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Investigation of Metal Toxins in Industrial Wastewater

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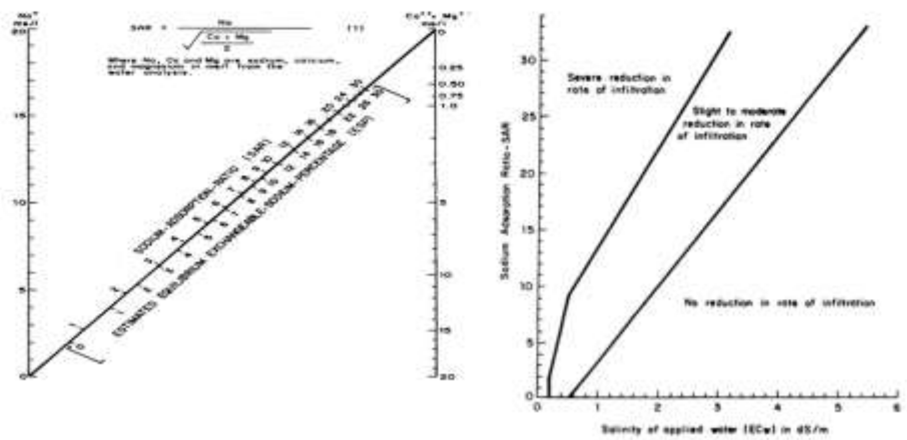
ABSTRACT

Industrial Wastewater due to its chemical and physical contents can be the source of positive and negative effects on irrigated soil. In this study, the quality of the effluent of the Malaysian refinery was studied and its long-term effect on the soil of the green space around the plant was investigated. The results showed that the effects of the use of mentioned industrial effluent in terms of salinity, chloride, sulfate and sodium adsorption ratio are more than normal irrigation water. In terms of BOD, COD and fecal coliforms, effluent conditions are acceptable. In terms of fat, the effluent is higher than the standard. For these conditions, it is recommended to apply physical filtration from the wood chips bed in the transmission channel and physical filtration in the central control unit of the drip irrigation system. In summary, the results of this study show that the use of refinery effluent is not limited if filtration and mixing are used to qualitatively modify environmental and irrigation problems. In addition, studies of this reseach show that the time factor is effective in changing the quality of wastewater and therefore qualitative evaluation is recommended in different seasons.

GRAPHICAL ABSTRACT



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INTRODUCTION

Properly use of wastewater, while it can control the problems caused by the spread of pollution in the environment and water sources, can increase the yield of products due to the nutrients in it. Industrial wastewater is very extensive and variable in terms of quality. Irrigation with industrial wastewater has long been common in Iran, but the effects of this use on the physical and chemical properties of soil should be studied. Due to the diversity of industrial wastewater quality, the effects of these effluents on the soil are also different. Iran is located in an arid and semi-arid region and its average rainfall with 240 mm of rainfall compared to the global average of about 830 mm of rainfall is lacking. On the other hand, the country's population is expanding and most of the country's population is concentrated in large cities, and as a result, distribution of population in the vast country of Iran is not balanced and population density around urban areas is very high. In this regard, many industrial centers are concentrated in these areas [1]. Therefore, the high volume of water required for use in drinking and industrial uses has caused the volume of fresh water required in the agricultural sector in these areas to be greatly reduced. Also, many soils that have been cultivated for years and have an acceptable level of fertility, unfortunately have been allocated to the expansion of industrial and urban areas or buried under thousands of tons of concrete and iron. Naturally, the green space and agriculture of these areas have shifted to poorer soils, and farmers are looking for ways to improve the fertility of these lands [2]. In addition, environmentalists, municipalities, service and environmental units of industrial units have designed green belts in order to achieve environmental standards around cities and industrial areas, which have also been in crisis due to lack of fresh water and low quality soil resources. On the other hand, the presence of population and industrial centers in the mentioned areas converts a significant volume of fresh water into sewage. In case of injection of wastewater into surface water or groundwater sources or uncontrolled injection into the soil, it causes many environmental problems. Many findings emphasize that most urban and industrial wastewater is renewable and can be used in green and agricultural areas [3]. Utilization of urban and industrial wastewater in green and agricultural areas should be with health and environmental considerations and as a result quality of soil and product of irrigation with wastewater should be considered [4]. Iran Environment Organization has provided a standard for the use of wastewater in green space and agriculture. According to this standard, minimum values are provided for some important parameters in wastewater, but what is important is that the conditions of wastewater use depend on various factors that without considering those factors, we will not have proper management of this resource [5-7]. Sewage accounts for five percent of the country's total surface water resources, which is very important for our country, which is located in an arid and semi-arid region, given that this resource is more abundant around large urban centers. Therefore, in addition to increasing the efficiency of wastewater use and maximizing the use of the source, on the one hand, there should be a concern about environmental conditions and on the other hand, excessive wastewater treatment, while imposing heavy costs on the country's economy. However, it should be mentioned that it is a useful food and organic that can help enrich agricultural soil [8].

Utilization of Sewage

The general structure of the wastewater utilization model is discussed in three levels as the origin of the effluent used, the treatment process and how to utilize it. The source of effluents used around large cities is mainly industrial, human and rainwater runoff in the city and industrial areas. Industrial wastes from refining, petrochemical, food and chemical, metal industries and so on can be divided. In areas where the groundwater level is high or there are impermeable layers near the ground level, drainage network is necessary in agricultural lands and the resulting drainage at lower levels should be reused [9-11]. Also, effluents from other agricultural and livestock activities such as livestock, slaughterhouses, etc. are highly polluted, which requires special management. Leachate from municipal wastewater is also a rich source of nutrients that, if used properly, can be useful in repairing infertile and alkaline soils. Selecting the amount of treatment required to improve the effluent quality before use, is the second level of the proposed structure [12]. At this level, in order to use the effluent in agriculture, different levels of treatment are provided. These levels include primary treatment which is mostly physical treatment, and secondary treatment, such as activated sludge and drip filtration, while at the final stage it can be an aeration basins which is mostly biological treatment. Slow treatment instead of rapid treatment such as stabilization ponds and ground treatment in many places depending on the conditions is recommended, which can be applicable in our country, while has a lot of desert land. In certain circumstances, higher levels of filtration, such as reverse osmosis, can also occur, which is naturally associated with higher costs and technology. How to use treated effluent or wastewater is the most important part of this structure. Accordingly, based on the quality of treated effluent and environmental conditions, the method of exploitation should be presented. Exploitation method includes type of plants under cultivation, cultivation frequency, irrigation method, amount of hydraulic load per unit area according to the organic load in the effluent, amount of leaching according to the amount of special washable salts and ions and finally, amount of fresh water required to compensate for the drop soil or crop quality [13].

Input Data

One of the most important input data is the quality characteristics of wastewater before reuse in irrigation. These properties are divided into three main categories including chemical, physical and biological factors. Chemical factors include EC, SAR, COD, pH-value, toxicity of special elements such as chloride, boron, carbonate and bicarbonate, nutrient concentration, heavy element and nitrate concentration, nitrite, phosphate, sulfate, phenol, cyanide, etc [14]. Biological properties include BOD_5, total number of coliforms, fecal coliforms, nematodes, total number of bacteria, etc. Physical properties include DO, TSS, turbidity, organic matter and dye. The values of these factors vary depending on the source of the effluent. Therefore, the input parameters can be changed according to the origin of the effluent. Climatic conditions will be one of the most important inputs in the proposed model. Temperature can affect the amount of BOD_5, microorganisms in wastewater and, by its nature, some organic and inorganic amounts, including nitrate [15-18]. Temperature factor in addition to daylight hours, relative humidity and wind speed are also important climatic factors due to their effect on the intensity of evapotranspiration. Wind is also important in choosing the irrigation method in the case of wastewater reuse and causes spraying methods such as sprinkler irrigation to be abandoned in windy areas. Also latitude and longitude, effective rainfall and irrigation time are among the requirements of input data to be able to calculate the water needs of plants. In addition, soil texture will affect application conditions while physical properties include soil structure and texture. The heavier the soil texture, the greater the reduction of pollutant characteristics under groundwater treatment. Permeability will affect the amount of waste water due to the application and intensity of the hydraulic load used [19].

Cultivated plants can be classified into plants that are consumed raw, industrial plants that are ultimately edible, and non-edible industrial plants and non-fruitful plants. Plants that are consumed orally according to the consumption process should be in the microbial threshold and also in terms of the accumulation of various elements such as heavy elements named as lead, cadmium, chromium, nickel, mercury, arsenic, cobalt, etc. Other ions such as nitrate, which can cause health problems for consumers, should also be considered. Another parameter that should be considered is the tolerance threshold of the plant to various chemical parameters of the effluent, such as salinity, adsorption ratio of sodium, chloride, sodium, barium. The possibility of the spread of some plant diseases due to microbial contamination of the effluent can also be considered. On the other hand, some plants play a good role in absorbing polluting elements and can be effective in treating contaminated soil due to the use of unconventional water sources [20].

Model outputs

The proposed model must have the following output:

1. Provide suggestions for repair and modification of wastewater before use according to the input data, including the amount of treatment required for different levels of wastewater application. These suggestions depend a lot on how the wastewater is used and how it is reused. Also, the volume of treatable wastewater, climatic conditions, cost and level of investment and finally land value are other effective factors in this field. Recommendations include additional pre-irrigation treatments such as filtration, ground treatment, aeration lagoons, disinfection, etc. Depending on the quality of the effluent and the type of irrigation method selected, part of the treatment can be assigned to the irrigation system process. Also, in conditions of low effluent quality, application of mixed effluent with fresh water or intermittent application of effluent and fresh water can avoid heavy treatment costs. The studies of Najafi et al. (2004) showed that application of subsurface drip irrigation filtration is significantly effective in reducing the load of effluent pollution and supplementary treatment.
2. Providing planting frequency in order to control soil quality conditions in terms of compliance with environmental standards and maintaining and improving soil fertility quality.
3. Determining the amount of water required in each irrigation according to the water quality conditions so that the solutes in the soil, the concentration of special elements in the soil and heavy elements remain at the desired level. At the same time, the amount of irrigation water should be determined in such a way that the mentioned source is used optimally and the water consumption efficiency is maximally possible. The amount of water injection into the soil is also important in terms of soil quality and environmental standards. Controlling the amount of entry into the soil can lead to controlling the concentration of toxic elements allowed in the soil. Also, controlling the input amount of organic load per unit area leads to the use of soil potential for wastewater treatment at the irrigation site. Studies show that based on the amount of BOD_5, the permitted effluent in the soil can be adjusted to determine the irrigation cycle by calculating readily available water and plant evapotranspiration. The calculation of evapotranspiration depends on the water quality conditions. In 2007, Najafi et al. introduced the EC parameter in

the evaluation of evapotranspiration potential by presenting the ET-HS model.

4. Provide suggestions on providing an irrigation system among the possible methods in the area, if the subsurface drip irrigation method is used.

Concentration of all salts

The concentration of salts (for practical purposes and total soluble salts) is one of the most important parameters in determining the quality of agricultural water. Water-soluble salts are associated with soil salinity, and therefore plant growth, yield and crop quality are affected by all water-soluble salts.

Electrical Conductivity

Electrical conductivity is used to indicate the amount of ions in water. Electrical conductivity is directly related to the sum of the anions or cations resulting from decomposition of chemicals and is generally related to the total salts. Electrical conductivity is usually expressed at a standard temperature that is 22 °C, which of course can be changed and adapted to other conditions. EC_w indicates the electrical conductivity of water and EC_e indicates the electrical conductivity of the soil saturated extract and its unit of measurement is dS/m which shows the components of salts in irrigation water and the conversion relationships of total soluble salts to electrical conductivity.

Much research has been done on the effects of salinity on plant growth. The FAO divides plant resistance to salinity into four categories: sensitive, semi-sensitive, semi-resistant and resistant.

Sodium uptake Ratio

Sodium is one of the most unique cations due to its many effects on the soil. Exchangeable sodium can alter the physicochemical properties of soil, especially its structure, when it is above its threshold relative to the total salt concentration. Exchangeable sodium tends to disperse in the soil and slows down the infiltration of climate into the soil. Also, this scattering of particles causes the formation of a layer of tubercles on the soil surface and prevents seed germination. Irrigation water can be considered as a source of increasing soluble sodium in the soil and should be evaluated in this regard. Table 2 shows the salinity and sodium problems in soil and plants.

Table 1. Resistance of ornamental flowers to soil saturated extract

Low tolerance	Moderate tolerance	High tolerance
EC_e less than 2.0 dS/m*	EC_e= 2.0-3.0 dS/m*	EC_e= 3.0-4.0 dS/m*
China Aster	Carnation	Rose
Geranium	Poinsettia	
Lily	Chrysanthemum	
Gardenia		
Azelae		

*Approximate tolerance ranges. *Very little research has been done on the salinity tolerance of flowers.*

Table 2. Effects of salinity on irrigation water in soil and plants

Types of salinity problems

Salinity hazard	$\xrightarrow{effects}$	Plants	$\xrightarrow{can\ lead\ to}$	Saline soil condition
Sodium	$\xrightarrow{effects}$	Soils	$\xrightarrow{can\ lead\ to}$	Sodic soil condition

The most reliable indicator for determining the effect of irrigation water on increasing soil exchange sodium is the parameter of sodium uptake ratio or SAR, which is defined as follows (eq. 1):

$$SAR = \frac{Na}{\sqrt{(Ca+Mg)/_2}} \quad \text{(eq. 1)}$$

In the above relation, the concentration of ions is expressed in meq/l. In addition, using equation 2, the SAR value of irrigation water can be determined. Also, from this equation, the percentage of exchangeable sodium (ESP) in a soil balanced with irrigation water can be obtained.

$$ESP = \frac{y^{1+LF}}{LF^{0.5}} SAR_{adj} \quad \text{(eq. 2)}$$

Under field conditions, the true ESP value may be higher than the value estimated from the figure because under field conditions, the total salt concentration is increasing by evapotranspiration.

The SAR value calculated from equation 1 predicts the effect of sodium ions on irrigation water before water enters the soil. If the amount of SAR usually changes after water enters the soil and it is soil water that affects the soil structure then the amount of sodium ions due to solubility remains more or less constant after the entry of water into the soil, but the concentration of Ca ions after the entry of water into the soil in relation to the amount of bicarbonate and carbonate anions in irrigation water and carbon dioxide pressure in soil air changes. To solve this problem, Ayers and Wescott (1989) proposed the modified SAR method (SAR_{adj}) which is calculated according to equation 3:

$$SAR_{adj} = SAR_{iw}[1 + (8.4 - pH_c) \quad \text{(eq. 3)}$$

where in:

Table 3. Parameter & definition

Parameter	Definition
SAR_{adj}	Modified sodium adsorption ratio
SAR_{iw}	Sodium absorption ratio of irrigation water
pK_2	Negative constant logarithm of the second ionization H_2CO_3 (corrected for ionic strength)
pK_{sp}	$CaCO_3$ solubility coefficient (corrected for ionic strength)
p (Ca + Mg)	Negative logarithm of molar concentration of calcium plus magnesium
p (CO_3 + HCO_3)	Negative logarithm of equivalence of carbonate and bicarbonate

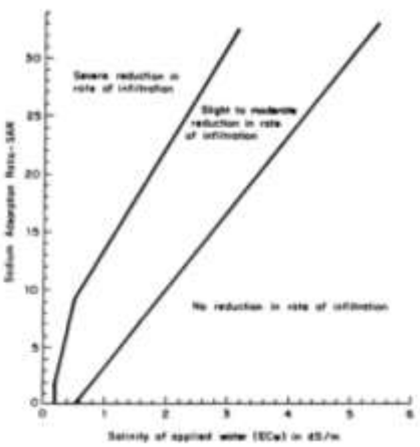

Fig. 1. Relation between sodium absorption and salinity

The mentioned values can be obtained by having the concentration of total cations from the second column (pK_2-pK_{sp},) having p(Ca + Mg) from the third column and having p (CO_3 + HCO_3) from the fourth column pH_c. In equation 3, the value 8.8-pH_C is known as the saturation index (SI). This parameter is important in direct drip irrigation conditions and if its value is positive, it indicates the deposition of calcium carbonate at the site of the drippers. The amount of SAR_{adj} can be evaluated based on the amount of soil EC and its effects on the permeability rate can be investigated (**Fig. 1**).

Toxic ions

Irrigation waters where the concentration of some ions is higher than the allowable level can cause problems in plant poisoning. Toxicity usually results in impaired root activity, reduced yield, deformed plant appearance, and even plant death. The severity of damage caused by poisoning depends on the type of crop, plant growth stage, toxic ion concentration, climate condition and soil conditions. The most important toxic ions are bor (Br), chloride (Cl) and sodium (Na). When wastewater is used for irrigation, it is necessary to measure and control the concentration of these ions.

Sodium

In addition to its effect on soil physics, sodium is also important for toxicity. Most woody and perennial woody plants are sensitive to even low sodium concentrations. Annuals are not as vulnerable and are likely to be vulnerable to higher concentrations. Sodium is absorbed by the plant along with water, and as water is removed from the leaves due to transpiration, the concentration of sodium in the leaves is increased. Leaf burn and formation of dead tissue in the margin of the leaf are obvious signs of poisoning. In the presence of calcium, the severity of sodium toxicity is adjusted. If the amount of calcium is not high, the degree of toxicity caused by sodium is probably reduced by a small amount, and if it is high, the problem will probably be prevented. Since the effect of sodium depends on both the amount of sodium and the amount of calcium, in assessing the potential toxicity problem, the sodium uptake ratio (SAR) for soil water and the adjusted sodium uptake ratio (SAR_{adj}) for irrigation are used (1).

ESP-susceptible plants usually tolerate less than 12, semi-resistant ESP plants between 18 and 30, and resistant ESP plants above 30. However, ESP above 25 creates unfavorable conditions for most plants in terms of physical properties.

Chloride

Most of the poisoning caused by irrigation water is due to the presence of chloride ions in it. Chloride ions are not adsorbed on the surface of soil particles but are transferred to the soil by moisture and after adsorption through the roots, like sodium, accumulate in the leaves. Tree and perennial plants are sensitive to low chloride concentrations, while most annuals are usually not.

Table 4. Permissible amounts of chloride on plant sensitivity in milligrams per liter

Sensitivity	Chloride (mg/l)	Affected crop
Sensitive	< 178	Almond, apricot, plum
Moderately sensitive	178-355	Grape, pepper, potato, tomato
Moderately tolerant	355-710	Alfalfa, barley, corn, cucumber
Tolerant	> 710	Cauliflower, cotton, safflower, sesame, sorghum, sugar beet, sunflower

Symptoms of chlorine poisoning start from the tip of the leaf in the form of burning and gradually spread to the surface and in the developmental stage, leaf burn, premature leaf fall and leaflessness occur (1). Table 3 summarized the levels and affected crops.

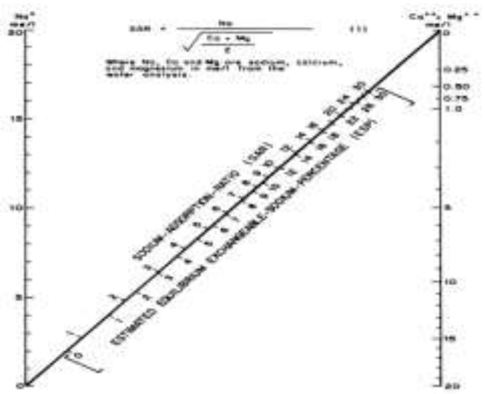

Fig. 2. Graph for determining the ratio of sodium adsorption ratio (SAR) and percentage of exchangeable sodium (ESP)

Miscellaneous effects

Physical Properties: Microparticles cause clogging of soil pores, but are probably useful in sandy soils. Organic matter in water can be collectively beneficial to the soil. Odor and color can be controlled by purification. Smell is a sign of incomplete purification and strong odor is a sign of non-purification. If secondary treatment is performed on wastewater, it is usually less associated with odors. Another physical property is temperature, which usually does not pose a problem for the plant.

Nitrogen

Nitrogen range in raw wastewater effluent varies between 15 to 80 mg/l, in primary effluent between 15 to 55 mg/l and in secondary effluent between 5 to 25 mg/l. Wastewater nitrogen includes organic nitrogen, ammonia, nitrate, and nitrite, which is usually less than 3 mg/l nitrite. The concentration of nitrate in wastewater is usually 7% of the total. In the United States, the concentration of nitrate in municipal secondary effluents is between (0-5) mg/l. Nitrogen is a nutrient necessary for the survival of living organisms that is usually added to the soil in agriculture to produce higher yields. Factors such as nitrogen consumption, time during plant growth period and nitrogen source, soil moisture, soil salinity, soil compaction, weeds, diseases and soil organic matter can all affect the efficiency of nitrogen in the cultivation of agricultural crops. Secondary wastewater causes a significant amount of nitrogen to enter the soil. Also, special conditions of wastewater effluent cause some factors affecting the efficiency of nitrogen to be provided spontaneously. Including the fact that wastewater nitrogen gradually enters the soil as a solution. Also, the presence of organic matter and microorganisms in the wastewater can have a positive effect on the efficiency of available nitrogen. In any case, the use of wastewater, plant nitrogen uptake, soil nitrogen uptake, gas nitrogen lost and leached nitrogen can affect the root area. Irrigation management has a significant effect on the above values. Studies have shown that fertilization with irrigation has a significant effect on crop yield. The use of wastewater, in addition to being a kind of fertilizer with irrigation, has the advantage that fertilizer is given to the product in full installments.

The average nitrogen content of plants is between 1 and 7% and may reach 10%. Crops can absorb and use NO^{3-} and NH^{4+} ions. The NO^{3-} form is adsorbed in the soil mainly due to the rapid conversion of NH^{4+} to NO^{3-}. Heat and anaerobic conditions such as submerging the soil for denitrification. Soil and heat ventilation is desirable for nitrification.

pH-value

The pH range of irrigation water changes from 5.5 to 77.5 in which the plant has good growth.

Toxicity of minor elements

Sewage, especially if it is industrial, probably contains a number of toxic elements including heavy metals. These toxic elements are usually found in small amounts and therefore they are also called trace elements. Some of these elements are removed in the refining process. But others are more stable and can cause poisoning problems. Therefore, municipal wastewater effluent should be tested and examined in terms of hazards caused by these elements, especially when it is questioned in terms of trace elements.

Zinc

The most important application of zinc in water supply pipes and industries is paint, rubber, pharmaceuticals, mines, inks, floor coverings and cosmetics. For this reason, too much zinc in fertilizers from municipal and industrial wastewater is problematic. Zinc is important in human and animal nutrition and is found in peptidase and plant dehydrogenase enzymes. The World Health Organization recommends a maximum daily intake of 1 mg/kg of body weight. Sludge and factory effluents can contain up to 5% zinc and, if added to the soil, upset the balance of ions and prevent the absorption of other elements such as iron. The symptoms of zinc poisoning appear in amounts of more than 250 mg/kg of plant dry matter. It can also cause poisoning if the zinc concentration in the feed exceeds 0.1%. Also, the taste threshold of zinc in drinking water is approximately 5 mg/l.

Copper

Too much copper is harmful to soil microscopic organisms. Therefore, high consumption of copper sulfate in farms reduces the activity of these organisms, and stops decomposition and decay processes carried out by microscopic organisms. The mobility of copper in the soil is very low and its movement is mainly achieved through the intense absorption of copper by organic matter and clay. Many plants, especially cereals and citrus fruits, are sensitive to copper deficiency in the soil, and the toxicity of copper to plants is double that of zinc. Plant contamination with copper is common in areas where there are copper-containing compounds or in industrial areas or lands exposed to industrial wastewater. According to a study, the permissible amount of copper entering the human body is 0.5 mg/l and its amount in drinking water is 2 mg/l.

Cadmium

Improper application of phosphorus fertilizer and the use of sewage sludge in the soil of agricultural lands and green space, increase cadmium in the soil. Cadmium is non-dynamic in soil and accumulates in shallow depths. Studies by Chaino (6) show that there is an average of 5 mg of cadmium per kilogram of superphosphate, so consuming 376 kg of superphosphate per hectare per year in New Zealand for 27 consecutive years increases cadmium from 53 to 1.41 mg/kg soil. It also depends on the phosphate source. Chino also shows that industrial wastewater sludge in Japan averages 7.2 mg/kg and domestic sewage sludge averages 2.17 mg/kg cadmium. In general, high concentrations of cadmium are toxic to plants, but in most plants it can accumulate in the plant without showing signs of poisoning, but the presence of this element in the human food chain is very dangerous.

The World Health Organization has set a limit of one microgram per kilogram of body weight per day in the human diet. In drinking water, a threshold of 0.005 mg/l is recommended. Except in these cases, USEPA considers the maximum permissible cadmium concentration to be 0.04 g/kg of agricultural dry matter.

Iron

Iron is a trace element needed by plants. The adequacy of this element in most plants is 5-300 mg/kg in plant dry matter. The critical limit of this element for a large number of plants is 300 mg/kg. In soil, the critical level at the absorbable level is between 20-25 mg/kg. Iron in soil solution is affected by soil pH-value and with increasing soil pH, the amount of soluble iron decreases. In the case of humans and animals, the absorption of 6-20 mg is acceptable and if it reaches 150 mg, it becomes poisonous and 7 to 35 g is lethal.

Manganese

Manganese adequacy in leaves varies from 10-40 mg/kg in adult leaf dry matter. Its amount in tissues reaches 200 mg/kg or more. Citrus is one of the plants that are sensitive to this element and its adequacy in the plant in the growing organ is between 18-50 mg/kg. This element also decreases with increasing pH-value and its absorption capacity and on the contrary at pH-values less than 5.5 symptoms of manganese toxicity may be observed.

Nickel

For decades, nickel was considered a toxic element because its concentration in various foods exceeded the amount needed for living organisms. It has recently been considered as a potentially essential element for plants, although its deficiency can occur under certain conditions. However, nickel in high concentrations can be toxic and cause problems in the soil. Adding lime to the soil is one way to reduce the usability of nickel. Too much nickel in the soil is usually caused by human activities. The amount of nickel in the soil is strongly dependent on the amount in the plant, because nickel is easily and rapidly absorbed by plants from the soil and is highly dynamic in plants. There are growing concerns about the toxicity of nickel because nickel is easily absorbed by plant roots and is also absorbed by airborne particles on the leaves.

Nitrate toxicity

Nitrogen removal and nitrogen cycles occur in natural systems in a complex set of processes. In secondary treatment processes, nitrogen is often removed to a small extent unless nitrification and denitrification steps are included in the treatment system. In this case, aerobic and anaerobic conditions should be applied alternately. Organic nitrogen is hydrolyzed more than the precipitation treatment process and part of it is eventually converted to soluble ammonia. Ammonia is also converted to nitrite nitrogen and finally to nitrate nitrogen during the nitrification process.

Nitrate nitrogen is not removed through ion exchange with soil particles due to its negative

If nitrate is not absorbed by plants and microorganisms do not remove it, it enters directly into surface and groundwater and causes environmental problems. Denitrification occurs in soil layers under anaerobic conditions and the presence of optional bacteria. In addition, the carbon to nitrogen ratio must be at least 2: 1 (based on TOC, TN) to complete denitrification. Therefore, for the treatment of secondary effluents in which the ratio is 1: 1, one cannot expect the removal of nitrate through denitrification. Nitrate accumulation in plants is a natural phenomenon and occurs at a time when nitrate accumulation in plants is greater than its reduction due to absorption and analysis.

Nitrate accumulation is regulated by plant hereditary capacity and varies by environmental factors, management, fertilization and agronomic operations. Nitrate and nitrite conversion in the digestive tract lead to nitrite toxicity, especially in infants as well as ruminants such as cattle. The most obvious symptom of acute poisoning is methemoglobinemia, in which hemoglobin is converted to methemoglobin. In this disease, the tissues are damaged due to lack of oxygen. Also, due to the continuous consumption of vegetables or drinking water with high nitrate content, nitrosamine is produced inside the digestive system, which is a toxic and dangerous substance and possibly cancerous. Animals may also suffer from symptoms of multiple complications and diseases due to high levels of nitrate in drinking water, such as methemoglobinemia, vitamin A deficiency, reproductive disorders, miscarriage and decreased milk production. Many environmental factors affect plant nitrate concentration by affecting the activity of nitrate-reducing enzyme as well as nitrate uptake.

In general, low light, high temperatures and humidity stresses reduce the activity of nitrate-reducing enzymes and increase nitrate accumulation.

Table 5. Permissible levels of heavy element concentrations in soil, presented by the Environment Organization of Australia and New Zealand (2019)

Parameter	Concentration (mg/kg)	Parameter	Concentration (mg/kg)
Zn	200	Hg	5
Cd	1	Ni	10
Pb	250	Cr	500
Cu	250	Ar	5
		Mg	350

Table 6. Normal limit and toxicity threshold of daily absorption of heavy metals and trace elements (mg / day) by humans

Element	Normal level	Onset of toxicity
Cd	0.001-0.005	0.02
Cr	0.05-0.2	10
Co	0.02-0.05	250
Pb	0.01-0.02	1
Ni	0.2	15
Se	0.02-0.07	2
Cu	2-3	100
Fe	10-20	150
Mn	3-5	20
Zn	10-15	500
Mo	0.15-0.5	5
Si	50-100	250

CONCLUSION

Oil effluents and oil-water emulsions are two of the main pollutants in the environment. Although their amount is small in volume, but they have a high level of contamination. In wastewater treatment, microorganisms are used to convert soluble and colloidal organic matter into substances that are easily separated from water and to convert them into simpler elements. The types of purification methods that are based on this are generally called biological purification. Although the use of biological treatment can remove about 85% of BOD2 and suspended solids, this method does not remove large amounts of nitrogen, phosphorus, heavy metals, non-degradable organic matter, bacteria and viruses. Advanced purification is used for this purpose. In biological treatment, conditions are created in such a way that microorganisms can grow well in those conditions, by feeding on the substances in the wastewater, these substances are decomposed, consumed part of their vital metabolism and the rest as simpler elements such as water and carbon dioxide. In general, wastewater can be treated in both aerobic and anaerobic modes. In aerobic biological treatment, the organic matter of wastewater is converted to methane gas and hydrogen sulfide. The only advantage of this method is the optimal growth of microorganisms and finally the small volume of sludge. This method is rarely used in municipal wastewater treatment due to problems caused by unpleasant odor and low BOD removal efficiency. It increases that this causes the possible accumulation of these elements in soil, plants and crops, and ultimately causes poisoning for users or plants.

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