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Comparison of the application of Heavy metals adsorption methods from aqueous solutions for development of sustainable environment

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Abstract: Pollution of water by heavy metals is a major problem such as mercury, lead, cadmium, cobalt, etc. The presence of toxic metals in the environment has detrimental effects on human and animal health and disrupts the balance and order of the ecosystem. Therefore, it is necessary to study the ways to eliminate these pollutants. The aim of this study was to compare nickel metal uptake by biological uptake methods with the help of bacterium and brown algae Sargasom, Focus and Grasilaria red algae and nanotechnology method. Based on the previous interpretations, It is compared the processes of removal and recycling of nickel metal from industrial wastewater. Research question is that which method is more effective for removal of heavy metals? Results show that biosorption, as an environmentally friendly method, has a brilliant performance and is a low-cost internal method for wastewater treatment. The biological treatment of effluents is carried out by bacteria, some fungi, algae and protozoa to examine the conversion of effluent into a harmless state. Also results show that Iron-based nanostructured particles are capable of decomposing highly stable contaminants such as perchlorate compounds, air nitrate, heavy metals (nickel and mercury) and radioactive materials such as uranium dioxide. Nanostructured particles are used for immediate treatment of sediments, water treatment and liquid waste.

Keywords: Biosorption, Sustainable Environment, Nanotechnology, adsorption, heavy metals, Water Pollution

Introduction

One of the most important issues in today's world is environmental pollution with toxic and dangerous metals (Harland 2012; Mahrol 1983; Arup et al. 1995).

The extraction of metals from mines and the widespread use of heavy metals in industry have led to the concentration of these metals in water, sewage, air and soil increase more than the baseline values. The mechanism of the toxicity of heavy metals is due to the strong tendency of the cations of these metals to sulfur. In this way, the activity of vital enzymes in living organisms is disrupted (Dabrowski and Hubicki (2004); Saioglu 2004).

Therefore, the removal of heavy metals from the aquatic environment is an important issue in public health, which in two respects. It is important:

A) Separation of heavy toxic metals from industrial effluents, agricultural drainage, mines and neutralizing their toxic effects

B) Rehabilitation and recycling of metals, which is essential with the gradual reduction of mineral resources. Heavy metals in the effluent of many industries such as zinc mining and other heavy metals from ore, petrochemical industries, oil refining industries, paper industries, pharmaceutical industries, paint industries, product industries. There are plastics, etc., and if they go to wastewater treatment systems on microorganisms and kinetics. Sewage treatment reactions, due to their toxicity, reduce system efficiency. This causes the concentration of these compounds in the effluent of treatment plants is not comply with the standard set by domestic and international authorities. On the other hand, navigation these heavy elements and compounds will have an irreversible effect on the environment and humans. With care to the mentioned cases, purification of these compounds and their removal in accordance with internal standards and international is very important. Heavy metals are basically a group of metals. They have a specific gravity greater than 6 g/cm^3 and an atomic weight of more than 55g. Some of them in quantities parts are considered essential elements and their presence in the food chain of humans and other organisms is necessary for this reason. They are called essential elements. The presence of these elements in excessive concentrations also has several adverse effects humans, as well as other organisms, pose pollution and environmental hazards. Heavy metals includes mercury, arsenic, cadmium, nickel, copper, lead, chromium, zinc, vanadium, etc., which have different boiling points.

Among the sources of environmental pollution associated with heavy metals include: Heavy metal mining, metal industry, foundry, plating, painting, battery making, tanning, textile, Paper making and other similar industries that repel and release elements such as cadmium, mercury, nickel, lead, zinc, chromium, copper and silver pollutes the environment. Heavy metals in municipal wastewater disrupt the wastewater treatment system and reduce purification efficiency and in acute cases, causes the cessation of biological activities of treatment systems. So given the effects harmful discharge of effluents containing heavy metals into the environment and its living organisms, wastewater discharge standards from The Environmental Protection Agency (EPA) have provided a variety of resources for discharging industrial wastewater. The presence of heavy metals in industrial effluents and environmental problems due to their improper disposal makes it necessary to treat such effluents before discharging them into the environment or entering the wastewater collection network. Surface and groundwater resources that are somehow contaminated with heavy metals need to be treated. Yet in order to remove heavy metals from the sewage industry, several different methods have been implemented, each of which is practical and economics has its advantages and disadvantages. In Iran, efforts to control plaque effluent, which contains heavy metals, are mainly aimed at sedimentation. Heavy metals are deposited and the resulting sludge is filled with these metals, so it is predictable that due to the large number of plating units in the country, every year relatively large amounts of these metals along with effluent or sludge to the environment should be drained. Of course, if implemented recovery and investment techniques in this area, the possibility of compensating part of the costs spent on wastewater treatment, while saving these metals, it will be created by industries. Recover copper, nickel, chromium, cadmium and zinc. It can be done using the ion exchange process. The high price of these metals makes them recover from industrial wastewater flows are very attractive. Today, ion exchange methods are used to recover effluents contains chemicals, especially heavy metals (process growth). Common methods of removing heavy metals from wastewater include chemical sedimentation with lime and soda, ion exchange process, chemical oxidation and reduction, surface adsorption, electrodealysis, filtration, and membrane processes such as reverse osmosis and nanofiltration. The physicochemical methods mentioned above are expensive and require a lot of investment in construction and operation, and in many cases, with the help of these methods, it is not possible to achieve the legal standards for effluent discharge. It should also be noted that the above technologies are used in places where the concentration of heavy metals is high, and if the concentration of heavy metals in the wastewater is low, these technologies will not have the necessary effectiveness and will be expensive. The most common method of removing heavy metals from wastewater is chemical precipitation. In this method, a large amount of chemicals must be used to achieve the discharge accumulate them. Sludge that increases the cost of treatment. Common methods of removing heavy metals from wastewater include: chemical deposition with lime and soda, ion exchange process, chemical oxidation and reduction, adsorption, electrodialysis, filtration and membrane processes such as reverse osmosis and nanofiltration.

The physicochemical methods mentioned above are expensive and require a lot of investment to build and operate. In many cases, with the help of these methods, it is not possible to achieve legal standards for wastewater discharge.

It should also be noted that the above technologies are used in places where the concentration of heavy metals is high, and if the concentration of heavy metals in wastewater is low, these technologies will not be effective and will be expensive. In conventional municipal wastewater treatment systems, the removal of heavy metals has been observed, but heavy metals at concentrations above the acceptance capacity have adverse effects on biological wastewater treatment processes. Therefore, conventional biological wastewater treatment systems are not suitable for detoxification of wastewaters containing high concentrations of heavy metals. Observation of the ability of microorganisms in biological wastewater treatment systems to remove heavy metals became the basis for further studies in this field. Bioaccumulation is the active and metabolism-dependent removal of heavy metals in resistant microorganisms and their ability to accumulate. Active adsorption of heavy metals by microorganisms is sensitive to environmental conditions (temperature, pH, etc). Bioaccumulation also requires nutrients for the survival of microorganisms. In addition, the active adsorption capacity of heavy metals by microorganisms is relatively small, as a result Bioaccumulation has low potential to compete with conventional heavy metal removal technologies from the aquatic environment (Dyre et al. 1997; Banshi 2002; Asmi 1999).

Thus, in order to effectively remove heavy metals from water and sewage, there is an urgent need to develop a new, inexpensive method. There are prices and economics. To meet this need in recent years, biosorption studies has intensified. Based on the above interpretations, in the following, we will compare the processes of removal and recycling of nickel metal from industrial wastewater. Considering that the purpose of this paper is to to compare nickel metal uptake by biological uptake methods with the help of bacterium and brown algae Sargasom, Focus and Grasilaria red algae and nanotechnology method. In this paper, research question is:

– Which method is more effective for removal of heavy metals?

Methodology

Common methods of removing heavy metals from wastewater include chemical sedimentation with lime and soda, ion exchange process, chemical oxidation and reduction, surface adsorption, electrodealysis, filtration, and membrane processes such as reverse osmosis and nanofiltration. Considering that the purpose of this paper is to to compare nickel metal uptake by biological uptake methods with the help of bacterium and brown algae Sargasom, Focus and Grasilaria red algae and nanotechnology method. In this paper, it is paid to which method is more effective for removal of heavy metals with studying of previous research?

ion exchange process

The phenomenon of ion exchange, like the processes of distillation, extraction and adsorption, is one of the branches of the science of separation. Although this phenomenon has many aspects in common with other branches of segregation, it differs from many of them in a very important way.

The difference between ion exchange and other separation methods is that this phenomenon occurs with the division of different types of charged species between different regions of a system. These regions are usually separate phases.

Dealing with pregnant species means that the ion exchange process is inherently a stoichiometric reaction because during each ion exchange process each of the phases in the system must maintain its electrical neutrality.

The ion exchange reaction can be defined as the internal exchange of ions in a system, including ions present in the solid phase of ion exchange and ions in the soluble phase. Ion exchangers are insoluble solids that contain anions or interchangeable cations. When ion exchangers come in contact with an electrolyte solution, these ions can be exchanged with ions in the solution with the same sign as the stoichiometric equivalent. To be. Materials with interchangeable cations, cation exchangers and materials with interchangeable anions, anion exchangers.

They are called materials that are able to exchange both types of ions (anions and cations), they are called amphoterics). Lost and so-called depleted can be solved with a solution of a sodium salt such as Na+ that all ions are regenerated. Due to ion exchange, the cations or anions present in the solution are replaced by the cations and anions in the resin so that both the solution and the resin remain electrically neutral.

In other words, some soluble ions and resins together without dissolving solids in the solution are exchanged.

Ion exchange resins can be divided into two main groups:

1- cationic resins

2- Anionic resins

And the pH of each group includes the weak and strong type. In general, strong type resins exchange ions in a wide range of pH. Weak resins operate in a small range of pH.

Resins are usually available in bulk. In general, anionic resins are more expensive than cationic resins. . The price of weak game resins is almost the same as the price of strong game

resins, but the price of weak acid resins is up to three times higher than strong acid resins.
Nickel recycling can be done using the ion exchange process. Recovering from ion exchange usually requires sewer separation. Especially if there is cyanide ion. The presence of this substance causes permanent contamination of resins.
Nickel is usually present in the form of its sulfate, so sulfuric acid is used for the resin recovery phase, but if nickel is recycled from wastewater from nickel refining units, the resin-reducing agent will be ammonium carbonate.
Nickel ions are absorbed on a strong acidic cationic converter. Resin reduction is two steps. The output of the first reduction step, which is rich in nickel sulfate and contains additional sulfuric acid, is neutralized with nickel carbonate and the result (which is actually recycled nickel solution) is returned to the plating tub.
The output of the second phase of the reduction is kept in the next cycle for the recovery of the first phase of the resin. After the cations are removed from the sewage, it is passed through the column of anion converter and the final deionized water is returned for consumption. The recovery effluent of this column flows into the sewer.
If the effluent has more complex compounds, special resins should be used. Chelating resin can also be used to recover nickel from the metal staining process. Aluminum ions were also present in these effluents (Shohoudi 2004).

Use of coagulation, flocculation and electric flotation process

In recent years, the processes used in the water and sewage industry in various physical, chemical and biological fields have undergone significant progress, and in the meantime, the share of biological and chemical processes has been higher than the advanced process. Coagulation and clotting process. In water and wastewater treatment today, it is usually done through chemical and adding organic, mineral and other coagulants to the water and sewage environment. Despite its relatively long history in the water and wastewater industry, due to limitations such as high operating costs and adverse environmental consequences, it has no significant advantages, so in order to find other appropriate solutions to replace the chemical deposition process, Numerous studies have been conducted in recent years, including the process of electrical coagulation and flotation, which is a significant innovation in the water and wastewater industry.
Electrical coagulation is the production of coagulants in a solution using the electrical decomposition of aluminum or iron electrodes. Metal ions are produced in the anode and hydrogen gas is produced in the cathode (Chen 2004).

In this method, by using electric current and installing chemical electrodes made of aluminum, iron, etc., which act as anode and cathode, the colloidal particles in the water or sewage environment are electrically neutralized by producing positive electric charges. As a result of Al3+, Fe3+, etc., the clotting process is provided. This process in
Various industries such as plating, metal extraction from mines, wood and paper, metal industries, automotive, chemical industries, pharmaceuticals, etc. have been designed and implemented on a real scale and in terms of treatment efficiency and elimination of various environmental pollutants from very high returns. It has been well received.
In 1995, Matson et al. described a project introduced in the 1940s called the Electrical Connector. Based on this design, the aluminum was electrochemically dissolved and combined with the hydroxyl ions released from the cathode, and the aluminum hydroxide was used for the coagulation process. A similar process was used in 1556 in the United Kingdom to purify water. In North America, this method is mostly used in wastewater treatment of wood and paper industries, mines and metal refining (Paul 1996).

The process of electrical coagulation is not cost-effective for small-scale purification systems. Using aluminum ingots can reduce costs in this way. With proper operation, this method can be used for a long time.
A comparison made at a factory in Iran shows that if iron electrodes are used in the electrical coagulation process, given the relatively low power consumption in Iran, the cost of this system in wastewater treatment is reduced by about one third of the chemical coagulation process.
Also, due to the fact that the volume of sludge in this method is much less than chemical coagulation, as a result, the costs of treatment and disposal are less, and consequently, the total cost of this process will be about one-third less than the chemical coagulation process.

Powdered Activated Carbon (PAC) Process

The combined process of activated carbon powder - activated sludge (PAC) is used as a process for the treatment of industrial wastewater with high organic load and the presence of late decomposing compounds or inhibiting microbial growth such as heavy metals. In the last three decades, the use of the PAC process for the treatment of industrial wastewater has expanded significantly.

Studies and experience show that the most important reasons for increasing the efficiency of heavy metal removal in such systems include increasing the adsorption and acceleration of bacterial growth and improving the sedimentation properties of the clots produced.

In their study of operating systems, Flyn et al. Concluded that adding activated carbon powder to the active sludge system increased the biological purification rate of organic matter, improved the diverse network of microorganisms and carbon particles, increased settling and condensation rates. Sludge, accelerating the removal of organic matter, controlling the concentration of organic matter fluctuations, the possibility of increasing the age of the sludge without the occurrence of wind conditions) Balking (sludge and thus increasing the possibility of late decomposition of organic matter)

It decomposes and minimizes the phenomenon of foam production by absorbing surfactants (Robertaccio and Flynn 1976).

The application of this process to remove various organic and mineral compounds, especially in the wastewater industry of plating and heavy metals, chemical industry, polymer production, oil refineries and paper, steel, textile and industrial paint industries has shown that in addition to reducing organic load, Activated carbon powder quickly absorbs pigments and aromatics, simplifies sludge dehydration, improves sludge digestion, and minimizes system sensitivity to sewage fluctuations (Adams, 1975).

Elimination of heavy metals using nanotechnology

Nanotechnology involves illustrating, measuring, and using the production of objects on scales between 1 and 100 nanometers. Benefits of nano include the production of new products, longer durability and low energy consumption.

The applications of nanotechnology in the environment are many. Nanoparticles have a high degree of flexibility in the treatment of pollutants. If conventional methods are used to purify organic solvents containing chlorinated compounds such as trichlorethylene, some dichloroethylene and vinyl chloride are always formed by side reactions, which are very harmful using nanostructured bipartite particles (nanoscale metals) to produce such products. An undesirable side reaches zero. Iron-based nanostructured particles are capable of decomposing highly stable contaminants such as perchlorate compounds, nitrates, heavy metals (Nickel and Mercury), and radioactive materials such as uranium dioxide.

Nanostructured particles are used for immediate treatment of sediments, water treatment and liquid waste. However, using nano-membranes, up to 99% of contaminants can be easily removed from the water. Research shows that the use of nanotechnology in water and wastewater treatment can greatly reduce treatment costs.

Therefore, nanofiltration is the separation of solute from solvent by passing a solution through a membrane whose pores are in the range of 0.5 to 2 nanometer.

The driving force in this process is to apply a pressure difference of 5 to 45 times. The diameter of the pores in this way, molecules with a molecular weight of more than 300 to 500 grams per mole are separated from the solution. The membrane surface has a small electric charge, and as a result, the electrical interaction between different ions and the membrane surface also plays a major role in separating these elements from the solution.

New technology enables mass-produced nanofiltrated water to produce water purified by nanofiltration as much as purified mineral water. With the use of nanofilters, the minerals needed for human health remain in the water and toxic and harmful substances are removed from it. Nanofiltration is a useful method between reverse osmosis and ultra filtration methods.

Ultra filtration has defects due to the higher amount of mineral and alkaline pollutants than the allowable temperature and the reverse osmosis method due to the production of excessive product purity and high price.

The baths are made of holes made of carbon nanotubes, which allow cheaper separation of gas and liquid. Currently, most existing membranes are made of polymeric materials that are not suitable for high temperature applications. But scientists have been able to use carbon nanotubes to bring the two seemingly opposite things together and provide good selectivity with high input.

Wastewater treatment with the help of optical nanocatalysts can remove plum and resinous compounds from the simultaneous rotation and turn wastewater into a suitable water source. But because these compounds are biodegradable, we have to use some kind of energy to break them down. This energy is obtained from ultraviolet light from the sun and is used in conjunction with optical catalysts (Garcia et al. 2001).

Nano-cavity ceramics are made of ceramic or glass materials with nanometer porosity; So that a single layer of molecules can be connected to each other. Single-layer and mesoporous layers have the ability to be programmed to remove certain contaminants. Nano-cavity ceramics have shown faster adsorption, higher capacity and better selectivity than many other absorbent membranes and technologies.

These compounds are designed to remove metal contaminants from drinking water, groundwater and industrial wastewater (Cainet and Morrell 2001).

Also, nanoparticle ceramics can be programmed to remove certain metals; But some metals, such as calcium, do not remove magnesium and zinc. Nano-cavity ceramics as a single layer is not effective for removing biological or organic contaminants. Nanospheric ceramics can be used in a wide range of applications for water treatment to industrial wastewater treatment (Savage et al. 2005).

One of the nano-cavity ceramics is zeolites, which have high porosity aluminosilicate compounds and the construction of various cavities, including a three-dimensional framework and a negative charge inside the network. The negative charge is balanced by a cation that can be replaced with some of the cations in the solution. The high ion exchange capacity, high specific surface area, as well as the relatively low price of zeolites are attractive for the removal of heavy metal ions. Adsorption of arsenic from aqueous solution on ceramics
can be inserted into membranes and used for external applications (Bolong 2000).

Zero iron nanoparticles have a very active capacity and a high specific surface area compared to zero iron has the capacity of granules and soil temperatures and pH values and is effective in a wide range of nutrients. Therefore, it can reduce a wide range of common environmental pollutants, such as chloromethane, chlorobenzene, pesticides, organic dyes, trihalomethanes, polycyclic, use

Nano-cavities have been studied at room temperature and the results have shown that the synthesized nanofiber ceramics are effective absorbers for the removal of arsenic ions at both high and low concentration levels (Chutia et al. 2009).

Tita Nano Nano-Oxide: Semi-conductors transmit an electron to the conduction layer under radiant energy and a cavity is created in the capacity layer. This process has the ability to oxidize and regenerate for particles.
It comes with. The TiO2, ZnO, and 2 Fe2O3 semiconductors perform this process under the influence of ultraviolet radiation.

Titanium oxide produces hydroxyl free radicals in the presence of water, oxygen, and UV radiation, which decompose organic contaminants into low-toxicity carbon compounds (Bahnemann 2004).

Titanium deoxygenated nanoparticles exhibit high-efficiency photocatalytic process; Because their inner surface is exposed to ultraviolet radiation and pollution, it provides a faster photocatalytic process than larger particles. Tita New Dioxide acts as both a photocatalytic regenerator and an adsorbent. Titanium dioxide decomposes almost all organic contaminants. This substance is very hydrophilic; Therefore, it has the ability to absorb biological contaminants and heavy metals such as arsenic. Its efficiency depends on titanium dioxide size, ultraviolet light intensity, water pH, water-soluble oxygen and pollutant concentration (Li and Somorjai 2010).

Zero-capacity iron nanoparticles: Zero-capacity iron nanoparticles are widely used to remove organic and mineral pollutants from groundwater and provide very high flexibility for on-site and off-site treatment. It is both an adsorbent and a reducing agent (Table 1), which also causes organic contamination with carbon compounds.
Break with less toxicity and remove heavy metals from the solution. Zero-capacity iron nanoparticles can be injected directly into groundwater sources for treatment at the site, or they
non-phenols, arsenic, nitrates and heavy metals such as mercury, nickel and silver (Wang et al. 2005).

Zero iron nanoparticles also have a dual-metal capacity in which iron nanoparticles are coated with a secondary metal such as palladium to
secondary metal such as palladium to increase iron activity. Zero iron nanoparticles with a capacity covered with palladium have been shown to reduce all chlorinated compounds

within eight hours below the allowable limit. Zero iron nanoparticles, on the other hand, require a normal capacity of 24hours to remove more than 99% of these compounds (Chicgoua et al. 2012).

Mohammadi Aloucheh et al. (2018) studied the effect of nanobiosensors in determination of environmental risks. They found that nanobiosensors could identify heavy metals an environmental contaminants.

Table 1. Remove contaminants using iron-based nanoparticles

Type of nanoparticle	Contaminant type	Delete efficiency	pH	Reference
Iron sulfide nanoparticles	Lindan	94	-	Wang et al. 2012
Zero capacity iron	Nitrate	100	-	Choe et al. 2000
Zero iron nanoparticle capacity	Perchlorate	100	6.5-6.8	Xiong et al. 2007
Iron nanoparticles	Ni (II)	100	-	Li and Zhang 2006
Iron / copper nanoparticles	Nitrate	100	-	Liou et al. 2005
Nickel / iron nanoparticles	Three Chlorothane	>90	-	Schrick et al. 2002
Nangaroo Maghamit	Ni (II)	96.5	7	Salmani et al. 2013
MnFe_2O_4	Cu(II)	95.0	5.3	Takafuj et al. 2004

Continuous Reactive Operators (SBR) Reactors

One of the methods used to remove heavy metals from industrial wastewater and thus protect the environment is biological treatment. Due to the proven ability of a group of microorganisms to separate heavy metals and their compounds, this method is in many cases superior to other methods of purification and removal of these compounds.

One of the suitable methods for biological treatment of effluents containing these compounds is the use of discontinuous reactor methods with successive operations, which in recent years has been considered by many experts and experts in the field of environmental engineering due to its unique characteristics. The method of discontinuous reactors with consecutive operations is a biological method of active sludge family that has high flexibility and efficiency of treatment. In fact reactors the discontinuity has been compounded by successive operations of sludge systems, now known as biodegradable and reactive biological reactors, which are characterized by time-varying stages (Hassani 2000).

In discontinuous reactors with successive operations, biological wastewater treatment is summarized in five stages: (1) filling the reactor with raw sewage, (2) aerobic and semi-aerobic biological reaction stage, (3) sedimentation stage and sewage, (4) sludge discharge stage, and finally (5) rest or cessation stage. First and fourth steps are necessary, but other steps can be modified or deleted (Malek Ahmad 2002).

Nickel heavy metal as salt of nickel sulfate ($NiSO_4$) with heavy chromium and lead metals as salt of these metals ($PB(NO_3)_2$) and ($K_2Cr_2O_7$) entered the system with a concentration of 0.1 mg/l. First, the elimination efficiency was 55% on the first day, then the nickel elimination efficiency increased, reaching 78% on the twelfth day. By adding a nickel concentration of 100 mg/l, although the elimination efficiency increases from the beginning to a few days later, the overall efficiency Nickel heavy metal removal is reduced. If on the sixty-third day, when the concentration of input nickel reaches 200 mg/l, the efficiency of nickel removal decreases and reaches 91%.

As with heavy metals chromium and lead, a decrease in the percentage of depletion of nickel heavy metal at the beginning of each concentration increase, then an increase in removal efficiency after a few days can be attributed to microbial habituation with changes made during this period (Malek Ahmad 2002).

Biosorption Method

One of the most important issues in today's world is environmental pollution with toxic and dangerous heavy metals. Common methods of removing heavy metals from the aquatic environment include chemical precipitation, ion exchange, surface adsorption, membrane processes, and oxidation and reduction processes, which are expensive and costly to invest and operate. Thus, there is an urgent need to develop a new, inexpensive, and economical way to effectively remove heavy metals from water and sewage. To meet this need, studies on bioresorption have intensified in recent years. Absorbent, physicochemical adsorption of heavy metals by non-living microorganisms (bacteria, fungi, algae) and other organic objects (such as rice bran, fruit peel, leaves and bark of trees, etc.). The advantages of the non-adsorption process compared to conventional methods of heavy metal removal include cost-effectiveness, selective adsorption property, bioadsorption and metal recycling capability, high process speed and no sludge production. Biosorbent performance can be improved using physical and chemical pre-treatment methods.

Studies of bioadsorption show that some bioabsorbents have a high adsorption capacity for heavy metals. The introduction of these organic objects into the industry has led to the production of some commercial products that are used on a real scale to remove heavy metals from sewage. Thus, with the spread of this cheap technology, an important step will be taken to improve the quality of the environment (Gupta et al. 2000; Volesky 2001).

Commercial bio attractants include $\mathrm{AMT-BIOCLAIM^{TM}}$, $\mathrm{AlgaSorb^{TM}}$ and Bio-Fix noted (Volesky 1990; Wase and Forster 1997; Gupta et al. 2000).

$\mathrm{AlgaSorb^{TM}}$ is manufactured using Chlorella vulgaris algae and is used to treat wastewater. This product is used to remove metal ions at initial concentrations of 1-100 mg/L.

The output concentration is less than 1 mg/L, and calcium and magnesium ions have no effect on its performance and do not reduce its adsorption capacity (Volesky 1990; Gupta et al. 2000).

$\mathrm{AMT-BIOCLAIM^{TM}}$ is made of granular biomass using Bacillus and is able to remove 55% of incoming metals. This product is non-selective and can be reconstituted and reused using sulfuric acid, soda, etc. (Wase and Forster 1997).

Bio-Fix is a mixture of organic matter including cyanobacteria (Spirulina), yeast, algae and plants (Lemna sp. Sphagnum sp.). These organic objects are mixed with gum and Xanthum gums and stabilized in polysulfone.

The Bio-Fix adsorption capacity for Zn^{2+} is four times that of ion exchange resins. The adsorption of bovine metals is a means of selecting this product and for some metals it is as follows: $Al^{3+} > Cd^{2+} > Zn^{2+} > Mn^{2+}$. Calcium and magnesium are absorbed in small amounts. This product can be used in more than 115 adsorption-adsorption cycles. Hydrochloric acid or nitric acid is also used to regenerate the adsorbent.

Table 2. The results of some studies conducted in the field of bioadsorption

Reference	Tempreture	PH	Max Adsorption capacity	Adsorption capacity	Metal ions	Gender and species	Organic mass type
Holan et al. 1993	-	3.5	-	1.17	Cd	Sargassum natans	Algae
Volesky and Kuyucak, (1998)	-	2.5	-	2.03	Au	Sargassum natans	Algae
Davis et al. 2000	-	4.5	-	0.68	Cd	Sargassum muticum	Algae
Davis et al. 2000	-	4.5	-	0.66	Cd	Sargassum filinendola	Algae
Jalali et al. 2002	30	4.5	1.38	-	Pb	Sargassum hystrix	Algae
Jalali et al. 2002	30	4.5	1.05	-	Pb	Pdina Pavonia	Algae
Diniz and Volesky (2005)	-	5	-	-	La	Sargassum Polycystum	Algae
Diniz and Volesky (2005)	-	5	-	-	Eu	Sargassum Polycystum	Algae
Diniz and Volesky (2005)	-	5	-	-	Yb	Sargassum Polycystum	Algae
Yan and Viraraghavan (2003)	-	5	0.12	-	Pb	Mucor rouxii	fangus
Yan and Viraraghavan (2003)	-	5	0.07	-	Cd	Mucor rouxii	fangus
Yan and Viraraghavan (2003)	-	5	0.11	-	Ni	Mucor rouxii	fangus
Yan and Viraraghavan (2003)	-	5	0.25	-	Zn	Mucor rouxii	fangus
Aksu et al. 2002	-	1	5.66	-	Cr^{6+}	Activated Sludge	Bacteria
Aksu et al. 2002	-	4.5	4.06	-	Ni	Activated Sludge	Bacteria
Loukidou et al. 2004	20	2.5	3.39	-	Cr^{6+}	Aeromonas caviae	Bacteria
Loukidou et al. 2004	20	2.5	3.49	-	Cr^{6+}	Aeromonas caviae	Bacteria
Loukidou et al. 2004	20	2.5	3.25	-	Cr^{6+}	Aeromonas caviae	Bacteria

The advantages of the non-absorbent process compared to conventional methods are the removal of heavy metals as follows [Baird 1995; Volesky 1990; Wase and Forster 1997; Davis et al. 2000, Loukidou et al. 2004, Brady et al. 1994]:

1. Affordability: Due to the abundance of bioabsorbents in nature and waste from various industries, these materials are inexpensive. The price of commercial bio-absorbers is about 10-15USD per a kilogram, while the price of resin exchanges is 30-35USD per a kilogram (Wase and Forster 1997). The price of commercial resin exchanges (AMBERLYST 15, ION-EXCHANGE RESIN) is about 236USD per a kilogram (https://www.rightpricechemicals.com, 2020).

Estimates show that the use of bioabsorbent methods reduces investment costs by 20%, operating costs by 18% and total treatment costs by 18% compared to conventional methods of heavy metal removal.

2. Selective property in metal removal: A study of the performance of bioabsorbents shows that these cases show a different tendency to absorb different metals, which depends on various factors such as biomass type, pre-treatment type, composition and conditions. Physico-chemical has a solution.

3. Ability to revive the adsorbent

4. Ability to recycle metals

5. High process speed

6- No sludge production, very high purification rate and observance of the strictest environmental discharge standards.

Ahmadi Asbochin (2015) reported that there is no restriction on the use of live cells in the industry in the use of the studied algae (Grasillaria, Cystosyra, and Focus). The amount of algae cystosyra and grasilaria.

There are many cheap and cheap beaches in the south of Iran, the Persian Gulf and the Sea of Oman. As the pH increases, so does the density of the OH^{-} ions, Metal ions reduce the percentage of adsorption by hydroxide.

It was also found that by increasing the initial concentration of the ion, the rate of metal adsorption increases and it can be concluded that the adsorbent sites are filled and no longer have the ability to absorb more nickel metal.

It also follows the adsorption temperatures to remove the nickel ion from the Langmuir temperature. Due to the linearity of the graphs, the adsorption coefficient of this adsorption coefficient has been proved. Microorganisms, algae, can be used as biological attractions in industrial use when, in addition to having a high potential for bonding metals, they are also used as a fixed or movable substrate and do not cause a large drop in the system for this purpose. Processes such as measurement, chemical modification, or stabilization and granulation are used, which help to create a suitable structure for the efficiency of adsorbents in the reactor and increase the adsorption capacity. More important work in the adsorption of metals by adsorbents, such as the role of ion exchange in metal adsorption, metal adsorption simultaneously, the use of real samples of industrial effluents. It must be made of metal.

The nickel metal adsorption kinetics are completely different from the biomass of focal algae, cystosyria, and grasilaria. In bacteria, the equilibrium time is about 121 minutes but in focal algae about 311 minutes, in cystosyria 351 minutes in Grasilaria is about 411 minutes (Figure 2). Determination equilibrium time plays an important role in industrial use.

The criterion for achieving equilibrium conditions is from the time perspective, after which time, the adsorption increase or, to be more precise, the removal of metal from the aqueous solution will no longer take place, and the rate of metal removal will no longer occur.

The solution remains constant.

Investigation of nickel adsorption by adsorbents in relation to the amount of metal concentration in the solution with the highest metal adsorption

It is especially important for absorbers. As shown in Figure 3, as the metal's environmental concentration increases, the adsorption of nickel ions by the adsorbents also increases.

According to the Longmoir model, 0.4 mmol/g in Bacillus is up to 0.9 mmol/g in focus (Figure 3). Experimental interpretation shows that by increasing the environmental concentration of the metal, the adsorption rate increases.

It takes place. This increase in adsorption until a specific concentration occurs is not due to an increase in the adsorption concentration.

Finally, for industrial use, the use of brown algae is recommended and has more advantages than other adsorbents.

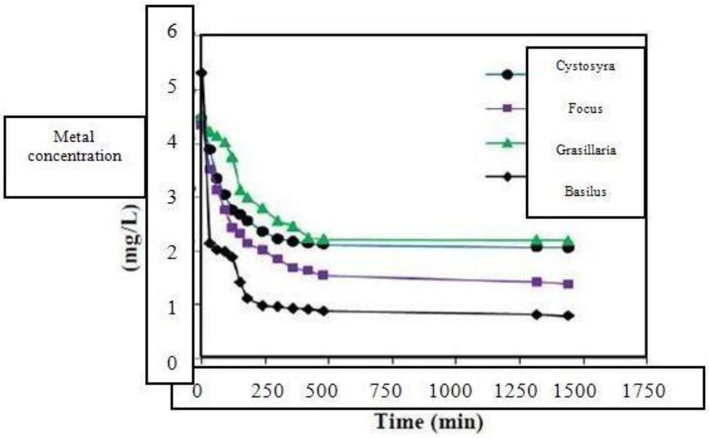

Fig 2. Synthetic study of nickel ion uptake by adsorbents. 22^{0c} temperature, the adsorption rate of 1 g/liter and pH about 6 (Ahmadi Asbochin 2015)

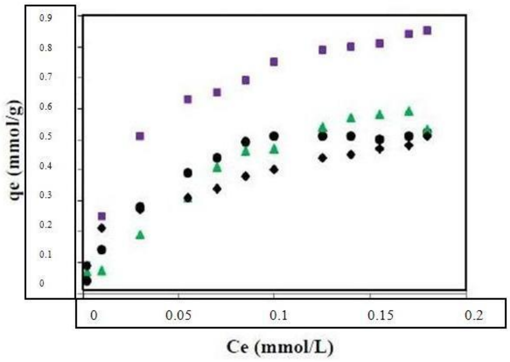

Fig 3. Comparison of nickel adsorption by adsorbents. 22^{0c} temperature, the adsorption rate of 1 g/liter and pH about 6 (Ahmadi Asbochin 2015)

Results

In general, the cost of treatment by biological methods is much lower than the cost of treatment with chemical methods such as commercial ion exchange resins, chemical precipitation and reverse osmosis to remove heavy metals from aqueous media. But the main disadvantage of biological treatment methods is that these are new and currently in the early stages of development.

there is a fact in heavy metal removal methods by biological treatment that the technology of its use in Iran and other parts of the world is very limited and its operating conditions are only on a pilot and laboratory scale and under controlled conditions. This new technology is in its infancy and is currently in the early stages of development, as expected in the near future with the acquisition of science and technology and knowledge of real-scale operation and improvement of its performance, as well as communication with industry. Production the manufacturer of similar products and the consumer industry of this technology, with the spread of this cheap technology, an important step will be taken to improve the quality of the environment.

It has been studied and it is very difficult to generalize the results and provide the mentioned conditions on real scales and it is necessary to spend the time and previous experience gained in the field of similar designs.

For example, with small changes in pH, the removal efficiency of metals will be different, assuming that other parameters are controlled, on the other hand, the adaptation period (adaptation of microorganisms to the environment) is long and the start-up of biological reactors requires time. It will be for the system to achieve so-called stability.

Also, changes in the quantity and quality of incoming sewage flow, such as decreasing or increasing the concentration of constituents and elements in it, changing the flow regime inside the reactor and incoming sewage, etc., cause unwanted fluctuations in the reactor and then cause growth disturbance and ultimately the percentage of metal removal is reduced. According to the above interpretations, it can be said that the growth curve of microorganisms will not be adapted to the new conditions, which will result in non-uniformity in the quality of effluent and instability in the removal of pollutants.

Discussion

Result of description and studies of different methods in removal of heavy metals from industrial wastewater such as Physico-chemical methods and biological methods showed that these methods are all effective in removing these elements according to the conditions provided. On a laboratory scale, these methods are able to remove these metals with varying degrees and different efficiencies.

Biological methods of removing heavy metals such as biosorption and removal by algae are new methods that can be used under controlled laboratory conditions (such as temperature regulation, pH adjustment and other effective parameters) with high removal efficiency above 90 % according to (Tsezos and Volesky 1982, Volesky 1990, Kuyucak and Volesky 1989).

Conclusion

The biosorption process is a good way to remove heavy metals such as chromium, cadmium, nickel, cobalt, zinc and plumbum from the aquatic environment. this process can produce metals with a concentration of µg/lit of metals, and its cost is much lower than the cost of commercial ion exchange resins. While biodegradable technology is still in the early stages of development, its price is expected to decline and its performance improve in the future, but for large-scale use, more research is needed to connect with industries producing similar products and the consumer industry is this technology.

Thus, with the spread of this cheap technology, an important step will be taken to improve the quality of the environment.

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Author Contributions

Hamid Goran OUrimi: Proposed the plan, Studied the previous experiments, analyzed the data, prepared figures, and tables, authored or revised drafts of the paper.

Mehdi Nezhadnaderi: Studied the previous experiments, analyzed the data(Tempreture, PH, max adsorption capacity, adsorption capacity and metal ions), contributed reagents, materials, analysis tools, prepared figures, and tables, approved the final draft.

Ethics Statement

The study was conducted by Tonekabon Branch Islamic Azad University.

Supplemental Information

There is no supplementary information on this paper. Any questions and request for more information should be addressed on correspondence author.

References

Adams AD, (1975) Activated carbon old solution toold problem part 1,2. J. w.s.w, 118(8-9): 46-48, 78-80.

Ahmadi Asbochin S, (2015) Comparison of nickel synthetic study and biological adsorption by bacteria and red algae and brown. Iranian Journal of Chemistry and Chemical Engineering. 34(3). 41-46.

Aksu Z, Acikel U, Kabasakal E, Tezer S, (2002) Equilibrium modeling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge. Water Res, 36: 3036-3073.

Arup k, Senguptx ED, (1995) Ion exchange technology: Advances in pollution control. Technomic Publishing Company, Inc., Lancaster, PA, U.S, 399..

Asmi N, (1999) Preventing the loss of chromium in the plating industry and examining the possibility of recycling it by ion exchange method, M.Sc. Thesis, University of Tehran.

Bahnemann D, (2004) Photocatalytic water treatment: Solar energy applications. Sol Energy, 77: 445-9.

Baird C, (1995). Environmental chemistry. W.H. Freeman and company. New York.

Banshi MM, (2002) Investigation of Anionic Resin Performance in Simultaneous Removal of Organic and Mineral Pollutants from Water. Master Thesis, Faculty of Health, University of Tehran.

Bolong N, (2000) A review of the effect of emerging contamination in wastewater and options for their removal. Desalination. 239: 229-46.

Brady D, Stoll A, Ducan JR, (1994) Biosorption of Heavy Metal cations by non-viable yeast biomass. Environmental Technology. 15: 248-249.

Cain M, Morrell R, (2001) Nanostructured ceramics: a review of their potential. Appl Organomet Chem, 15: 321-30.

Chen G, (2004) Electrochemical technologies in wastewater treatment, separation and purification. Technology, 38: 11-41.

Chicgoua N, Sabine C, Richard C, (2012) Nanoscale Metallic Iron for Environmental Remediation: Prospects and Limitations. Water Air Soil Pollut, 223:1363–82.

Choe S, Chang Y.Y, Hwang K.Y, Khim J, (2000) Kinetics of reductive denitrification by nanoscale zero-valent iron. J Chemosphere, 41(8): 1307-11.

Chutia P, Kato S, Kojima T, Satokawa S, (2009) Arsenic adsorption from aqueous solution on synthetic zeolites. J Hazard Matter, 162: 440-47.

Dabrowski A, Hubicki Z, (2004) Selective removal of the heavy metal Ions from waters and Industrial waste waters by Ion-exchange method. ChemospHere, 91-106.

Davis T.A, Volesky B, Vieira R.H.S.F, (2000) Sargassum seaweed as biosorbent for heavy metals. Water Res, 34: 4270-4278.

Diniz V, Volesky B, (2005) Biosorption of La, Eu and Yb using Sargassum biomass. Water Res, 39: 239-247.

Dyer A, Hudson MJ, Williams PA, (1997) PROGRESS progress in ion exchange advances and applications. 1st Edition, Kindle Edition.

Garcia S, Ake C, Clement B, Huebuer H, Donnelly K, Shalat S (2001) (Garcia S, C. Ake, B. Clement, H. Huebuer, K. Donnelly, S.Shalat. Initial results of environmental Monitoring in the Texas Rio Grande Valley. Environ Int, 26(7-8): 465-74.

Gupta R, Ahuja P, Khan S, Sexena, R.K, Mohapatra H, (2000) Microbial biosorbents: Meeting challenges of heavy metal pollution in aqueous solutions. Current Science, 78:967-973.

Harland C.E, (2012) Ion Exchange: theory and practice, 2nd Edition.

Holan Z.R, Volesky B, Prasetyo I, (1993) Biosorption of Cd by biomass of marine algae. Biotech. Bioeng, 41: 819-825.

Hassani A.H, (2000) PhD Thesis in Environmental Engineering. Investigating the Performance of Continuous Operating Continuous Reactors (SBR) in the Treatment of Industrial Wastewater containing Phenolic Compounds.

Jalali R, Ghafourian H, Asef Y, Davarpanah, S.J, Sepehr S, (2002) Removal and recovery of lead using nonliving biomass of marine algae. Journal of Hazardous Materials, 92: 253-262.

Kuyucak N, Volesky B, (1989) Desorption of cobalt-laden algal biosorbent. Biotechnol. Bioeng, 33(7): 815-823.

Li X.Q, Zhang W.X, (2006) Iron Nanoparticles: The Core-Shell Structure and Unique Properties for Ni(II) Sequestration. Langmuir, 22(10): 4638-42.

Liou Y.H, Lo S.L, Lin C.J, Kuan W.H, Weng S.C, (2005) Chemical reduction of an unbuffered nitrate solution using catalyzed and uncatalyzed nanoscale iron particles. J of Hazard Mater, 127 (1): 102-10.

Li Y, Somorjai G.A, (2010) Nanoscale advances in catalysis and energy applications. Nano Lett, 10(7): 2289–95.

Loukidou M.X., Zouboulis A.I, Karapantsios T.D, Matis K.A, (2004) Equilibrium and kinetic modeling of chromium (VI) biosorption by Aeromonas caviae. Collids and Surfaces A: Physicochem. Eng. Aspects, 242: 93-104.

Malek Ahmad A.H, (2002) Master Thesis. Investigating the performance of continuous sequential operation (SBR) reactors in the treatment of industrial effluents containing heavy metals, mercury and cadmium.

Marhol M, (1982) Ion Exchangers in analytical chemistry. Their properties and use in inorganic chemistry. Volume 4, 1st Edition. Elsevier Science, 585.

Mohammadi-Aloucheh R, Alaee Mollabashi Y, Asadi A, Baris O, Golamzadeh S, (2018) The role of nanobiosensors in identifying pathogens and environmental hazards, Anthropogenic Pollution Journal, 2 (2): 16-25.

Paul AB, (1996) Electrolytic treatment of turbid water in package plant. 22nd WEDC conference. NewDehli.

Paul, AB, (1996). Electrolytic treatment of turbid water in package plant. in: Pickford, J. et al. (eds). Reaching the unreached - Challenges for the 21st century. Proceedings of the 22nd WEDC International Conference, New Delhi, India, 9-13.

Robertaccio F.L, Flynn B.P, (1976) Truth or consequences: biological fouling and other consideration in the PAC-AS system. 31th purdue industrial waste conference, 855-862.

Salmani M.H, Ehrampoush M.H, Aboiian M, (2013) Comparison between Ag (I) and Ni (II) removal from synthetic nuclear power plant coolant water by iron oxide nanoparticles. J Health Eng Sci, 11(1): 21.

Sarioglu M, (2004) Removal of ammonium from municipal waste water using natural Turkish (Dogantepe) Zeolite. separation and purification Technology, 41(1):1-11.

Savage N, Diallo M.S, (2005) Nanomaterials and water purification: opportunities and challenges. J Nanoparticle Res, 7: 331–42.

Schrick B, Blough J.L, Jones A.D, Mallouk T.E, (2002) Nanotechnology for water treatment application. Chem. Mater, 14: 5140.

Shohoudi M, (2004) Investigating the possibility of removing copper and nickel from industrial plating wastewater and recycling it as salts using T.M.A. type mineral mineral resin. Master Thesis. University of Tehran.

Takafuj M, Ide H, Ihara S, Xu Z, (2004) Noncrystalline L-Phenylalanine-Silica Hybrid Composite Materials. Chem. Mater, 16(10): 1977-83.

Tsezos M, Volesky B, (1982) The mechanism of uranium biosorption. Biotechnol. Bioeng, 24: 385-392.

Volesky B, (1990) Biosorption of Heavy Metals. CRC Press, Boca Raton, USA.

Volesky B., Kuyucak, N, (1998) Biosorbents for gold. US Patent, No 4, 769, 223.

Volesky B, (2001) Detoxification of metal-bearing effluents: biosorption for the next century. Hydrometallurgy, 59: 203-216.

Yan G, Viraraghavan T, (2003) Heavy metal removal from aqueous solution by fungus Mucor rouxii, Water Res, 37: 4486-4496.

Wang L, Li J, Jiang Q, Zhao L, (2012) Water-soluble Fe3O4 nanoparticles with high solubility for removal of heavy-metal ions from waste water. Dalton Trans, 41: 4544-51.

Wang L.Y, Luo J, Maye M.M, Fan Q, Qiang R.D, (2005) Iron oxide-gold core shell nanoparticles and thin film assembly. J Mater Chem, 15(18): 1821-32.

Wase J, Forster C, (1997) Biosorbents for Metal Ions. Taylor and Francis Ltd.

Xiong Z, Zhao D, Pan G, (2007) Rapid and complete destruction of perchlorate in water and ionexchange brine using stabilized zero-valent iron nanoparticles. Water Res, 41(15): 3497–505.