

Original Article: Investigating the Effects of Environmental Applications on Decomposition of Zein Nanoparticles in Adsorbents in Industry

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ABSTRACT

This study has investigated the environmental effects of the decomposition of zein nanoparticles in adsorbents in the petrochemical industry. Zein is a fibrous and protein polymer that has a small amount of acidic and basic amino acids, but is rich in amides, leucine, proline, and alanine. This protein is found in corn germ, is commercially extracted from corn gluten by alcohol, and is a byproduct of the bioethanol industry. Zein particles in the diameter range of 1-2 micrometers are called the main proteins of corn spores. Three separate components of zein including α , β and γ zein can be identified by their different solubility in alcohol solutions. Commercial zein is a mixture of proteins with different molecular mass, solubility, and charges. Biodegradable polymers from renewable sources have attracted a lot of attention due to their positive impact on the economy and the environment. Since oil resources are running out, new energy sources are needed. Therefore, more attention has been drawn to the conversion of biomaterials into useful products.

Introduction

Zein is a polypeptide with a molecular weight between 25000-21000. A structure with α -9 hexyl was proposed by Argos *et al.* based on hydration ability, polarity, and secondary structure. Commercial zein has a high concentration of α -hexyl structure in alcoholic water solution. Timashev's research shows that most solvents such as ethanol can increase the structure of α -hexylzein [1]. Due to the hydrophobic properties of zein, many efforts

have been made recently to prepare zein grains and zein hydrogens, which cause the survival of the network structure [2]. Due to its insolubility in water, zein is a suitable candidate for use in transport systems or in other words drug delivery. A number of proteins are used as barriers or carriers of food components, drugs, and food supplements, and this is due to the characteristics of biodegradability, low side, proper absorption, and eating ability. Among the proteins, zein can be changed into a film due to chemical modifications or physical softening or similar processes [3]. Zein film can

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be prepared simply by evaporating the solvent from the Zein solution due to its properties such as hardness, glossiness, hydrophobicity, resistance to the passage of fat, and resistance to microbial attack. These physical characteristics of decorative film have made it used as a coating in food and pharmaceutical packaging. Zein is used to produce microsome proteins for capsule drugs, insecticides. For example, in the food industry, zein is used to create a coating on nuts and sweets to prevent the evaporation of moisture. Zein is usually used as a coating for tablets due to delaying the release of drugs and protecting drugs from the acidic environment of the stomach, and this is largely due to its surface characteristics due to its surface form, structure, and surface hydrophilicity. Previous researches show that the characteristics of the surface with fine grains have a special effect on the loading and integration with active compounds [2].

Nanoparticles and nanoparticle synthesis methods

1- Nanoparticles: Different definitions of nanotechnology have been provided. The National Institute for Nanotechnology Advances in America provides the following definition. Development of research and technology at the atomic, molecular and macromolecular levels with an approximate length from 1 to 100 nanometers to provide a basic understanding of phenomena and materials at the nanoscale and to create and use structures, parts and systems that are small due to their size. Or the medium itself has new properties and functions [4]. Nanoparticles have been used for a long time. During the last few years, the applications of nanoparticles separately and independently of the nanotechnology technology have made significant progress and are considered as one of the main dimensions of this technology. These advances have been in the fields of biomedicine, pharmaceuticals and drug delivery, cosmetics, composites and coatings, and include the use of mineral nanoparticles as antibacterial agents in bandages, labels for diagnosing diseases, drug carriers, bone materials, and isolation equipment. Bio is magnetic. Likewise, in recent years, there have

been advances in the possibility of making and controlling the size, composition and uniformity of nanoparticles. The diversity in the types of nanoparticles is related to the diversity in its applications. Besides the mentioned cases, nanoparticles have very wide applications in human life, industry, etc. [5].

2- Nanoparticle production methods: There are many different methods to produce nanoparticles, which include:

- A) Steam condensation.
- B) Chemical synthesis.
- C) Solid state processes.
- D) The use of supercritical fluids as a medium for the growth of nanoparticles.
- E) Using microwave and ultrasonic waves.
- F) Using bacteria that can produce magnetic nanoparticles.

After the production of nanoparticles, according to the type of their application, common field methods such as coating or chemical modification can also be used.

A) Steam condensation: This method is used to produce metal ceramic and metal oxide nanoparticles. This method includes the evaporation of a metal, and then its rapid condensation, during which the nanometer clusters are deposited in the form of powder. One thing that should be noted is that oxygen is used to prepare metal nanoparticles to prevent oxidation from inert gases and to prepare metal oxide ceramic nanoparticles. Finally, the particle size is controlled by changing parameters such as temperature, evaporation rate, and environment. The most important advantage of this method is the low level of pollution and the preparation of transparent metal oxides that are resistant to scratches and defects and its cost. Another type is the vacuum evaporation method on liquid liquids. In this method, by creating a vacuum in a circular cylinder covered by a thin film of viscous material such as oil or polymer, the target metal is evaporated, and dispersed in the vacuum. Suspended particles form in liquid and grow in different forms (Figure 1).

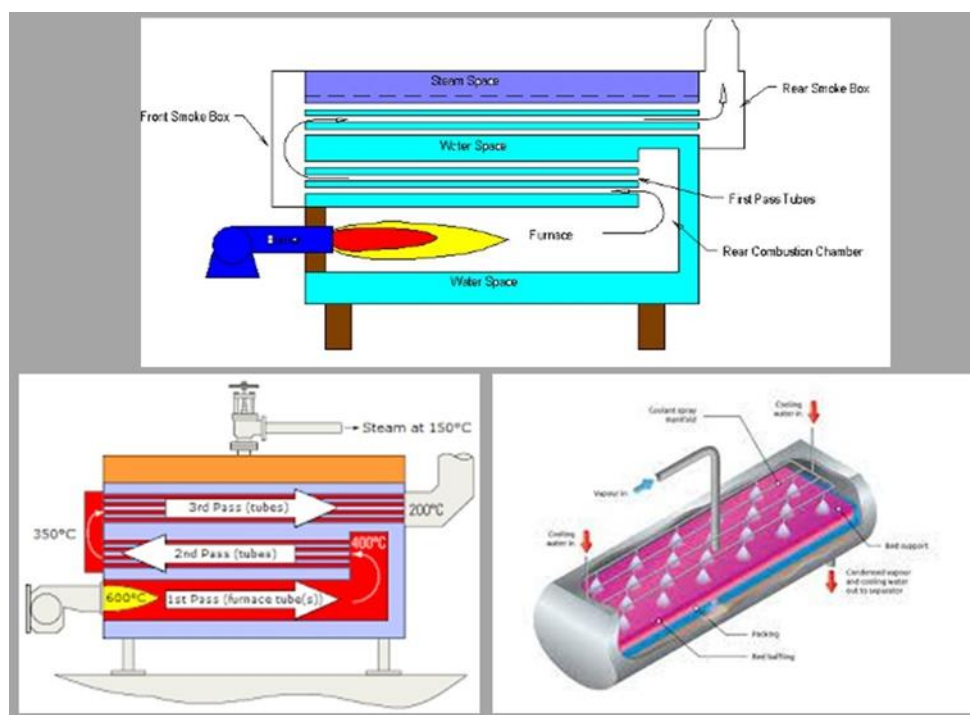


Figure 1: Steam condensation.

B) Chemical synthesis: The chemical synthesis method or the solution method includes the growth and precipitation of nanoparticles in a liquid medium containing a variety of reagents, and the most common example is the sol-gel method. To control the final shape and size of the particles, the process can be stopped by choosing chemicals that form stable particles. This method is also used to create quantum dots. The advantage of this method is its high controllability. Furthermore, this method is low-cost, but the problem is the contamination from chemicals, which makes it difficult to bake nanoparticles for coating.

C) Solid state processes: In this method, micrometer particles are transformed into smaller particles by direct application of energy, such as pulverizing or grinding. The properties of nanoparticles obtained by this method are affected by the grinding material, time and atmospheric environment of the mill. This method is used to prepare nanoparticles that are not easily produced in the previous method, but the important issue is the

contamination from grinding materials or thermal environment.

D) Applications of supercritical processes in the production of micro- and nanoparticles

Due to some gas and liquid properties of supercritical fluids such as permeability and density, it is possible to use supercritical fluid processes in the production of various materials on a micro- or nano-scale in various industries. One of the important applications of such processes is the production of various substances such as drugs, proteins, biopolymers, as well as chemicals on a micro or nano scale [5].

Water

Being aware of the fact that water is the only and most important vital substance that cannot be replaced in any other way, and on the other hand, having it available in sufficient quantity and quality is one of the basic needs of life, the quantitative and qualitative protection of the country's water should be done. It should be

put it at the top of the priorities. In this century, mineral and organic chemical elements and substances such as oil, detergents, pesticides, and industrial substances such as heavy elements have entered the environment cycle. Unfortunately, along with the gradual decrease in the volume of usable water reserves, various pollutions are also continuously adding to the water problems. According to Clause H of Article 104 of the National Development Program Law, to reduce the factors that pollute the environment, especially in the case of natural resources, production units are required to adapt their technical specifications to environmental regulations and reduce pollution. Concerning the increase in the costs of obtaining new water sources, saving, recycling and reuse of existing sources can meet various water needs in a more economical way. To preserve the health of people and the environment and the economic use of all available water sources, the process of polluting water sources should be changed to increase and improve water quality.

Water pollution

Pollution is the introduction of substances or energy by humans into the environment, so that as a result of this act, vital resources or the health of humans, animals, and plants are endangered. The presence of materials or energy in different environments is permitted

and sometimes desirable within certain limits. Pollution happens when these values suddenly increase significantly and this increase causes disturbances and creates problems in the natural and usual process of the existing phenomena. For example, phosphorus and nitrogen are both elements that are necessary for life, and even some of their compounds are added to the ground as chemical fertilizers in agriculture, but if the amount of these substances exceeds the permissible limit and some of them are If the water is washed and poured into different rivers or lakes, it will cause excessive growth of some weeds, which is harmful to the life of aquatic organisms and may cause premature aging of lakes, especially artificial lakes. The idea of purification also creates difficulties [6].

Features of fluoride

Fluorine is a chemical element represented by the chemical symbol F and is found in diatomic form. This element in its pure form is a yellow and corrosive gas considered as a strong oxidizing agent. This element is more electronegative and reactive than all elements. Fluorine is seen in aqueous solutions as fluoride ion (F⁻). Table 1 lists some physical characteristics of fluoride [7].

Table 1: Properties of fluoride

F	Chemical symbol
9	Atomic number
Gas	Physical state
1/7 g/L	Density
53.53K	Melting point
3.85K	Boiling point
6.62 kJ/mol	Heat of vaporization
31/304 J/mol.K	Specific heat capacity
3.98	Electronegativity
Cubic	Crystal structure

Ways of entering fluoride into water

Fluoride is widely present in natural waters at low concentrations. The approximate concentration of fluoride in drinking water is about 1 mg/L, and this amount of fluoride in

water is necessary to prevent osteoporosis and tooth decay, without having a bad effect on body health [8]. The high concentration of fluoride in water is known to be harmful to human health, and its concentration in underground water in different parts of the

world is increasing, and this can be due to the dissolution of minerals containing fluoride, including fluorite, biotite, topaz, and other minerals from this group. It includes granite, basalt, syanite, and other rocks containing fluoride, which causes this ion to enter groundwater [9]. In addition to these minerals and rocks containing fluoride, which causes fluoride to enter the water, the effluent of some industries including glass, ceramic, semiconductor production, electroplating, iron, and brick factories increases the concentration of fluoride in underground water. The fluoride introduced by industrial effluents is much more than the fluoride introduced by the dissolution of rocks and minerals. Fluoride is used in mouthwash, toothpaste, fruit juice, canned food, and Teflon containers, and one of the ways of fluoride entering water is aluminum industry, insecticides, pesticides, herbicides, and fungicides for fruits and vegetables.

It is used and causes environmental contamination with fluoride [10]. Fluoride is used in the combination of rat and cockroach poison, sedatives, anesthetics and sleeping pills, psychoactive drugs, and war gas. Chlorine has been replaced by fluorine in the composition of DDT insecticide so that its effect is stronger. The antiseptic effects of inorganic fluoride can cause enzyme disorders. Enzyme changes can be effective in carbohydrate and fat structure changes. Fluoride disrupts the shape and function of proteins and nucleic acids by forming a strong hydrogen bond with the amide group. Evidence shows that the water consumed by more than 200 million people in the world contains fluoride more than the permissible limit declared by the World Health Organization (WHO), i.e. 1 mg/L [11].

Problems caused by increased fluoride concentration in water

The high concentration of fluoride causes many diseases, such as a decrease in hemoglobin, stomach and intestinal disorders, loss of teeth at a young age, an increase in hip fractures in the elderly, osteoporosis, infertility, a certain form of arthritis, and weak tooth structure and yellowing, Insulin secretion

disorder, decrease in urine concentration, immune system disorders, genetic damage, learning disorders, decrease in IQ, thyroid function disorders, and prevalence of cancer, and Alzheimer's [12]. Reports show that fluoride causes disruption in DNA synthesis and also disrupts the metabolism of carbohydrates, lipids, proteins, vitamins, and minerals [13].

Fluorosis

Chronic poisoning caused by inhaling or swallowing more than 6 mg of fluorine daily causes severe fluorescein and its symptoms include weight loss, bone fragility, anemia, general health decline, and joint stiffness. The change in the color of the teeth also occurs if this poisoning occurred during the formation of the teeth [14]. If the amount of fluoride in the drinking water of an area is too much, white spots can be seen on the teeth, or the teeth become yellow-brown, which is called fluorosis. When the fluorosis is very severe, the tooth enamel is soft and pitted like a pebble [15].

Ways to remove fluoride from water

Traditional methods of removing fluoride from water include the use of lime and its co-precipitation in the form of fluorite [16]. Co-precipitation and flocculation process with Fe (III), activated alumina, and calcium have been widely investigated. In addition, ion exchange, reverse osmosis and electrodialysis have been used to remove excess fluoride from water. However, these methods have weaknesses such as complexity, high cost, and pollution production. In a detailed discussion, Ayub *et al.* have presented materials on the comparison of different methods of removing fluoride from water and compared the strengths and weaknesses of these methods. According to the results, flocculation methods are an effective method to remove fluoride, but with this method, the fluoride concentration cannot be reached to the desired level. Furthermore, they found that setting up electrochemical methods requires a high cost and maintaining them for use is costly and difficult. Besides, membrane methods have been used to remove fluoride, which does not require an additive, but setting

up and preparing this method for implementation is costly and time-consuming. The Nalgonda technique is one of the popular techniques for removing fluoride, which is widely used to remove fluoride from water in developing countries such as India, Kenya, Senegal, and Tanzania. This method consists of adding accurate amounts of Alum, lime, and disinfectant chemicals to the water, and then these materials are quickly stirred and aluminum hydroxide is precipitated along with fluoride and placed at the bottom of the container (Figure 2). One of the disadvantages

of this method, which is stated in various reports, is that the concentration of fluoride remaining at the end of the test is 2-7 mg/L, which is very high compared to the limit declared by the World Health Organization (WHO), which is 1 mg/L among the various methods used to remove fluoride from water, the absorption process is widely utilized, and this is due to the simplicity of its design, its application, and the low price of the used adsorbents [10].

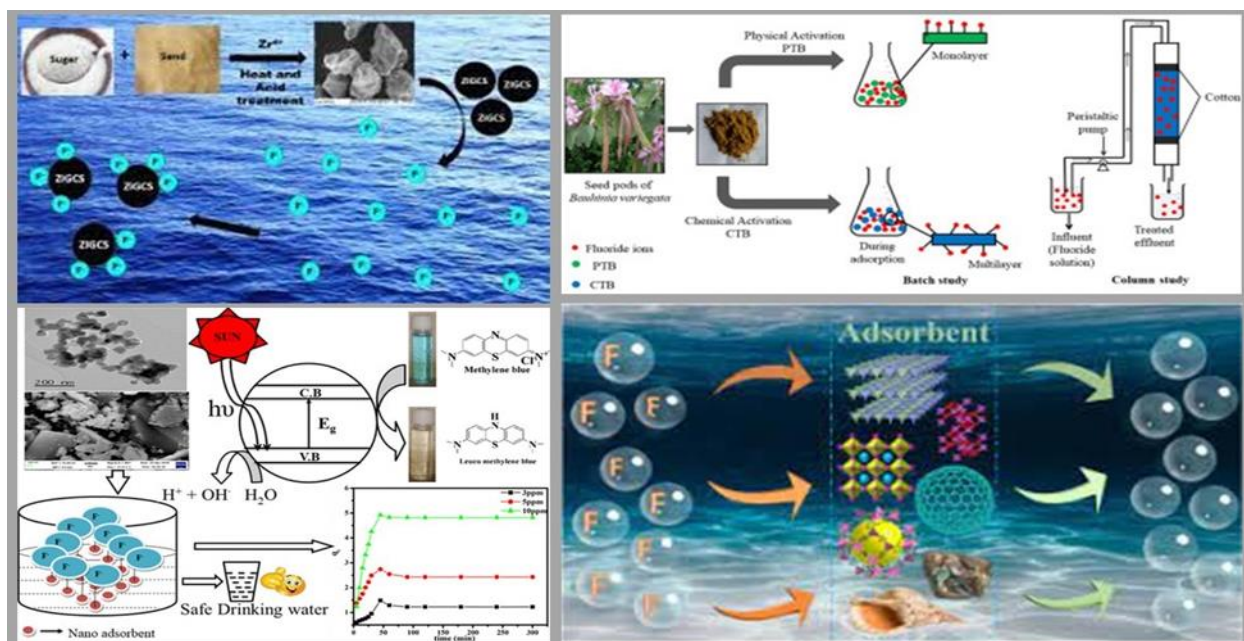


Figure 2: Remove fluoride from water.

Fluoride determination methods

1- Titration: In this titration method, a rare earth metal such as thorium is usually added to a fluoride solution, and then it is allowed to react with fluoride. Thereafter, the solution is reacted with a color indicator such as Alizarin Red-S or Spadence. Color changes caused by the reaction of residual thorium are detected visually with a color indicator. The pH and composition of the solution are carefully controlled and initial isolation is performed before detection to avoid interference from other substances. This method is accurate, but it is boring. In addition, the results obtained

from this method require high skill and experience [3].

2- Potentiometric method: Fluoride concentration in aqueous solutions is estimated by direct potentiometric method by fluoride ion selective electrode [3]. This electrode is made using a single crystal of fluor lanthanum impregnated with europium II as a solid membrane. The role of europium II is to increase the electrical conductivity of the crystal. Such a membrane is installed on the end of a fixed tube and filled with a control solution of sodium fluoride saturated with AgCl. The potential of such a solution is a function of the chloride ion activity in the internal solution. The electrode prepared in this way is floated

along with the other control electrode in the test solution containing fluoride ion. The measurement of the potential difference between two internal and external control electrodes gives figures that depend on the fluoride ion activity in the external solution according to the following relationship:

$$E = K - 0.0591 \log a_{F^-}$$

In this equation, K is the electrode constant and a_{F^-} shows the activity of the fluoride ion in the solution. The use of a negative sign in the above equation indicates that the selected electrode belongs to an anion. With this electrode, the fluoride ion activity can be measured in the concentration range of 1 micro to 1 mol/L in solutions. The use of this electrode requires adjusting the pH of the test solution to a certain level. Because acidic pHs cause the conversion of F^- ions to HF and the destruction of the lanthanum fluoride crystal, and alkaline pHs also cause the intervention of OH^- ions instead of F^- ions in creating the potential and also the destruction of the crystal [1].

3- Spectrophotometric method: In this method, a combination of metals such as aluminum, iron, thorium, zirconium, lanthanum, or cerium reacts with a color indicator and forms a complex with a low-resolution constant, which forms a new complex in the presence of fluoride. and causes color change [3]. In this method, due to the change in the structure of the complex, the absorption spectrum changes, and these changes can be identified using a spectrophotometer. One of the important dyes used in this method is trisodium 2-parasulfophenylazo-1.8-dihydroxy-3.6-naphthalene disulfonate, which is known as spadence. Eri chromium cyanine R is another common dye reacting with metal ions and produces a colored complex. In the spadence method, zirconium reacts with spadence and produces a colored complex, fluoride destroys the red color of the complex and causes a change in absorption, which can be measured using a spectrophotometer [9].

Adsorption

In the absorption process, atoms or molecules in a liquid or gas are in contact with a solid surface. This absorption occurs by the forces of adhesion and cohesion. Surface adsorption begins with weak long-range forces such as Van der Waals force and ends with strong short-range forces such as ionic and metallic forces. It should be noted that the covalent force is associated with chemical reaction and acts not only on the surface, but also in the mass of the substance, and therefore it is not one of the surface attractions forces [2]. In surface absorption, gas molecules are absorbed on the surface of a solid body, and in another type of surface absorption, the body dissolved in a solution is absorbed on the surface of a solid body.

1- Adsorption and related chemistry:

Surface adsorption refers to the process of accumulation of materials in the solution phase on a suitable interface. Adsorbed substance refers to a substance that is being removed from the solution phase at the interface [4].

2- Types of surface absorption of materials on solids:

In the study of surface absorption, it is easy to recognize that the types of absorption can be placed in one of two categories. This classification is based on having basic physical forces holding gas molecules on the solid surface or the possibility of chemical bonds that cause such a connection. The classification of surface absorption into physical or chemical originates from here. Table 2 summarizes the empirical aspects that can be used to categorize a phenomenon based on the above. Distinguishing the different behavior of two types of surface adsorption should be based on having the characteristics of a physical phenomenon such as condensation of vapor to liquid or the characteristics of a chemical reaction [5].

3- Physical absorption: The basis of this type of absorption is the existence of electrostatic forces between the absorbed and absorbent molecules. Physical reactions between molecules based on these forces include interactions between dipoles, weak Van der Waals forces. Physical surface adsorption occurs below the boiling point of the absorbent,

Table 2: Physical and chemical surface absorption characteristics

Physical surface absorption	Chemical surface absorption
<p>The heat of absorption is less than about 80 kJ/mol. Absorption occurs significantly only at temperatures below the boiling point of the adsorbed substance. The increase in the amount of adsorbed substance on the surface is added with each increase in the pressure growth of the adsorbed substance.</p> <p>The amount of absorption is more dependent on the absorbing body than the adsorbing body.</p> <p>It is not much involved in the absorption process of activation energy.</p> <p>Physical surface absorption takes place in several layers.</p>	<p>The heat of absorption is more than about 80 kJ/mol. Absorption can take place at high temperatures. The increase in the amount of adsorbed object on the surface decreases with the increase in the pressure of the adsorbed object.</p> <p>The amount of absorption is one of the characteristics of both adsorbing and adsorbing bodies.</p> <p>The activation energy may be involved in the absorption process.</p> <p>Chemical surface adsorption leads to a maximum of one layer.</p>

but in chemical surface absorption, absorption can also occur at higher temperatures. Physical surface adsorption enthalpy is lower than chemical surface adsorption enthalpy. In physical surface absorption, the amount of absorption is one of the properties of the absorbing body. Physical surface absorption takes place in multilayers, but chemical surface absorption leads to a maximum of one layer [2].

4- Chemical adsorption: In chemical surface adsorption, the adsorbed molecules are kept on the surface of the material with bonds that are comparable to chemical bonds. In the process of forming a bond with the adsorbent, the molecules that are chemically adsorbed undergo a change in the internal electron configuration. The bonds inside some molecules are stretched and weak, and even the bonds of some of them are broken. This type of absorption is further caused by the existence of electrostatic forces and the difference between two types of physical and chemical absorption cannot be distinguished. In chemical absorption compared to physical absorption, the bonds are stronger and the bond length is shorter. The chemical bond of the adsorbed substance on the adsorbent usually cannot be more than one molecular layer due to the nature of the bond. The bond energy of different adsorption mechanisms is approximately from strong to weak, in order of electrostatic chemical bond with more than 10 kcal/mol, Van der Waals

force and hydrogen bond with 10-2 kcal/mol and mutual effects of dipoles with less than 2 kcal/mol. Calories are per mole. Most of the absorption phenomena are a combination of two forms of absorption and, as a result, different force and distinguishing between physical and chemical absorption is not so simple.

The most important factors affecting surface absorption

1- The nature of the adsorbent: the amount of material adsorbed on the surface depends on the specific surface area of the adsorbent. The adsorbents that are mainly used are generally in the form of spherical plates, a point with a diameter of 0.5-10 mm, which the results show, with the increase of the specific surface area of the adsorbent, the capacity of the adsorbent increases.

2- The nature of the adsorbed substance: In the surface adsorption process, the solubility of the soluble substance is an important issue, which largely controls the balance of the surface adsorption. In general, there is an inverse relationship between the amount of material adsorbed on the surface and its solubility in the solvent, which is the Landelius law. Weber and Morris showed that larger compounds of one chemical family are

absorbed much faster than small molecules of another family.

3- Solution conditions: Conditions such as pH, ionic strength, and solution concentration are among the effective factors on the surface absorption of the solution, the most important parameter of which is the pH of the solution, and this is due to its effect on the adsorbent and how it affects the electron density and Impregnation of the adsorbent and its effect on the substance and the degree of ionization of that substance.

4- Temperature: In all cases of surface absorption, heat is released and the reaction heat of the surface absorption process is negative. However, surface absorption heat is usually written without a sign. The heat of physical surface absorption is about the heat of evaporation and is usually less than 40 kJ/mol, and concerning that physical absorption may lead to the formation of several layers of the absorbed substance, the mentioned heat depends more on the nature of the absorbed substance than to the solid absorbing body. On the other hand, the heat related to chemical surface adsorption is comparable to the heat of normal chemical reactions. In other words, the heat of chemical surface adsorption can have any value up to about 630 kJ/mol.

Absorption Equilibrium

As a result of the action of absorbing some of the dissolved substance from the solution to the solid phase and vice versa, a dynamic equilibrium is established between the dissolved substance remaining in the solution and the amount of the same substance on the adsorbent surface, and thermodynamically balanced in such a system when it is established that the adsorbent, adsorbant, and solvent reach the minimum free energy. The distribution of the dissolved substance between the solution and the adsorbent surface is expressed as a function of C_e (adsorbed equilibrium concentration in mg/L) and q_e (mg absorbed per unit of adsorbent mass in mg/g equilibrium conditions) at a constant temperature. Because the temperature is constant, it is called adsorption isotherm. The

adsorption isotherm is a function of the concentration of the dissolved substance at a constant temperature, and usually the value of q_e increases with the increase of the concentration of the dissolved substance in the solution.

$$q_e = f(C_e)$$

Surface adsorption isotherms

In general, there are two types of surface adsorption isotherms:

- 1- Langmuir surface adsorption isotherm.
- 2- Freundlich surface adsorption isotherm.

1- Langmuir surface adsorption isotherm:

In 1961, Langmuir presented a model for the surface adsorption phenomenon and especially the chemical surface adsorption phenomenon and was able to achieve a simple but important theoretical explanation about the surface adsorption isotherm curve. He assumed that there is no interaction between the adsorbed molecules and the solid has a uniform surface. The Langmuir surface adsorption isotherm is much better and more common. Because it is possible to optimize it with mathematical equations to generalize it to be two-layer, and there is no need for the adsorbent concentration in the equations. For example, in surface adsorption chromatography, the Freundlich isotherm is not used at all, and the adsorption process is best described by the Langmuir equation. Because the Langmuir adsorption isotherms give a small amount of adsorption of one layer of molecules on the adsorbent as a function of the concentration of the adsorbed substance in the solution that contains it, and in the optimized equations, even two-layer adsorptions can be obtained.

The general form of the Langmuir equation is as follows:

$$q_e = \frac{q_m b c_e}{1 + b c_e}$$

The Langmuir relation can be written as the following equation:

$$\frac{1}{b q_m} c_e = \left(\frac{1}{q_m} \frac{c_e}{q_e} \right) + \frac{1}{q_m} \left(\frac{1}{c_e} \right) = \left(\frac{1}{b q_m} \frac{1}{q_e} \right)$$

Where, q_e , C_e , q_m , and b are, respectively, mg absorbed per unit mass of adsorbent in equilibrium conditions, equilibrium concentration of adsorbed in mg/L, mg absorbed per unit mass of adsorbent needed to complete the coating Monolayer surface, and constant b represent surface absorption heat.

Freundlich adsorption isotherm

Another equation for isothermal surface absorption is the Freundlich isotherm, which is used like the previous isotherm to quantitatively determine equilibrium surface absorption systems.

The general form of the Freundlich equation is as follows:

$$q_e = K_f c_e^{\frac{1}{n}}$$

Where, q_e and C_e are similar to those mentioned in the Langmuir relation, and the values of K_f and n are constants determined experimentally.

The Freundlich relation can be written as follows:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln c_e$$

From plotting $\ln q_e$ in terms of $\ln C_e$, n and K_f can be obtained [11].

Chemometrics

Chemometrics has developed rapidly in the last two decades, and this rapid development is due to the use of smart devices, advanced computers, and suitable software. Chemometrics is widely used in analytical chemistry, and analysts use a significant amount of statistical and mathematical methods. The origin of chemometrics goes back to 1969, when Jares, Kowalski and Eisenhower published a series of articles on the application of linear learning machines in the field of classification of mass spectra with high overlap in the Journal of Analytical Chemistry. A Swedish scientist named Svant Veld first chose the name chemometrics for this technique in the 1970s. His collaboration with Kowalski, who was working in the field of pattern

recognition in chemistry, led to the establishment of the International Chemometrics Society in 1974. There are different definitions for chemometrics, the most common of which is that chemometrics is a chemistry technique that uses mathematics, statistics, and logic for the following purposes [13]:

- 1- Designing or choosing optimal laboratory methods.
- 2- Obtaining information about chemical systems.

ICS definition of chemometrics: Chemometrics is a mathematical, statistical, graphical, or symbolic method for improving chemical information.

Experiment design

Experiment design is a very broad field that has expanded a lot in the last two decades. Although all chemists are aware of their need to design basic experiments, systematic and codified statistical or chemometric rules are rarely considered as an essential part of chemistry. Comparing a biologist with a physiologist, he often spends weeks building a regular statistical plan, before paying attention to the issue of spending months or years of time and conducting often unrepeatable experiments. The simplest experiments in chemistry are relatively convenient and repeatable, while chemists do not necessarily see the need to design regular experiments in their profession under slightly different conditions. For instance, there are rare cases that spend a week designing a series of experiments that only take a few hours to complete. This lack of expertise in systematic design has entered all levels from management to professors and students. However, most real-world tests are very expensive. For example, to optimize the conditions for synthesis, to test compounds for a study (QSAR), or to improve the separation rate of isomers in chromatography, days and months may be spent, and under such conditions, an acceptable increase in the field of basic and fundamental experimental design seems necessary [15]. There are several important key factors that

explain how a chemist can be much more efficient if they know the basics of the experiment.

Practical areas of experimental design

Design of experiments is a tool to conduct experiments in principle, because if the experiments are done randomly, the results will also be random. Therefore, experiment design and optimization are essential in conducting experiments. In this context, there are some technical terms that are mentioned as follow:

- 1- Test area: The range discussed in the test.
- 2- Factors: Test variables that can be changed independently.
- 3- Independent variables: Independent variables are the same factors.
- 4- Continuous variables: Independent variables that can change continuously.
- 5- Separate variables: Independent variables that change step by step.
- 6- Answer: The measured values as the results of experiments.
- 7- Remainder: The difference between calculated values and experimental results [6].

These include the following four sections:

1- Screening: This type of testing includes cases where the tester observes factors that are important for the success of his testing process. Examples of this can be the study of chemical reactions, dependence of solvent ratio, catalyst concentration, temperature and pH, speed of stimulation. Typically, 10 factors or more may be related to each other, in which one can be eliminated and the other should be studied in detail.

2- Optimization: This is one of the most common applications in chemistry. How to improve the product of a synthetic process or the separation rate in chromatography? Systematic methods can be optimized in a better way and also give a faster response. The simplex method is a classic method for optimization, although several designs such as

mixed designs and central hybrid designs can also be used to perform optimization.

3- Saving time: In the industry, this is probably the main motivation for designing experiments. There are clear and obvious examples in the field of optimization and screening. Even in basic cases such as a quantitative relationship between a feature and a structure from the structural and fundamental data of existing molecules, it is possible to predict a small number of compounds for further tests on behalf of a larger group of molecules, which saves a lot of time. Factorial designs and Bormann's platelet design are its good instances, although all experimental designs more or less incorporate this feature.

4- Quantitative modeling: Almost all experiments, from simple linear calibration in analytical chemistry to complex physical processes where a series of observations require a mathematical model for the system, have benefited from a good experimental design. Most such designs are based around composite design, although calibration designs are also useful. An example of cases where systematic experimental design is valuable is the optimization of reaction product as a function of reactant concentration.

Five basic principles in experiment design

1- Degrees of freedom: The basis of learning experiment design is degrees of freedom. One of the important results in many tests is measuring errors. This can tell how reliably a phenomenon can be predicted. For example, is it really possible to estimate the activity of an unknown compound from its molecular descriptors? In addition, which is the weak link in the tests? Each experiment includes a series of observations that allow it to answer a number of such questions. Of course, more degrees of freedom can make the researcher more confident about the answers. Whenever time is limited, it is very important to provide information that allows all questions to be answered. Most experiments respond to multiple categories of the model, which is a mathematical way to relate an experimental

response to the value or state of a number of factors. An example of a response may be the product of a synthetic reaction, and the factors may be pH, temperature, and catalyst concentration. An experimenter always wants to conduct a reaction under a given set of conditions and predict the product. Now, how many tests should be done to make reliable predictions of the product in each combination of three factors? five? ten? Or maybe twenty tests? Of course, increasing the number of tests is equal to improving predictions, but at the same time, the amount of time spent and also the cost will increase.

2- Analysis of Variance: The ultimate goal of the experiment is to answer the question of how important a factor is. In general, an experiment can be designed in such a way as to allow measuring the importance of a factor using a sufficient number of degrees of freedom. Various situations may occur in which this information is very important [17]. Analysis of variance (ANOVA) is a very powerful statistical method that can be used to isolate and estimate different causes of variation. This method can check whether the change of the factor with the controlled effect leads to a significant difference between the obtained mean values. ANOVA can be further used in cases where there is more than one source of random error and is used to isolate and estimate sources of variation [18].

3- Matrix design and modeling: Experiment design is a key concept. A design may include a series of experiments performed under different conditions. Usually, experimental data are shown in the form of mathematical relationships between factors or independent variables such as synthetic product, time of a reaction, or percent purity. A type of equation with three factors may be as follows:

$\hat{Y} = b_0 + b_1X_1 + b_2X_2 + b_3X_3$ (linear expressions depending on each of the three factors)

$b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2$ (quadratic sentences depending on each of the three factors)

$b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3$ (interaction sentences between factors)

The existence of the sign (\hat{Y}) on y means that the corresponding values are estimated by the equation, which naturally will not be the same as the real values, which indicates the existence of errors in the experiment. There are ten parameters in the above equation that many chemometrics users can easily find these parameters using matrices. Although most of the classical texts have refused to express matrix concepts, but with new computer packages, the use of matrices has become much easier.

4- Determining significance: In many classic books on statistics and analytical chemistry, major sections deal with significance tests. In chemistry, only one whole book can deal with significance tests. Most of these tests are basically based on (t-test) and (f-test), but they have been developed along with the progress of advanced computers. In general, different methods such as t-test and f-test can be used to determine the importance of a factor or a parameter.

5- The power and reliability of the models: A basic question in carrying out the experiment may be using the data obtained in an experiment, to what extent the required quantitative information can be predicted. For example, if our observations in the field of temperature are between 40 and 80°C, how can we comment on the temperature of 90°C? The usual practice in such cases is to cut the model in the area outside the experimental area, but this method loses a lot of important information. Often, the ability of the model to predict slowly decreases by moving away from the central area of the experiments, that is, for instance, in the example above, at 60°C, it has the best possible prediction ability, and the further away from the central area, this ability also decreases, but This in no way means that one cannot express an opinion about a temperature of, for example, 90°C, simply because it is less reliable in prediction than a temperature of 80 °C. It is very important to be able to recognize how the ability to predict a response such as synthetic product or concentration changes with independent factors such as temperature and pH. When only one factor is involved in an experiment, the

ability to predict is expressed with confidence bands, the size of these confidence bands depends on the magnitude, and significance of the experimental errors.

Ion Selective Electrodes (ISE)

Electrochemistry is the measurement of the electrical signal produced by a chemical system in an electrochemical cell. There are three types of electrochemical techniques: potentiometry, voltammetry, and coulometry, the most common of which is the potentiometric method, that includes measuring the potential produced by cells in equilibrium conditions. Studies on ion selector electrodes have started since 1900 and those studies show that these electrodes have advantages such as high selectivity, high sensitivity, and short response time. These electrodes are used in medical analysis and in simple analysis control of a number of ions and biological species, and this is due to their easy use and high selectivity (Figure 3). These electrodes are prepared quickly and at a low price, and the sample can be analyzed without

the need for initial separation. Due to the widespread use of potentiometric titration and direct potentiometry in the simple chemical analysis of ions and biological, environmental, and clinical species, many studies have been carried out on ionophores and selective electrodes that have high selectivity towards specific ions or new ions [9]. The ISE response is produced by the complex selection of the ion to be measured by an ionosphere dispersed in a polyvinyl chloride (PVC) matrix. Due to the selection of different sensitive elements according to the charge, the size of the target ions, the electrodes with polymer membrane are one of the sensitive and very useful methods in environmental and clinical tests [50]. Fast response, easy preparation, simple tool to prepare the electrode, wide linear range, low detection limit, and reasonable selectivity and usability of this electrode in colored and turbid solutions are the advantages of these electrodes.

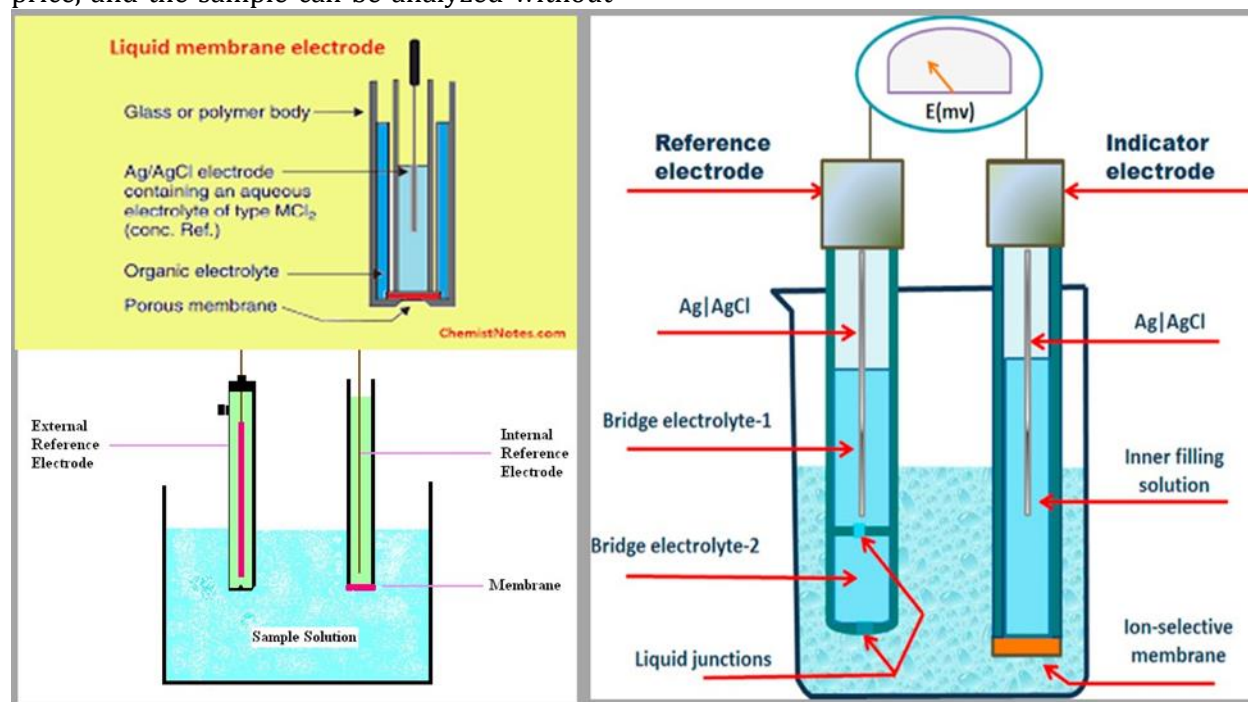


Figure 3: Ion Selective Electrodes (ISE).

Literature Review

1. Absorbents used to remove fluoride

In 2001, Yan Hui Li *et al.*, from Tsinghua University in China, have used carbon nanotubes supported by amorphous alumina to

absorb fluoride from water. The absorption isotherms of this process show that the maximum absorption of fluoride by this adsorbent occurs at pH 5-9. The ability of this adsorbent to remove fluoride is 14.9 mg/g. The high pH range and high capacity of this adsorbent have made this adsorbent to be introduced as a suitable adsorbent for fluoride removal [3].

In 2007, Yaping *et al.* used flax cellulose exchanged with Fe (III) ligand Fe (III) (LECCA) as an adsorbent for fluoride removal, and parameters affecting the experiment such as pH, contact time, temperature, the effect of ions, and flow rate were investigated. The results of adsorption, desorption, and reabsorption show that this adsorbent has a high potential for fluoride removal and has high mechanical stability [13].

In 2009, Xiaoli Zao *et al.* from China University have used $\text{Fe}_3\text{O}_4/\text{Al}(\text{OH})_3$ magnetic nanoparticles to remove fluoride from water. This adsorbent has the advantages of aluminum hydroxide and iron oxide and shows a high tendency to remove fluoride from water. Another advantage of this adsorbent is the easy separation of this adsorbent from the solution by creating an external magnetic field. The capacity of this adsorbent was obtained by the Langmuir equation of 8.4 mg/g at a pH of 6.5. Parameters affecting this test such as solution pH, temperature, absorption time, initial concentration of fluoride, and the effect of other anions have also been investigated in this research. The adsorbent ability enhances with increasing temperature and the kinetics of this reaction is the second order. Enthalpy changes and entropy changes of this reaction are 6.836 kJ/mol and 41.65 kJ/mol, respectively, which indicates the endothermic and spontaneity of this process. In addition, the residual fluoride concentration after absorption for the initial fluoride amount of 20 mg/L is equal to 0.3 mg/L, which corresponds to the permissible limit declared by the Environmental Protection Organization.

In 2009, Samadi *et al.* from Hamedan University of Medical Sciences used bone charcoal to remove fluoride from drinking

water. The results obtained from their experiments indicated that bone charcoal has a high ability to remove fluoride and the amount of fluoride removal is directly related to the amount of adsorbent and contact time of the adsorbent with the solution and pH. The amount of removal is low at low pH and the amount of absorption increases with increasing pH.

In 2010, Karthikian *et al.* from a university in India have used a biopolymer material to remove fluoride from water. Polyaniline chitosan and polypyrrole chitosan are the names of two materials used in this research to remove fluoride from water. The parameters affecting the test include the initial concentration of fluoride, amount of adsorbent, contact time, pH of the solution, temperature, and the effect of the presence of other ions. The adsorption capacity of 5.9 mg/g for polyaniline chitosan and 6.7 mg/g for polypyrrole chitosan at 50 °C has been obtained for an initial fluoride concentration of 10 mg/L. Thermodynamic parameters show that fluoride removal from water is an endothermic process.

In 2010, Biswas *et al.* from a university in India synthesized a ternary oxide compound of iron (III), chromium (III), and aluminum hydrate (HIACMO) and investigated its properties. FT-IR studies have confirmed the existence of M-O-M bonds in this substance. This material was used to remove fluoride and different conditions governing the experiment were investigated. Investigations showed that this reaction is sensitive to pH and the best pH for this experiment was between 4-7. The time required to reach the equilibrium is 1.5 hours and the kinetic studies show the compliance of the data with the second-order kinetics. The Langmuir isotherm equation explains the equilibrium governing this process. Thermodynamic studies show that the fluoride absorption reaction by HIACMO from water is an exothermic and spontaneous process. It is possible to regenerate the adsorbent up to 90% using 0.5 M NaOH. 0.2 grams of this adsorbent can bring 50 ml of 10 ppm fluoride solution to the limit declared by the Environmental Organization.

In 2010, Sanjay P. Campbell *et al.* from India have conducted their studies on the absorption of fluoride by natural alumina oxide, and in this study, they performed the removal process in two continuous and column stages. The effect of the parameter's affecting absorption has been investigated in this experiment. In this test, with the increase in fluoride concentration, the absorption percentage also increases. Thermodynamic studies show that fluoride absorption by alumina alkoxide is an exothermic and spontaneous process. The kinetic results also show that the mentioned process is of the pseudo-second order. The process of removing fluoride by column method shows that with the increase of the flow rate and the initial concentration of fluoride, the output graphs become sharper and the output time and the amount of absorbed fluoride are reduced. Likewise, by increasing the length of the column, the output graphs become sharper [12].

In 2010, Khatibi Kamal *et al.* from Tehran University used electric flocculation method to remove fluoride from industrial wastewater. In this process, it is suggested to use aluminum electrodes to remove fluoride. The test conditions such as temperature, pH, voltage, hydraulic retention time (HRT), and the number of aluminum plates between the cathode and anode plates have been investigated in this research. The results of the experiment show that the percentage of removal increases with the increase of HRT up to 5 minutes, but after that it shows insignificant changes. High holding time requires high electric current to achieve constant voltage and system temperature. The pH of the solution also decreases from 6.91 to 4.6 during the first ten minutes and then increases to 9.5 during 50 minutes. After purification, the amount of fluoride increases from 4-6 mg/liter to 0.5 mg/liter. The pH of the solution has a great effect on the removal of fluoride, and the optimal pH range in this test is 6-7. Kinetic studies indicate that the reaction kinetics is of the second order.

In 2010, Chen *et al.* from the University of China have used ceramics as fluoride adsorbents from aqueous solutions. The effect

of various parameters on the test, such as contact time, initial fluoride concentration, pH of the solution, and the effect of the presence of other anions in this test have been investigated. The optimum value for pH is 4-11. The experimental data show that the surface adsorption process of fluoride fits both Langmuir and Freundlich isotherm models. The maximum adsorbent capacity is 2.16 mg/g. Kinetic data indicate that the reaction is of the pseudo-second order. Experiments show that fluoride absorption decreases in the presence of phosphate and carbonate ions, but the presence of nitrate and chlorine ions does not have much effect on fluoride absorption [18].

Fluoride ion selective electrodes reported in scientific references

In 1996, Hirokazu from Shiga University, Japan, prepared an ion-selective electrode for the determination of low-concentration fluoride ions with a suitable buffer composition and used it for rainwater analysis. In the measurement of fluoride ion, the pH of the solution is usually adjusted using acetate buffer at 2.8. In this research, a new buffer is proposed to adjust the pH, which is a combination of glycine and hydrochloric acid, and this buffer is suitable for rainwater analysis [16].

In 2007, Pietrzak prepared polymer membrane electrodes with high fluoride selectivity using tetraphenyl propylene Al (III) and Zr (IV) derivatives. The response of this electrode is also almost fast and less than 80 seconds, and if tetraphenyl propylene Al (III) is used as an ionizer, the life of the electrode is about 7 months [17].

In 2009, Gorski used the tetra-tert-butyl-tetraazaprocine (TAP) complex with Al (III) and Zr (IV) cations as a fluoride-selective ionophore. The selectivity of this electrode increases in the presence of cationic and anionic materials added to the electrode membrane. Electrodes with Al (III)-TAP membrane act as pseudo-Nernst and measure the fluoride concentration in a short time, while the electrode with Zr (IV)-TAP membrane as an ionophore in the electrode membrane indicates super-Nernst and this electrode is slow in identifying

fluoride. Electrode with Al (III)-TAP membrane with 20% anionic lipophilic mol as additive has high selectivity with high selectivity coefficient in the presence of interfering ions [4].

In 2010, Gorski *et al.* from Poland have used different structures of Zr (IV) and Al (III) ionophores to prepare a fluoride selective electrode. They tested new structures of aluminum and zirconium cellophanes as anion-selective ionophores and showed that these compounds have high selectivity towards fluoride ion. The results of potentiometric and spectroscopic measurements show the influence of the stability of cellophane ligands on the work of electrodes. Increasing the lipophilicity of cellophane ligands maximizes the life of the electrode. Ion-selective electrodes with Al (III) cellophanes are stable, fast, and exhibit Nernst-like responses for fluoride [18].

Conclusion

As nanotechnology in various industries is moving toward larger-scale production, this should be done before significant release of nanoparticles into the environment. The possible ways to deal with these products during their entire survival cycle in nature are:

- ✓ Discharge and leakage during production/transportation and storage of final and intermediate products.
- ✓ Drainage and leakage from waste.
- ✓ Release of particles during product use.
- ✓ Penetration, transmission, and movement in air, soil, and water.

Some applications such as cosmetics and food products are also a source of penetration of nanoparticles. In addition, certain applications such as environmental purification with the help of nanoparticles can lead to the intentional entry of nanoparticles into the environment. This is one of the fields that will lead to the release of significant amounts of nanoparticles into the environment in the coming years. The main criterion used in the evaluation of risks related to chemicals, their toxicity for the environment, their resistance, and bioaccumulation can directly cause the

destruction of tissues. In fact, these substances break down very slowly in the environment and can be concentrated in fatty tissues. For engineered nanoparticles, specific properties of nanoparticles should be considered for effective risk management. The available information on the properties of bulk materials is not sufficient to classify the environmental risks of similar materials in nanoparticle form. The possible environmental effect should be further evaluated specifically for each of these nanomaterials. There are only a few studies in this field. From a scientific point of view, the results should be considered as indicators, not fundamental for decision making. In the first study of the toxicity effect of nanoparticles in an aqueous solution of organic substances, fish were exposed to fullerene 60. Fullerenes are one of the types of nanoparticles produced artificially, which are produced in several tons every year. Rapid oxidation has been observed when exposed to 0.5 ppm of fullerene 60 when these substances come into contact with the brain. This study shows that the produced nanoparticles have an adverse effect on the other organs of the body. Nanoscale iron particles are also considered as a new generation of environmental purification technologies. Due to their high surface activity and high surface area, they can be used to convert and neutralize contaminants such as PCBs. Field tests in the United States indicate that nanoparticles remain active in soil and water for several weeks, and that they can enter groundwater up to 20 meters under the surface. The risks related to free nanoparticles on the ecosystem cannot be done until full papers are published in this field. A specific environmental issue with nanoparticles is their tendency to bind to other substances such as naturally occurring toxic substances such as cadmium. Their high surface area can lead to their binding to molecular contaminants. Colloids are famous for their transparency and ability to retain pollution. Absorbed pollution can be transported to long distances by these materials. In other words, nanoparticles have a lower mobility than what we imagine. It appears that their motion is very specific and generally less than the mobility of coarser particles. It should be mentioned here that their

high surface area and chemical interaction because this decrease in mobility. Their sticky nature significantly slows their transport through porous materials such as soil. In brief, it should be stated that the information about nanoparticles and the environment is only in the initial stages. Among the research needs of this field, issues such as the effect of nanoparticles on non-human species should be investigated. Furthermore, issues such as the effect of these substances on air, water, and soil or their ability to accumulate in the food chain should be investigated. Concerning the large number of parameters that influence nanoparticle properties, it is necessary to devote significant research efforts to fill the scientific gap. To obtain faster and more effective results, coordination between researches requires focusing on the most important materials, parameters, and nanoparticles produced more often.

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