Reusing industrial iron wastes in production of ferrous Sulphate that utilizes in manufacturing of food supplements by selective leaching method

Mohammed Abdulateef Ahmed
Production Engineering and Metallurgy, University of Technology/ Iraq-Baghdad
E-mail: 70051@uotechnology.edu.iq

Abstract. After do the research in variety sources for get some information about food supplement which belong to ferrous Sulphate and how can get this material that got from industrial material waste by selective leaching method, by reaction between industrial waste of iron with sulfuric acid. Iron waste used here got from work shop. After preparation these wastes then processing and recycling by dissolving these industrial wastes in sulfuric acid. According to standard diagrams of X-ray diffraction (XRD) for ferrous Sulphate found that results of ferrous Sulphate are conformable. Besides hydrogen gas was resulted from that reaction as by-product and utilizable. Thereupon the environment protection from industrial wastes will be done. In addition, this method does not consume electrical energy, and industrial iron waste is invested in it instead of using expensive iron ores, meaning it is an economical method that supports the environment and sustainability.

Key words: Industrial waste, Iron waste, Food supplements, Nutritional support, Selective corrosion and Ferrous Sulphate.

1. Introduction:
1.1. Human Blood and Minerals
Fundamental minerals and minor components have very much described physiological capacities inside the body (see Table 1) and should be provided by the eating routine. Dietary Reference Intakes for the different minerals and by life stage bunches have been inferred by the North American Institute of Medicine. Unseemly admissions as well as raised necessities coming about because of a scope of conditions, including infection, mal ingestion, a few medications, and inordinate misfortunes, will in the end prompt a condition of inadequacy or poisonousness with related way physiology. For some minerals, there are no basic, delicate and explicit biomarkers of status, so insufficiency or poisonousness may not be analyzed until genuinely all-around cutting edge, so, all in all the patient may give clinical signs or manifestations. With a less than stellar eating routine, all things considered, numerous micronutrient inadequacies will happen, yet there are additionally uncommon hereditary transformations that influence the digestion of single minerals or minor components; these are typically random to eat less carbs [1]. In this work, it is important to study food supplements containing iron metal only as Sulphate.

1.2. Nutritional Supports or Food supplement
A Food supplement is characterized under European Union (EU) enactment as ‘food stuffs the motivation behind which is to enhance the typical eating routine and which are concentrated wellsprings of supplements or different substances with a nourishing or physiological impact, alone or in blend, promoted in portion structure, to be specific structures like cases, pastilles, tablets, pills and other comparable structures, sachets of powder, ampoules of fluids, drop administering bottles, and other comparative types of fluids and powders’ [2].
Table 1: Major functions of minerals and trace elements [3].

| Minerals | Major Functions |
|----------|----------------|
| Na       | Liquid equilibrium, stomach corrosive creation |
| Cl       | Liquid equilibrium, nerve transmission, muscle compression |
| K        | Bone and teeth wellbeing upkeep, nerve transmission, muscle, constriction, blood coagulating |
| Ca       | Bone and teeth wellbeing upkeep, corrosive base equilibrium |
| P        | Protein creation, nerve transmission, muscle withdrawal |
| Mg       | Protein creation, nerve transmission, muscle compression |
| S        | Protein creation |
| Fe       | Conveys oxygen, aids energy |
| Zn       | Protein and DNA creation, wound mending, development, invulnerable framework work |
| I        | Thyroid chemical creation, development, digestion |
| Se       | Antioxidants |
| Cu       | Coenzyme, iron digestion |
| Mn       | Coenzyme |

Food supplements that are showcased in an EU Member State need to agree with all significant parts of EU food enactment and a particular EU Member State public enactment regarding their organization, production and control [2]. As food supplements are intended to supply supplements, especially micronutrients, and other healthful or physiologically dynamic substances in foreordained sums, expert abilities and gear are by and large utilized in the assembling of most of such items [2].

It is a group of vitamins, minerals and proteins that are used to meet the need of the body of food, whether this need therapeutic or simply to improve the performance of a specific function in different sports or personal reasons related to the same person and despite the benefit provided by supplements, but there are those who use it wrongly to obtain on the results of rapid and effective, which causes damage may be serious in some cases so all countries seek to regulate the use of these substances and strict control of production and trafficking [3].

Minerals and strong inorganic substance that from precious stones and are arranged relying upon the amount of them we need. Minor elements, like molybdenum, selenium zinc, iron, and iodine, are just needed in a couple of milligrams or less and large-scale minerals, like calcium, magnesium, potassium, sodium, and phosphorus, are needed in many milligrams [3]. Numerous minerals are basic for chemical capacity, others are utilized to keep up liquid equilibrium, fabricate bone tissue, blend chemicals, communicate nerve motivations, contract and loosen up muscles, and secure against hurtful free extremists (cancer). Table (1) Minerals and their Major Additional Functions [3].
1.3. Iron Sulphate
Iron Sulphate has two types; Ferric Sulphate and Ferrous Sulphate. The two types used as a medicine, one of them is an antiseptic for wounds and the second is a food supplement (nutritional supports). Iron Sulphate may refer to [4]:

- Ferrous Sulphate, FeSO₄, Iron (II) Sulphate.
- Ferric Sulphate, Fe₂(SO₄)₃, Iron (III) Sulphate.

Iron (II) Sulphate (British English: iron (II) Sulphate) or ferrous Sulphate signifies a scope of salts with the equation FeSO₄•XH₂O. These mixtures exist most regularly as the heptahydrate (X = 7) however are known for a few estimations of X. The hydrated structure is utilized medicinally to treat iron insufficiency, and furthermore for modern applications. Referred to since old occasions as copperas and as green poison (hostility is an antiquated name for Sulphate), the blue-green heptahydrate (hydrate with 7 particles of water) is the most well-known type of this material. All the iron (II) Sulphates break up in water to give a similar water [Fe (H₂O)₆]²⁺, which has octahedral atomic math and is paramagnetic. The name copperas dates from times when the copper (II) Sulphate was known as blue copperas, and maybe in similarity, iron (II) and zinc Sulphate were referred to separately as green and white copperas [4].

Other names Ferrous Sulphate, Green vitriol, Iron vitriol, Copperas, Melanterite, Szomolnokite. It is on the World Health Organization's List of Essential Medicines, the main drugs required in a fundamental wellbeing framework [5]. Ferrous Sulphate utilized Medical as Iron enhancement. Along with other iron mixtures, ferrous Sulphate is utilized to strengthen food sources and to treat and forestall iron inadequacy pallor. Stoppage is a successive and awkward result related with the organization of oral iron enhancements. Stool conditioners regularly are endorsed to forestall obstruction [5]. (See Figure 1).

Figure 1: Iron (II) Sulphate [5].

Ferrous Sulphate production in case of by-product, such as in the completing of steel before plating or covering, the steel sheet or pole is gone through pickling showers of sulfuric corrosive. This treatment delivers enormous amounts of iron (II) Sulphate as a result [6].

\[
H₂SO₄ + Fe \rightarrow H₂[FeSO₄] \quad (1)
\]

Iron (III) Sulphate (or ferric Sulphate), is the Chemical compound with the equation Fe₂(SO₄)₃. Typically yellow, it is a salt and dissolvable in water. An assortment of hydrates is likewise known. Arrangements are utilized in coloring as a stringent, and as a coagulant for modern squanders. It is likewise utilized in shades, and in pickling showers for aluminum and steel [7]. Ferric Sulphate is produced from the reaction of sulfuric acid and hematite as in the following equation [7]:

\[
Fe₂O₃ + 3 H₂SO₄ \rightarrow Fe₂(SO₄)₃ + 3 (H₂O) \quad (2)
\]
Ferric Sulphate is used as a dietary supplement for plants and cannot be used as a dietary supplement for humans, it is toxic and causes blood clots, an acid compound used in dentistry and gum surgery. It acts as an anti-inflammatory and a blood clot (cut off bleeding), where it interacts with the blood protein forming blood clot. Therefore, it cannot be used as a food supplement for humans, but is used in surgery as a cutter for bleeding, especially dentistry and gums. It should therefore be mentioned here to avoid its use as a dietary supplement such as iron Sulphate [7]. (See figure 2).

Figure 2: Iron (III) Sulphate [7].

1.4. Ferrous Supplement
J.M. BLANCHARD and M. MURAT, in 1980, accomplish research in “Recuperation of Chemicals from Waste Iron Sulphate. A Laboratory Test of The Production of Iron Chloride or potentially Electrolytic Iron”, this examination summed up with; Waste iron Sulphate is delivered in titanium dioxide make and in steel pickling with sulfuric corrosive. Numerous cycles have been proposed to utilize this loss as a wellspring of synthetic substances or crude materials [8].

In 2014 the researcher Pedro Jorge Walburga Keglevich and others conducted a research that summarized in; spent pickle alcohol from steel makers is generally used to create ferrous Sulphate in the course of corrosive recuperation. This work proposes another interaction to be utilized mechanically by which clean plant scale is utilized as crude material for the creation of ferrous Sulphate by corrosive draining. Interaction effortlessness and bounty of crude material might be conjured as variables that empower its execution. In this work, after portrayal, an example of plant scale from a semi-coordinated steelmaking plant is filtered with sulfuric corrosive (at centralizations of 5%, 10%, and 15%) inside permeation segments; by distribution of the corrosive arrangement, an alcohol wealthy in Fe²⁺ is created. Close to the filtering step, the alcohol is gathered by dissipation at the temperature of 80 °C and, in the succession, is left to cool normally until room temperature. This strategy takes into consideration the crystallization of ferrous Sulphate. To complete, the precious stones are gathered, purged with ethanol, and portrayed by X-beam diffraction. X-beam examination demonstrate Melanterite (FeSO₄.7H₂O) as the fundamental compound present in the strong portion, trailed by Szomolnokite (FeSO₄.4H₂O) and Rozenite (Fe SO₄.4H₂O) [9].

In 2017, thesis is prepared by Birhan Getachew, entitled: "Creation, advancement and portrayal of ferrous Sulphate from nearby iron mineral", intrigued by iron Sulphate has a broadened utilizes in horticulture, synthetic ventures and waste water treatment plants. In spite of the fact that Ethiopia has a gigantic stores of iron mineral. Thusly, this examination researches the capability of the nation to create iron Sulphate from neighborhood iron metal and sulfuric corrosive [5].
Shahnila Nadir and others in 2015 studied; "The Effect of Ferrous Sulphate on the Gross and Histological Changes in the Body of Gastric Mucosa of Adult Albino Rats", to notice the impacts of Ferrous Sulphate on the collection of gastric mucosa of grown-up pale skinned person rodents. A trial study was completed on 30 grown-up pale skinned person Wistar rodents for 12 weeks. Two gatherings were made; An and B. They were partitioned further into A1, A2, B1 and B2 for subjective boundaries and factual purposes [6].

1.5. Corrosion and Selective Leaching

Corrosion is the dangerous assault of a metal by synthetic or electrochemical response with its current circumstance. Disintegration by actual causes isn't called corrosiontion, yet is depicted as disintegration, erosion, or wear. In certain examples, synthetic assault goes with actual disintegration, as depicted by the accompanying terms: erosion – corrosion, corrosive wear, or fretting corrosion. Nonmetals are excluded from this meaning of consumption. Plastics may grow or break, wood may part or rot, stone may dissolve, and Portland concrete may filter away, yet the term corrosion, is confined to synthetic assault of metals. "Rusting" applies to the corrosion of iron or iron - base alloys with development of corrosion items comprising generally of hydrous ferric oxides. Nonferrous metals, hence, corrode, however don't rust [10].

Selective leaching or on the other hand (Dealloying) is a corrosion interaction wherein one component is specially eliminated from an alloy. This happens without considerable change in the size or state of the part; yet the influenced territory gets powerless, weak, and permeable. The most significant instances of dealloying are the special expulsion of zinc from copper zinc alloy (dezincification), i.e. dealloying is the particular expulsion of one component from a combination by corrosion [10].

1.6. Metal Recycling

Metal recycling is one of the important elements in the sustainable development of natural mineral resources, which contains: Reduce consumption, reuse and recycling. The recycling process goes through multiple levels that start with collecting, sorting, chemically and / or thermally treating mineral wastes to separate the desired minerals from them. In any case, the economic cost of recycling is much lower than the cost of mining and extraction processes [11][12][13].

By following the recycling processes, it will modify the economies of the governments, especially when some taxes and fees are eliminated, as well as the design and production of recyclable metal equipment [12]. Waste metals, after being recycled and converted into castings, metal products and industrial waste are invested and reused. Minerals are non-renewable natural resources and are important in agriculture, industry, medicine, pharmacy, construction, energy, space sciences and other different areas of life. The sustainable development of mineral wealth aims to consume as little as possible of the mineral reserves in mineral mines (ammunition) without a negative effect on the economic growth and the growth of the country. This occurs through the best use of mineral resources in addition to recycle metal waste, this contributes to support sustainable development that protecting the natural environment from the damages that comes with mineral extraction, this helps in preserving biological diversity and not occur the environmental pollution in the future [13].

1.7. Pharmaceuticals and Nutritional Supports Synthesis

The Pharmaceutical manufacturing is a multi-billion-dollar endeavor which influences and improves the existences of individuals around the world. In the wide sense, the drug business incorporates all parts of medication configuration, testing, and conveyance. Albeit the business is profoundly serious, the innovative work of another medication into a last measurements structure is costly and delayed. Because of tough
testing and exacting legislative controls, a newfound medication may require as long as twelve years to arrive at the commercial center. From the great many new synthetic elements recognized yearly, just a modest number are really brought to the patient [14].

A few minerals are remembered for drug arrangements as the medicament or dynamic fixing. These minerals are for the most part as gastric acid neutralizers, adsorbents, intestinal medicines, skin drugs and healthful backings (minerals particularly) [14].

Since minerals supplements very important for human’s body and life, therefore many countries interested in pharmaceutical manufacturing especially minerals nutritional supports or minerals food supplement [2],[14].

1.8. Problem of Nutritional Supports

Youthful competitors are searching for enhancements to give them an edge over the opposition. Be that as it may, numerous buyers know almost no about the thing they are taking and the results. As quite a while client of dietary enhancements, they have regularly felt the wooziness and here and there ascribed nerves of taking enhancements firsthand what most shoppers don't know is that dietary enhancements can prompt gentle results or even dangerous issues and now and then passing. For instance, a few enhancements that contain fixings like caffeine, ephedrine, or GHB (gamma hydroxybutyrate) can prompt expanded pulse, parting cerebral pains, and expanded odds of a warmth stroke. Ephedrine is frequently sold as "home grown energy" items and advanced for weight reduction and jolts of energy [15]. The disadvantage is that ephedrine can have: genuine results on the heart and focal sensory system, just as raising center internal heat level and diminishing the body's capacity to cool. In certain examples, dietary enhancements might be connected to death. For instance, in 2002, Douglas Page composed on an article illustrating the flood of the expanding heat stroke passing among football players. In spite of the fact that enhancements may not be the immediate reason for death, Julian Bails, M.D. also, seat of neurosurgery at West Virginia University, expresses that heatstroke fatalities may, partially, be inferable or disturbed by the utilization of dietary enhancements [16].

The aim of project: Reusing industrial iron waste that has been taken from workshops to production of ferrous Sulphate dietary supplement. Purification of the environment from industrial waste, i.e., the research aims to purify the environment from industrial waste and invest it in the manufacture of a chemical compound used in pharmaceutical manufacturing at low costs without consuming the stock of mineral ores with high costs, starting from their extraction.

2. Experimental work:

2.1. Materials and Chemical Solution:

1- Industrial Iron Waste: The product from industrial processes (lathing process and filing process), this waste be on small balls and reticulate shapes. 1.5 kg Industrial iron waste was taken from work shop, this considered as sample. This waste considered as source to iron.

2- Sulfuric acid (H$_2$SO$_4$): It’s concentration of 99% purity and 99.09 g/mole molecular weight was use in leaching solution and was purchased from the local market and be colorless.

3- Laboratory tools: Which includes beakers that use as container for leaching solution with the materials (industrial waste), The suitable solution was pulled by a pipette, sensitive balance to scale the weight of the materials.

4- Distilled water: Used to mitigate the acid.
2.2. Materials preparation:
The one type of industrial waste is used to product iron compound that use in food supplement (ferrous Sulphate). These wastes are collected from workshops (lathing processes and drilling processes) that have shapes like small ball and reticulate, as shown in the figure 3. 1.5 Kg from these wastes was taken (this quantity used as sample).

After collecting iron waste by magnetic bare (magnetic separation); the iron waste must be cleaned from dust, oil and grease with worm water then using acetone, to prepare this material (iron waste) to subsequent processes.

2.3. Production of iron Sulphate:
The good absorbability of blood to metals in food supplement for that must be metals as Sulphates model [13]. Iron Sulphate was resulted by leaching method (using selective leaching corrosion phenomenon).

To product the source of iron food supplement, industrial iron waste was used here from the workshop. Food supplement when product be ferric compound ferrous compound, both compounds be as Sulphate of iron. To extract these compounds, extraction by leaching was used.

Use Sulfuric acid (H₂SO₄) as dissolvent solution to leaching process. Mitigation of sulfuric acid concentration by Distilled water in the beakers. After mitigation of sulfuric acid in the beakers, put and diving the industrial waste (0.25kg) from workshop in the solution of sulfuric acid, after a period from start reaction the color of the solution converts into transparent green color, as shown in the figure 4.

After 24 hours from reaction the waste converts into very small black particles, precipitate in bottom of beakers, as shown in the figure 5.
Figure 3: Shapes and Collect Waste of Workshop.

Figure 4: Immersing a workshop wastes in diluted sulphuric acid.

Figure 5: Particles precipitate from the waste of iron in solution.
The iron waste in the solution (corrosive medium) was leaved in the beaker and put that beaker in ice path because the reaction was exothermic reaction, then survives the beaker for one day. Also, the same reaction generating hydrogen gas (toxic and flammable gas). After finish the dissolving of wastes in the sulfuric acid some particles of waste not dissolving in solution (super saturated solution). The solution filtered by filter paper, the remaining waste that not dissolved in solution was remain on the paper and the solution passes from it. The color of the solution was sky bluish, as shown in the figure 6. After finish from the selective leaching and filtering processes, the container (beaker) of the filtered solution was cooling in water bath (at room temperature) to get on crystals of ferrous Sulphates (FeSO₄). These precipitated crystals were obtained by filtering technique and reusing to the remains solution in similar another reaction. The experimental parameters to prepare ferrous Sulphates were shown in table 2.

![Figure 6: The solution after filtration and the remain Particles of waste iron.](image)

Table 2: Experimental parameters to prepare ferrous Sulphates.

| Parameter                  | Value |
|----------------------------|-------|
| Acid concentration (M)     | 3     |
| Time (hours)               | 24    |
| Distilled Water (ml³)      | 60.6  |

3. Results and Discussion:

3.1. Sulphate Results Feature:
The ferrous Sulphate crystals (product) were precipitated from filtered reaction solution. The color of this product was sky bluish and crystallized shape, these precipitated crystals were virtuously, in various sizes, transparently, bad odor, and hydrous molecules since crystals uncage water when these putted on the heat source [8][9]. figure 7 shown ferrous Sulphate crystals. It is worth noting that hydrogen gas is liberated from reaction as a byproduct, has a distinctive smell, is toxic and flammable, and this was explained by the researcher Pedro [9].
3.2. XRD Results:
The XRD analysis for resulted crystals (from reactions above); observed that a high concentration of ferrous Sulphate compound evidenced by the peaks of ferrous Sulphate crystals at 2θ values of 12, 22, 30 and 38, as shown in the figure 8. The XRD pattern showed numbers of Bragg reflections that may be indexed on the basis of the face-centered structure of ferrous Sulphate. These values agreed with the provided standard data [17]. This proves to form ferrous Sulphate (FeSO₄·7H₂O) from industrial iron waste that have been worked on.

4. Conclusions:
The ferrous Sulphate crystals produced from the industrial iron waste that taken from workshop. The ferrous Sulphate crystals already have been obtained by investing a selective leaching corrosion phenomenon. It was found that ferrous Sulphate crystals have a many of special properties, ferrous Sulphate crystals which were used as essential supply to manufacturing iron food supplement as observed after XRD tests.
The resulted chemical reaction is an exothermic reaction and therefore the beaker must be placed in an ice bath to reduce the reaction temperature and to reduce the risk of the reaction.

In addition, there is a by-product that must be paid attention to, due to its dangerousness from the toxic side and from the other side, which is safety (because it is explosive able).

This method does not require the use of electrical energy, and industrial iron waste is invested in it. Therefore, it is considered an economical method that supports the environment and sustainability because it helps to purify the environment from industrial waste without returning to the use of raw materials stored in the ground at high costs.

5. Recommendations:
The research steps must be completed from the biological side by conducting biological experiments after obtaining approvals to conduct experiments on animals to find out what effect this compound has on animals and what is the effective percentage.

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