morganella* produces copper nanoparticles from wastes. Factors like microorganisms, particle sizes, temperature, and pH affect the bioleaching process. Bioleaching is a substitution for recycling methods of electronic wastes. Wastewater treatment and photocatalytic degradation of microplastics are two critical applications of produced nanoparticles.

Keywords: Biosafety, Nanoparticle Producing Bacteria, Bioleaching, Heavy Metals, Microplastic.

Introduction

With the advancement of technology and the demand for new products, the amount of wastes has also increased. Among the masses, toxic substances, heavy metals, and microplastics have a special place. The primary source of these hazardous substances is electronic wastes. E-waste are discarded electronic devices. They have a complex composition of different hazardous materials (1). According to the International Telecommunication Unions report, 781 million mobile phones were produced in 2015 (2). The toxic nature of these wastes makes them one of the most hazardous ones for the environment. For this reason, their removal from nature seems necessary. Toxic metals like lead, zinc, nickel and cobalt can affect the kidney or causing metal fever, Nickel itch, asthma, and pneumonia (1). Besides, precious metals in wastes such as gold, copper, and palladium have made their recycling very important and necessary. That is why e-waste is considered the core of urban mining (2). There are several disposal methods to eliminate e-wastes. However, these methods are ineffective in neutralizing the toxicity of heavy metals and microplastics. For example, incineration is not an ecofriendly approach (1). This method emits hazardous components and gases, depending on the design of incinerators and the composition of wastes (3). So this technique can lead to water and air pollution (1). Like NO_2, HCl, PM, SO_X, incomplete combustion byproducts, dioxins may be emitted into the atmosphere (1,3).

Inhalation of these compounds increases the concentration of heavy metals and certain organic materials in the bloodstream. It also increases the chance of getting cancer (3). Landfilling is another traditional way to dispose of wastes. This method has some disadvantages. For instance, dangerous heavy metals like lead, zinc, nickel, leak out to the environment. Aside from this, it can release hazardous gases into the atmosphere (1).

Electronic devices contain 60 elements, including valuable materials that need to be recycled. The heterogeneous blend of plastics, fiber glasses, metals, and organics makes the recycling process a severe challenge. There are different recycling processes. However, some of them have certain disadvantages that limit their application. For example, slow progress and time consuming of the process have limited their application in the industry. Besides, some of the recycling processes harm the environment. Moreover, some of these techniques are expensive (4). Apart from this, the stability of plastics in the environment is a great challenge. They are high-chain hydrophobic polymers with high molecular weight, and that is the main reason why they are resistant in the environment (5).

Microplastics are less than 5 mm in their size, and they have been made by breaking down those synthetic polymers. Microplastics have been found in fish, birds, fresh aquatic systems, sediments, and even Arctic and Antarctic sea ice. Therefore, they are one of the leading global concerns (6). Microplastics are very dangerous. Many organic chemicals (like dioxins, DDT, pesticides) floating in the ocean concentrate on their surface by their hydrophobic nature. When a marine organism accidentally swallows microplastics, the toxic chemicals on their surfaces would enter the body and accumulate in tissues, increasing concentration as the pollutants are transferred up the food chain. Yin et al. found that polystyrene microplastics reduce swimming and exploration

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ability, energy reserve, feeding activity, and growth (7).

That is why plastics and microplastics are some of the unresolved challenges of humankind. By considering these issues, there is a need for a new eco-friendly method. Bioleaching is a biological treatment that seems to be a good substitution of the existing conventional methods (1). One of the advantages of using the bioleaching method is extracting metals like copper from low-grade leftover ores of previous mining, which is not achieved by traditional methods (8). Besides removing heavy metals from the environment, this method is also used to produce metallic nanoparticles (1). These nanoparticles have several applications, For example, wastewater purification (9), and the photocatalytic degradation of microplastics (5).

1. Bioleaching as a way for metallic nanoparticle production

Bioleaching is a process in mining that extracts valuable metals from a low-grade ore with the help of biological systems like microorganisms. It is a principle mechanism in extraction metals like zinc, nickel, and cobalt (10). By this process, an insoluble metal is converted to a soluble form. When this happens, the metal dissolves in water then it can be extracted easily. For example, the conversion of CuS (an insoluble form) into the $CuSO_4$ (a soluble form) is a bioleaching reaction. The basis of this process is oxidation (8). This method has a special place in mining technologies. Developing countries are the primary resources for minerals. So bioleaching can be considered as a cost-effective and manageable method suitable for these countries. From 1950 to 1980, bioleaching was considering the most appropriate technology for copper and certain metals recovery from low-grade unrefined rocks (11).

The roman writer, Gaius Plinius Secundus wrote about a Cu leaching process. This report was one of the earliest writing on bioleaching subject. Georgius Agricola was a german mineralogist who published a report on the Cu leaching process using leachates from mines. The Rio Tinto mines in Spain have been used since the pre-Roman era to extract Au, Ag, and Cu. Gold biomining has been more efficient compared to other precious metals. Some conventional Au extraction methods use a higher amount of cyanide which is highly toxic to the environment (12). Cyanide is a chemical solution that dissolves gold (Figure 1).

The reaction between gold and cyanide is gold cyanidation (Equation 1) (10).

When the gold is surrounded by an insoluble metal sulfide, using the cyanide solution is not useful. By applying the bioleaching technique, the sulfide film is removed and gold recovery is obtained (11).

The potential of bioleaching in microorganisms can be investigated through the microbial sulfur and iron cycle. In this case, metal sulfides act as electron donors for aerobic sulfur-oxidizing microbes. The product of this reaction is soluble metal sulfate. So this reaction is a kind of bioleaching process. The biomining microbes are usually chemolithoautotrophic organisms. They grow under acidic conditions in the pH range of 1.5-2. They use minerals as fuel (13). All of them fix CO_2 to provide the carbon they need. They tolerate a wide range of metal ions. Some of them can fix atmospheric nitrogen (8).

Both the mesophilic and thermophilic microorganisms are used in the process of bioleaching (13).

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Equation 1. $4Au + 8CN^{-} + O_2 + H_2O \rightarrow 4Cu\,(CN)^{-}_2 + 4(OH)^{-}$ (10)

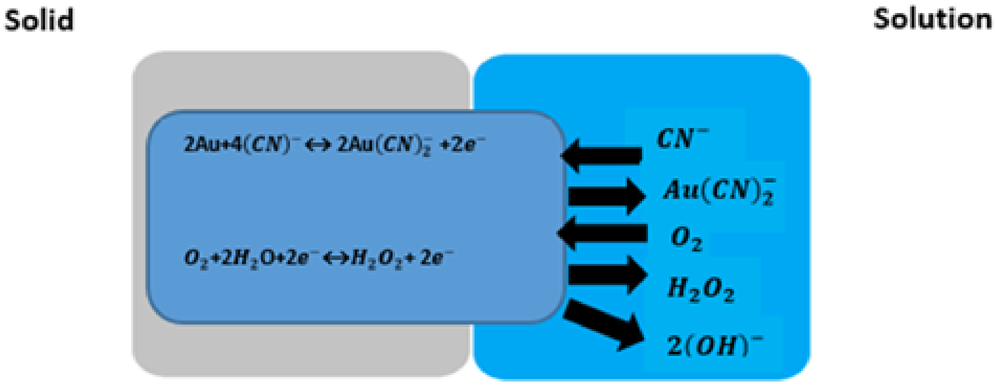

Figure 1. The cyanidation reaction.

During this process, alkaline cyanide solutions dissolve metals like gold to form the anionic complexes that are stable in the solution. This process occurs by various reactions that take place at the solid's surface. Diffusion of cyanide and oxygen are controlling factors.

Some microorganisms extract metals from electronic devices by the bioleaching process. For instance, bacteria like *Chromobacterium violaceum*, *Pseudomonas* species, *Sulfobacillus thermosulfidooxidans*, and *Acidiphilium acidophilum* bioleach gold, silver, nickel, and copper. Different fungi like *Aspergillus niger*, *Penicillium simplicissimum*, *Aspergillus fumigatus*, and *Aspergillus flavus* generate organic acid to leach out metals like copper, lead, nickel, and aluminum. Some of these microorganisms bioleach nanoparticles from e-wastes. The biosynthesize of nanoparticles by microorganisms is a way for green synthesizes of these materials. Microorganisms like *actinomycetes*, fungi, bacteria, and viruses are used for this process. Bacteria like *Morganella* produce copper nanoparticles from waste materials (1).

For metallic and nano metallic production, the attachment of the bacteria on the surface does not take place randomly. For example, *A. ferrooxidans* adhere to sites with surface scratches. The highly motile bacteria like *Leptospirillum ferrooxidans* and *A. thiooxidans* have a chemosensory system that can detect gradients of oxidizable metallic substrates like Fe^{2+}/Fe^{3+} ions or thiosulfate. This chemotactic response attracts microorganisms to the specific site of the surface. Most leaching bacteria usually attach to the metallic surface by extracellular polymeric substances (EPS) (13). You can find information about nanoparticles produced by the bioleaching process in the table 1. Although bioleaching is considered as a bioremediation method, it is also essential for nanoparticle production (1). Using this method to produce nanoparticles is to minimize the physical and chemical usage methods, that are not eco-friendly and relatively ineffective in terms of energy and financial costs. Various examples of chemical and physical methods include chemical precipitation, photo/electro-chemical methods and radiation (14).

Table 1. Nanoparticles bleached by bacteria from e-wastes.

Nanoparticles	e-waste Type	Microorganism	Ref.
Gold	Electronic waste/printed circuit boards	*Acidithiobacillus ferroxidans* and *Acidithiobacillus thioxidans*	(5)
Gold, Copper, Iron, Zinc and Silver	Ground powder of printed circuit boards from personal computers	*C. violaceum*, *P. aeruginosa* and *P. fluorescens.*	(15)
Gold, Silver and Copper	Video card and random access memory	*Paenibacillus sp.*	(16)
Copper, Zinc, Nickel, Palladium and Cadmium	Printed circuit boards	*Leptospirillum ferrooxidans* and *L. ferriphillum*	(17)

Besides, chemical and physical methods do not always yield higher products. In some cases, produced nanoparticles possess low stability, and controlling their aggregation and crystallization is hard (18). Generally, there are two different methods for metallic nanoparticle production: the bottom-up or atom by atom and the top-bottom (19). The bottom-up method is based on self-assembly, and the resulting nanoparticles are more homogenous. As a result, bioleaching as a bottom-up, eco-friendly, and cost-effective nanoparticle is a production method and can be used for the e-wastes removal from the environment (1).

2. Essential factors in the bioleaching process

Bioleaching is affected by different factors like microorganisms, particle sizes, temperature, and pH. There are specific bacterial species that accelerate the leaching process. The most common one is *Thiobacillus ferrooxidans* which is a gram-negative and chemolithotrophic bacteria. These bacteria oxidize ferrous ions and reduced sulfur compounds (20). Thermophilic and Archea also increase the rate of bioleaching (11). Mixed cultures have a better result than simple cultures. Most *T. ferrooxidans* strains are mesophilic bacteria with an optimum range of 30^{oc}-40^{oc}. However, this temperature can be increased by more than 60^{oc} in a heap due to the metabolic heat release. So a fantastic temperature gradient is established from the surface to 55^{oc}-70^{oc} in the center. As a result, different bacterial species can be established to cross the gradient. This phenomenon is considered a significant advantage in large-scale leaching. Particle size affects the rate of metal extraction and the cost of bioleaching. Decreasing the particle sizes by gridding leads to an increasing in the number of active sites. As a result, the leaching rate is increased (20).

pH is of great significance, which would affect the growth activities of microorganisms and structure of microbial communities, thereby influencing the leaching rate. On the one hand, bioleaching microorganisms are extremely acidophiles; high pH environments would be harmful to the oxidation ability of microorganisms. Besides, during heap leaching, elevated pH would reduce permeability of bioheap due to ferric ion precipitation. On the other hand, low pH values are also detrimental to bioleaching, inhibiting microbial growth and oxidative activity (21). Besides, inorganic nutrients of ores are the primary materials' sources for bacterial growth and they are limiting factors for their population. Because of the low concentration of elements like Mg, Ni, and phosphor (20).

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3. Nanoparticles in water treatment

About 3.1% of death happening annually because of the contamination of drinkable water. It is predicted that more than 75% of the population will have been struggling to access water in 2050. Increasing population, industry, and agriculture development lead to water pollution (22). The different herbicide is used in agriculture and farming. For instance, Mesotrione is a kind of herbicide used for weed control. This toxic compound can quickly enter the groundwater during farming. So it has destructive effects on the aquatic ecosystem (23). Besides that, increasing the concentration of heavy metals and organic pollutants, the presence of harmful bacteria like *Salmonella typhosa*, *Vibrio cholera*, and *Escherichia coli* are dangerous. So the removal of toxins and impurities from water seems essential. There are different purification methods, for example, the adsorption method (22). The elimination of toxic pollutants from the environment has been a great challenge for scientists (23). Nanoparticles have a large surface area to bind with different molecules. So they are applied in water purification. For example, the magnetic nanoparticle is used for this purpose. After treatment, the use of a magnetic field makes the removal of nanoparticles after treatment easier and cost-effective (22). Photocatalytic degradation is presented as an effective way for the degradation of organic contamination from water. Metal oxide nanoparticles like TiO_2 serve as a potent photocatalyst. Features like being non-toxic, low-cost, resistant to photo corrosion, insolubility in water, acids, and bases, chemical and biological stability and availability make it one of the best photocatalysts (23). Exposure of a nanoparticle to a specific wavelength of light stimulates it to form a hole-electron pair in its structure. This electron participates in the degradation process. There are some nanoparticles like TiO_2 which have a large band gap that limited their application. The fast recombination of electron-hole pairs in these kinds of nanoparticles decreases the efficiency of photocatalytic degradation. Changing the visible part of the spectrum by using other metals like Cu, Ni, Co and Ag can be considered as a solution. For example, in Au-TiO_2 nanoparticles, the absorption of photons by Au leads to electron excitation and the formation of electron-hole. This electron is shifted to the TiO_2 conduction band. Then it participates in degradation (Figure 2) (23).

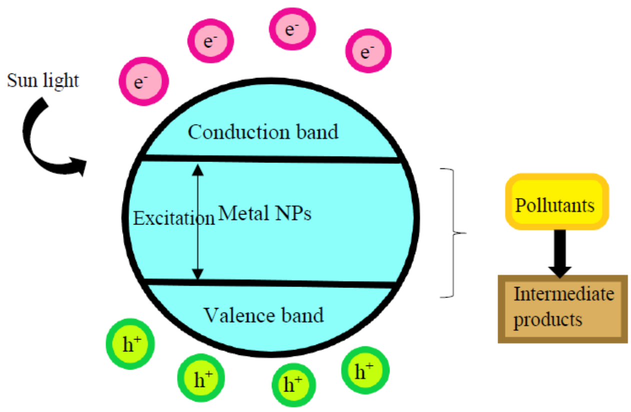

Figure 2. General mechanism of pollutant degradation by metal nanoparticles.

4. Photocatalytic degradation of microplastics

Plastics are the main components of electronic devices. The breakdown of these synthetic polymers into microplastics (<5mm) is a severe issue of the global environment (6). As particles reduce in their size, the proportion of the surface areas to volumes increase. As a result, the chemical behavior of small particles is affected more by their proportion of surface area to volume than by their constitute substances. Most of the microplastics are resistant to biodegradation because they have a long chain structure and high molecular weight and are hydrophobes. This polymer is consumed by humans and enters into different tissues (5). Seafood, drinking water, and commercial salts are examples of microplastics sources (6). There are different chemical, physical, and biological degradation methods (5). The conventional wastewater purification methods have some problems in controlling the elimination of microplastics in the wastewater. Photodegradation and biodegradation are two degradation methods. Biodegradation is dependent on the microbial species (24).

Different species of heterophilic microbes like *Streptomyces*, *Pseudomonas*, *Corynebacterium* and *Micrococcus* are be used in the biodegradation method. Apart from this method, the use of photocatalysts has a special place among different degradation strategies. The advantage of this method is producing a useful intermediate product by solar radiation and apply it to synthesis a new product (5). In other words, photocatalysis is the advanced oxidation process for pollutant removal (24). ZnO and TiO_2 are the two examples of photocatalysts. These photocatalysts usually work under UV lights (5,24). However, some researches showed removing low-density polystyrene under visible light by TiO_2 nanotubes (24). Figure 3 shows different mechanisms of photocatalytic degradation by metal oxide nanoparticles. These nanoparticles can kill microorganisms like bacteria and fungus, and protozoa by producing free radicals. They can detoxify heavy metals by different strategies, including reduction, adsorption, and ion exchange. They also reduce various aromatic compounds to neutralize their effects (25).

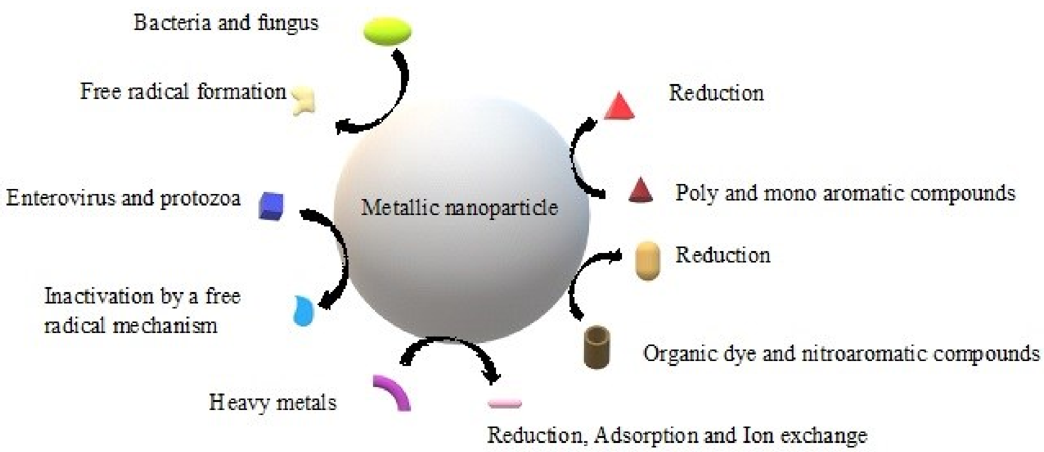

Figure 3. The mechanism of photocatalytic degradation by metal oxide nanoparticles.

Conclusion

Bioextraction of precious metals from e-waste is an important substitution of the expensive conventional recycling methods. Electronic devices have a multiplex constitution of heavy metals, plastics, and toxic substances. So it is necessary to remove them from the environment. By applying the bioleaching method, the removal of toxic substances and the recovery of precious metals are possible simultaneously. Some of the bioleaching can produce nanoparticles from heavy metals of electronic waste. Some of them are photocatalysts which can be used in wastewater treatment and photocatalytic degradation of microplastics.

Research about this field of study is ongoing. It is hoped that more of these bioleaching microorganisms will be discovered.

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بیولیچینگ برای تولید نانوذرات به‌عنوان راه‌حلی برای آلودگی‌های محیطی

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صفحه ۷۰-۶۱

چکیده

آلودگی محیط با پلاستیک و فلزات سنگین ازچالش‌های بزرگ قرن است. زباله‌های الکترونی باعث افزایش فلزات سنگین و پلاستیک در محیط می‌شوند که تهدیدگر زندگی موجودات هستند و حذف آنها از محیط ضروری است. روش‌های دفع مانند دفن و سوزاندن به محیط آسیب وارد می‌کند. فلزاتی مانند طلا و نقره، بازیافت زباله‌های الکترونی را ضروری می‌سازد اما به دلایل اقتصادی، استفاده از جایگزین ضروری است. هدف این مقاله معرفی بیولیچینگ به‌عنوان روش بازیافت زباله است که برای حذف فلزات سنگین و تولید نانوذرات استفاده می‌شود. در انتها به کاربرد این نانوذرات در تصفیه‌ی آب و تجزیه‌ی میکروپلاستیک اشاره شد. تبدیل فلزات غیرمحلول به محلول توسط میکروارگانیسم را بیولیچینگ می‌گویند. باکتری‌های *Chromobacterium violaceum*، *Pseudomonas*، *Sulfobacillus thermosulfidooxidans* و *Acidiphilium acidophilum* طلا، نقره، نیکل و مس را از زباله‌های الکترونی بیولیچ می‌کنند. *Aspergillus niger*، *Penicillium simplicissimum*، *Aspergillus fumigatus* و *Aspergillus flavus* که با بیولیچ مس، سرب، نیکل و آلومینیوم، اسیدآلی تولید می‌کنند. *Morganella* نانوذرات مس را تولید می‌کند. نوع میکروارگانیسم، اندازه ذرات، دما و pH روی این پروسه اثرگذار است. بیولیچینگ جایگزین سایر روش‌های بازیافت زباله الکترونی است. تصفیه‌ی آب و تجزیه‌ی فوتوکاتالیستی میکروپلاستیک‌ها از کاربردهای نانوذرات تولیدشده، هستند.

واژه‌های کلیدی: ایمنی زیستی، باکتری‌های تولیدکننده نانوذره، بیولیچینگ، فلزات سنگین، میکروپلاستیک.

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