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Dedication

I dedicate this humble work

To my parents, for gifting me the power to dream and the ability to realize them.

For my teachers, who saw potential in a quiet student and ignited that spark into a roaring flame.

To my friends, who became family.

To my family members who knows the untold chapters.

To all those who have an interest in this work, to you my dearest readers, thank you for giving my words a chance.

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LIST OF ABBREVIATION

Abbreviation	Meaning
HM	Heavy Metal
EDTA	Ethylenediaminetetraacetic acid
WWTP	Wastewater Treatment Plant
SWC	Soil Water Content
SOM	Soil Organic Matter
OC	Organic Carbon
TOC	Total Organic Carbon
HCl	Hydrochloric acid
HNO_3	Nitric acid
HF	Hydrofluoric acid
EC	Electrical Conductivity
XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction
FTIR	Fourier Transform Infrared Spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectroscopy
DTPA	Diethylenetriaminepentaacetic acid
GLDA	Glutamic acid di-acetate tetra sodium salt
EDDS	Ethylenediaminedisuccinic acid
SGS	Sewage Sludge Soil
CEC	Cation Exchange Capacity
LL	Liquid Limit
PL	Plastic Limit
PI	Plasticity Index
PSD	Particle Size Distribution
MB	Methylene Blue
SSA	Specific Surface Area

Abstract

Soil pollution by heavy metals is a pervasive environmental issue, posing significant risks to human health and ecosystems. Heavy metals can persist in the soil for centuries, bioaccumulate in the food chain, and contaminate water sources. Anthropogenic activities such as mining, industrial processes, and improper waste disposal are primary sources of these metals contamination in soils. This study focuses on the application of chelating agent ethylenediaminetetraacetic acid (EDTA), in soil washing for different periods of time, as a remediation technique. The effectiveness of EDTA in removing heavy metals from contaminated soils is evaluated through laboratory experiments. The results of this research provide valuable insights for environmental scientists, soil remediation practitioners, and policymakers working towards the restoration of contaminated soils, into the potential of soil washing with chelating agents as a viable method for reducing heavy metal contamination in soils with optimal conditions identified for maximum heavy metal removal while minimizing environmental risks, ultimately contributing to the preservation of ecosystem quality., ultimately contributing to the preservation of environmental quality.

Keywords : Heavy metals, soil pollution, EDTA, ICP-OES, acid digestion, WWTP.

ملخص

يعد تلوث التربة بالمعادن الثقيلة مشكلة بيئية منتشرة على نطاق واسع، مما يشكل مخاطر كبيرة على صحة الإنسان والنظم الإيكولوجية. ويمكن أن تستمر المعادن الثقيلة في التربة لقرون، وتتراكم بيولوجيًا في السلسلة الغذائية، وتلوث مصادر المياه. وتُعد الأنشطة البشرية مثل التعدين والعمليات الصناعية والتخلص غير السليم من النفايات من المصادر الرئيسية لتلوث التربة بهذه المعادن. تركز هذه الدراسة على استخدام عامل مخلب حمض الإيثيلين ديامينيتراسيتيك (EDTA) في غسل التربة لفترات زمنية مختلفة كتقنية علاجية. يتم تقييم فعالية حمض الإيثيلين ديامينيتيتراسيتيك في إزالة المعادن الثقيلة من التربة الملوثة من خلال التجارب المخبرية. وتوفر نتائج هذا البحث رؤى قيمة لعلماء البيئة وممارسي معالجة التربة وصانعي السياسات الذين يعملون على استصلاح التربة الملوثة، حول إمكانية غسل التربة بالعوامل المخلبية كطريقة قابلة للتطبيق للحد من التلوث بالمعادن الثقيلة في التربة مع تحديد الظروف المثلى لإزالة المعادن الثقيلة إلى أقصى حد مع تقليل المخاطر البيئية إلى أدنى حد ممكن، مما يسهم في نهاية المطاف في الحفاظ على جودة النظام البيئي.

كلمات مفتاحية : المعادن الثقيلة، تلوث التربة، EDTA، ICP-OES، الهضم الحمضي للتربة، محطة معالجة مياه الصرف الصحي.

Résumé

La pollution des sols par les métaux lourds est un problème environnemental omniprésent, qui présente des risques importants pour la santé humaine et les écosystèmes. Les métaux lourds peuvent persister dans le sol pendant des siècles, se bioaccumuler dans la chaîne alimentaire et contaminer les sources d'eau. Les activités anthropiques telles que l'exploitation minière, les processus industriels et l'élimination inappropriée des déchets sont les principales sources de contamination des sols par ces métaux. Cette étude se concentre sur l'application d'un agent chélateur, l'acide éthylènediaminetétraacétique (EDTA), dans le lavage des sols pendant différentes périodes de temps, en tant que technique de remédiation. L'efficacité de l'EDTA dans l'élimination des métaux lourds des sols contaminés est évaluée par des expériences en laboratoire. Les résultats de cette recherche fournissent des informations précieuses aux scientifiques de l'environnement, aux praticiens de l'assainissement des sols et aux décideurs politiques qui travaillent à la restauration des sols contaminés, sur le potentiel du lavage des sols avec des agents chélateurs en tant que méthode viable pour réduire la contamination par les métaux lourds dans les sols, avec des conditions optimales identifiées pour une élimination maximale des métaux lourds tout en minimisant les risques environnementaux, contribuant ainsi à la préservation de la qualité de l'écosystème.

Mots-clés : Métaux lourds, pollution du sol, EDTA, ICP-OES, digestion acide, STEP.

General Introduction

Introduction

The environment we live in is facing severe problems caused by human activities. The pollutants we generate not only impact our own well-being but also have far-reaching consequences for the diverse array of plants and animals surrounding us.

As we know, there are mainly three kinds of pollution, air, water, and soil pollution, each one of them has significant importance, but the latter is playing a crucial role in our lives nowadays, where it alters the biodiversity of soils, decreasing soil organic matter and its ability to act as a filter. Additionally, it contaminates the water stored in the soil and groundwater, leading to an imbalance of soil nutrients. Thus, it harms our health and causes serious diseases such as cancer, kidney failure, nervous system damage, …

Typical soil pollutants encompass heavy metals, persistent organic pollutants, and emerging contaminants including drugs and personal care products. Heavy metals, in particular, are notorious for their persistence and toxicity, means that they can remain toxic for extended periods, even after the source of pollution has been removed. Even low exposure to these metals can affect plant growth and pose significant health risks, such as, organ damage, neurological disorders, respiratory problems, and even cancer.

Besides mining, industrial wastes, pesticides, and fertilizers, the main inputs of heavy metals to land are sewage irrigation and sewage sludge generated in wastewater treatment plants, which is not taken into consideration much.

This highlights the importance of addressing soil pollution through proper waste management, remediation, and monitoring. That’s why efforts to decontaminate soil with heavy metal pollution are crucial and may involve strategies like phytoextraction, bioremediation, and thermal desorption.

However, these techniques may not be suitable at high contamination rates, need a lot of energy and time, and some are even high in cost, therefore, there’s another method that is more effective, less expensive and faster, which is soil washing (leaching) by chelating agents such as, DTPA, EDTA, GLDA and EDDS. In contrast to other agents, EDTA can effectively dissolve and remove existing mineral deposits or sediments by binding tightly to metal ions forming a stable complex.

Our study consists of carrying out qualitative and quantitative analysis of soil and sludge samples, as well as determining the amount of heavy metals existing and removing them by chemical leaching using EDTA as chelating agent.

This work has three chapters, the first one is a bibliographic review on soil, sludges, and wastewater treatment plants. The 2nd part or the experimental part presents the materials and products used, as well as the analysis methods and techniques used.

CHAPTER I

Literature Review

I. Soil

I.1. What is soil ?

Soil is an indispensable element within the Earth's ecosystem, serving a pivotal function in numerous natural cycles and processes. Its diverse roles are fundamental for the health of the environment and human communities [1,2].

Over time, influenced by climate factors and living organisms, soil develops specific characteristics and properties that enable it to serve as a foundation for plant roots, deliver essential nutrients, regulate air and water quality, moderate temperature, and furnish minerals necessary for optimal growth [3].

I.2. Soil formation

Pedogenesis, the intricate process of soil formation, involves the gradual transformation of soil under the influence of various factors. These factors encompass the parent material (unconsolidated material or solid rocks), climate, organisms, topography, and time [4].

The physical disintegration of rocks and the chemical weathering of minerals work in tandem to drive soil development. This process occurs through the simultaneous weathering of parental rock and the decomposition of plant residues [5–7].

In essence, soil formation is a multifaceted interplay of biogeochemical processes, weathering, organic matter accumulation, and humification, collectively contributing to the evolution of soil from parent material over an extended period [8,9].

I.3. Soil horizons

Soils typically exhibit a stratified structure composed of distinct layers referred to as soil horizons. According to the Soil Science Society of America, a soil horizon is described as a soil layer or material that is roughly parallel to the earth's surface and displays variations in physical, chemical, and biological attributes compared to neighboring layers that share a genetic relationship. These distinctions can include differences in properties such as color, structure, texture, consistency, types and quantities of organisms present, as well as the level of acidity or alkalinity [10].

The primary soil horizons, arranged from the surface downward, include [11]:

- O horizon: Comprised of organic matter like decomposing leaves and humus, with a predominance of organic material over minerals.
- A horizon (topsoil): A fertile layer rich in organic matter and mineral particles, well-weathered and recognized as the topsoil.
- E horizon (eluviated): Notable for the depletion of clay, iron, aluminum, or organic matter, resulting in a lightened appearance.
- B horizon (subsoil): Accumulates materials like clay, iron, aluminum, or organic matter that have percolated from upper layers.
- C horizon (parent material): Composed of largely unaltered, loose mineral material serving as the source material for upper horizons.
- R horizon: Comprises solid bedrock forming the base of the soil profile.

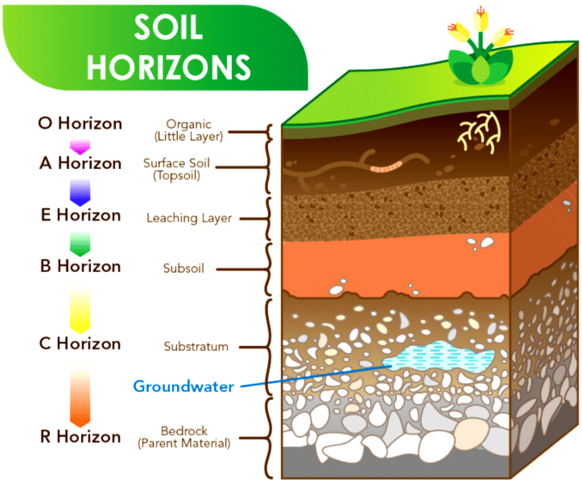


Figure 1. Soil horizons

I.4. Soil texture

Fine earth can be categorized into three particle size fractions: the sand fraction, ranging from 50 to 2,000 µm in equivalent diameter; the silt fraction, spanning from 2 to 63 µm; and the clay fraction, less than 2 µm in size [12].

The relative proportions of these fractions in fine earth define the soil's texture, a critical characteristic influencing the available volume for the gaseous (soil-air) and aqueous (soil-water or soil solution) phases. Sandy soils, with their higher water and air content, facilitate enhanced water movement and evaporation, leading to rapid fluctuations in soil moisture and aeration levels. Further breakdown of clay and sand can result in the formation of nanomaterials, impacting plant and animal life significantly. Soil texture and pore size play a vital role in determining the distribution of soil organisms within the soil ecosystem [12].

I.5. Soil pollution

Human actions have significantly altered the structure and arrangement of soil on our planet. The improper disposal of industrial and urban waste, along with the indiscriminate use of substances on agricultural lands, has led to ecosystem contamination [12].

I.6. Heavy metals

The term "heavy metal" is used to describe metallic chemical elements that possess a relatively high density and exhibit toxic or poisonous properties. These elements have a density at least five times that of water, distinguishing them from light metals, which have densities lower than this threshold. Examples of light metals include sodium, magnesium, and potassium, whereas heavy metals encompass a range of elements such as mercury, cadmium, thallium, lead, copper, aluminum, arsenic, chromium, and mercury, known for their high density and potential toxicity [12,13].

Through multivariate statistical analysis, potential geogenic origins are indicated for nickel, chromium, copper, and zinc, while anthropogenic sources like vehicle emissions and agricultural activities are implicated in the presence of arsenic, mercury, and lead [14].

I.7. Trace elements in soil

The buildup of trace metals in soil poses a significant environmental concern, leading to hazards when these metals are transferred to water or plants. To assess the movement and accessibility of trace metals, it is essential to determine their concentrations and distributions across various physical and chemical phases within the soil [15].

I.8. Soil contamination with heavy metals

Each year, surface sediments on Earth accumulate a significant volume of pollutants from diverse geogenic and anthropogenic origins, transforming soil components into both a repository for pollutants and a regulatory mechanism that influences pollutant dispersion in the environment [16,17].

Activities such as mining, manufacturing, and the utilization of synthetic products like pesticides, paints, batteries, and industrial waste, as well as the application of sludge to land, can introduce heavy metal pollutants into urban and agricultural soils. While heavy metals can occur naturally, they are seldom found at toxic levels in the environment [12].

Elevated levels of arsenic (As), chromium (Cr), cadmium (Cd), mercury (Hg), and lead (Pb) in soil pose toxicity risks to the majority of plants and animals [14,18].

I.9. Soil sampling

The significance of soil sampling lies in its ability to assess a wide range of chemical, biological, and physical soil attributes, providing farmers with valuable insights into the health of their soils and crop systems [19,20].

Historically, soil sampling techniques have primarily focused on characterizing soil properties in general, with their development predating the widespread issue of soil contamination from human activities. However, the inherent anisotropy of soil within its matrix makes it challenging to establish a universal method that can effectively sample soil across different locations, even in the absence of anthropogenic contamination. The task of monitoring soil for environmental contaminants is further complicated by the complexity of soil matrices, site-specific variations in soil types, and the unpredictable fate of pollutants in soil, making it a particularly daunting task [21].

I.9.1. Sampling Process Design

This soil sampling protocol outlines the equipment usage and procedures for handling and processing samples following material retrieval. Samples can be collected using hand augers, a Geoprobe, or a similar drilling rig.

I.9.2. Manual Soil Sampling Methods

These methods are primarily used to collect soil samples from the surface and shallow subsurface layers using spoons or hand augers. The specific intervals are defined as follows [22]:

- Surface Soils

Surface soils are generally classified as the soils located between the ground surface and a depth of 6 to 12 inches below ground level. The most common interval sampled is 0 to 6 inches; however, the data quality objectives of the investigation may dictate a different interval, such as 0 to 3 inches for risk assessment purposes [23].

- Shallow Subsurface Soils

The shallow subsurface interval may be considered to extend from approximately 12 inches below ground surface to a site-specific depth at which sample collection using manual methods becomes impractical.

- Sample Collection Considerations

If a thick, matted root zone, gravel, concrete, or other materials are present at or near the surface, they should be removed before the soil sample is collected. The depth measurement for the sample begins at the top of the soil horizon, immediately following any removed materials.

I.9.3. Direct Push Soil Sampling Methods

The main purpose of these techniques is to gather soil samples from both shallow and deep subsurface layers. Within the Division's direct push tooling inventory, there are three samplers ready for use. Each of these sampling tools is designed to collect and retrieve soil samples enclosed within a thin-walled liner [22].

I.9.4. Split Spoon/Drill Rig Methods

Split spoon sampling techniques are primarily utilized for obtaining soil samples from shallow and deep subsurface layers.

These samplers consist of split cylindrical barrels with threaded ends. One end features a beveled threaded collar acting as a cutting shoe, while the other end has a threaded collar for attachment to the drill rod string.

Two main methods are commonly employed: the standard split spoon with a smaller diameter, driven by a drill rig safety hammer, and the continuous split spoon with a larger diameter, advanced alongside the lead auger during hollow stem auger drilling [22,24].

I.9.5. Shelby Tube/Thin-Walled Sampling Methods

Shelby tubes, known as thin-walled push tubes or Acker thin-walled samplers, are utilized for gathering subsurface soil samples in cohesive soils and clays during drilling operations. Apart from obtaining samples for chemical analysis, Shelby tubes are instrumental in acquiring relatively undisturbed soil samples for geotechnical assessments like hydraulic conductivity and permeability. These analyses aid in the hydrogeological characterization of hazardous waste sites and other locations [22].

I.10. Soil Washing

Soil washing is a remedial method employed to purify polluted soil by segregating pollutants from the soil matrix. This technique entails rinsing the contaminated soil with diverse fluids such as water, surfactants, chelating agents, or organic solvents to extract and intensify the concentration of contaminants. By leveraging the affinity of pollutants to bind more strongly to fine particles, soil washing enables the segregation of contaminated fines from uncontaminated coarse-grained soils. It is a proficient approach for treating soils tainted with a diverse range of organic and inorganic pollutants, encompassing heavy metals, hydrocarbons, and pesticides [25,26].

I.11. Chelating agents

Chelating agents are compounds that form stable complexes with metal ions, enabling their removal from polluted soils [27]. Various types of chelating agents have been studied and applied in soil remediation processes:

- **Synthetic chelating agents**: such as EDTA (ethylenediaminetetraacetic acid), are widely used in soil washing due to their potent metal-chelating abilities. However, these non-biodegradable agents may have adverse environmental impacts [28].
- **Biodegradable chelating agents (BCs):** including iminodisuccinic acid (ISA) and glutamate-N,N-diacetic acid (GLDA), have emerged as promising

alternatives to conventional washing agents for heavy metal-contaminated soil remediation. These BCs can achieve high removal efficiencies for metals like cadmium (Cd), lead (Pb), and zinc (Zn) under optimized conditions [29].

- **Natural amino acids**: particularly threonine, aspartic acid, and histidine, have demonstrated metal-chelating abilities comparable to EDTA when applied to heavy metal-polluted soil samples. The structure-functional correlations of amino acids as chelators have been identified and found to be independent of the specific soil samples [30].
- **Organic acids and humic substances** derived from green waste compost have also been investigated as effective washing agents for removing heavy metals like cadmium (Cd) and nickel (Ni) from contaminated sediments.

The selection of an appropriate chelating agent depends on factors such as the target metal ions, soil characteristics (e.g., pH, organic matter content), and the desired level of environmental friendliness. Chelating agents can enhance soil remediation processes by increasing metal solubility and mobility, enabling their subsequent removal from the soil matrix [27,28,31].

I.11.1. EDTA

EDTA, also known as ethylenediaminetetraacetic acid, serves as a widely utilized chelating agent across diverse industries and applications [32].

This compound demonstrates potent metal-complexing capabilities, leading to the formation of stable metal-EDTA complexes. Its primary applications include enhancing cleaning products, detergents, and processes within the pulp and paper industries [33].

Moreover, EDTA plays a pivotal role in addressing heavy metal toxicity, notably lead poisoning, by facilitating chelation therapy in medicine [34].

Additionally, in the realm of biochemistry, EDTA is employed to effectively inhibit metalloenzymes, showcasing its versatility and significance in various scientific and industrial settings [33].

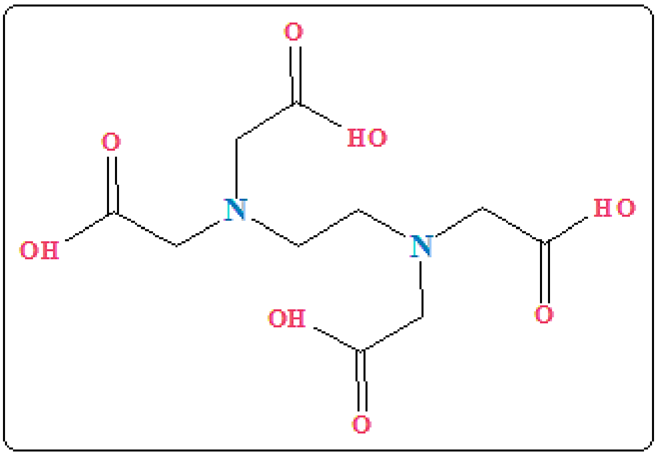


Figure 2. EDTA structure

II. Water

II.1. Wastewater

Wastewater is the term used to describe water that has been utilized in a variety of applications and now contains contaminants that require treatment before being discharged back into the environment or recycled for further use. This water can originate from numerous sources, including industrial facilities, agricultural operations, residential properties, and municipal treatment plants. Treating wastewater is of paramount importance to mitigate environmental pollution and safeguard public wellbeing [35,36].

II.2. Wastewater treatment plant

A wastewater treatment facility is an essential infrastructure that purifies contaminated water from diverse origins, including industrial operations, to safeguard the environment. These sophisticated plants leverage a multistep process to guarantee that the treated effluent adheres to stringent quality benchmarks, thereby preventing potential ecological damage upon release. By meticulously removing pollutants and contaminants, wastewater treatment plants play a pivotal role in preserving the integrity of natural water bodies and ensuring the sustainable management of water resources [36–38].

The wastewater treatment process involves a multi-step approach, incorporating physical, chemical, and biological methods to eliminate pollutants and contaminants from wastewater. This comprehensive process is typically structured into four distinct stages: preliminary treatment, primary treatment, secondary treatment, and tertiary treatment, each playing a crucial role in the thorough purification of wastewater [39].

- Preliminary Treatment

This initial stage focuses on the removal of large debris, grit, and sand particles to safeguard equipment and prime water for subsequent purification steps. It encompasses roughing filtration, desanding, and degreasing procedures.

- Primary Treatment

This stage targets the elimination of suspended solids and organic matter from the water. It employs decanter centrifuges to separate particles and may involve the strategic addition of chemicals such as coagulants and flocculants. These substances facilitate the aggregation of fine particles into larger, more easily removable flocs, enhancing the overall efficiency of the separation process [39].

- Secondary Treatment

This phase is dedicated to the elimination of organic matter and nutrients such as nitrogen and phosphorus from the water. It predominantly relies on a biological process that harnesses the power of bacteria and microorganisms to break down organic substances. The activated sludge process is a prevalent method employed, followed by a settling process designed to separate and remove the resulting biological sludge, ensuring the water is further purified before final treatment stages.

- Tertiary Treatment

  Tertiary treatment is the final stage in the water purification process, designed to elevate the quality of water to a level suitable for environmental discharge or reuse. This advanced stage involves several key processes [35,36]:

  - Filtration with Sand Beds

    Sand filtration is an effective method for removing any remaining suspended solids and particles from the water, polishing it to a high degree of clarity. As the water passes through layers of sand, the fine particles become trapped, leaving behind a clear, refined liquid.

- Disinfection with Chlorine or UV Light

  To eliminate any lingering pathogens and ensure the water is safe for its intended purpose, disinfection is a crucial step in tertiary treatment. This can be achieved through the addition of chlorine or by exposing the water to UV light. Both methods effectively neutralize harmful microorganisms, making the water safe for discharge or reuse.

- Other Advanced Treatments

  Depending on specific requirements and regulations, tertiary treatment may also involve other advanced processes to further refine the water quality. These may include reverse osmosis, which removes dissolved salts and minerals, ion exchange, which selectively removes specific ions, or advanced oxidation processes, which break down persistent organic compounds [40].

By incorporating these tertiary treatment steps, the water is brought to a level of purity that meets the necessary standards for safe and responsible discharge or reuse. This helps minimize environmental impact and maximizes the efficient use of this valuable resource.

III. Sludge

III.1. What is sludge?

Sludge, as per the US EPA, encompasses solid, semi-solid, or liquid waste produced by municipal, commercial, or industrial wastewater treatment plants, water supply treatment plants, or air pollution control facilities, excluding treated effluent. This EPA definition diverges from the conventional English interpretation of sludge, which denotes a dense, soft, moist mud or a thick mixture of liquid and solid elements. The EPA highlights that sludge can manifest in diverse physical states and arises from procedures aimed at eliminating pollutants from air or water [41–43].

III.2. Sewage sludge

Sewage sludge is a multifaceted amalgamation of inorganic and organic substances, as well as pathogens, generated through the treatment of domestic wastewater [41]. It stems from municipal sewage facilities that treat wastewater from residential and industrial sources. It comprises distinct components of the wastewater, such as sediments from the mechanical treatment phase, surplus biomass from the biological treatment phase, and sludge from the tertiary treatment phase containing precipitated phosphates [44].

III.3. Sewage sludge and heavy metals

Crop production on soils amended with sludge is particularly vulnerable to the negative impacts of four heavy metals: cadmium (Cd), copper (Cu), nickel (Ni), and zinc (Zn). The high concentrations of these metals in sludges make them significant contributors to soil pollution. However, research has consistently demonstrated that the transfer of heavy metals from sludge-amended soils to crops is significantly lower compared to inorganic sources, such as metal salts or mining wastes [45].

CHAPTER II

Methodology

I. Introduction

This chapter outlines the materials, equipment, and procedures employed in executing the experiments described in this study. The primary objective is to furnish ample information to enable other researchers within the field to faithfully replicate the methods utilized and corroborate the findings presented.

II. Description of study area

Figure 3. Geographical location of M'sila city and the WWTP (Google Earth 2024)

The M'sila (**WWTP**) is strategically located about 9 kilometers south of the town center, on the right bank of M'sila valley, at the geographic coordinates 35°40'N and 4°30'E. The plant covers an area of 4.16 hectares, reflecting the scale of wastewater treatment required for the local community.

Three soil samples were taken at 20 cm depth, from the entrance and exit of the station, as well as the soil on which the sludge was placed.

A fresh and 5 years stock sewage sludge samples, additionally two samples of water from the station's entrance and exit as an auxiliary indicator in the study.

Figure 4. Samples used in the experiment

III. Samples preparation

Samples were air-dried then grounded and sieved using a 0.4mm sieve, a mixing process was performed to ensure homogeneity.

IV. Soil characteristics

The nature and quality of soil are defined by its physical, chemical, and biological properties, known as soil characteristics.

1. pH and Electrical conductivity

Soil pH is a quantification of the acidity or basicity of soil, which is an essential determinant for plant thriving and nutrient accessibility. Soils with a pH below 7 are deemed acidic, while those above 7 are alkaline. The pH of soil significantly impacts the availability of essential nutrients for plant growth, as well as the activity of soil microorganisms. Maintaining optimal soil pH is crucial for maximizing agricultural productivity and promoting a healthy, balanced ecosystem. On the other hand, soil electrical conductivity (EC) indicates the soil's capacity to conduct electrical current, which mirrors salinity levels, nutrient content, and soil texture [46].

pH and EC were determined using 1:5 soil to water suspension, while stirring for 60 min [47].

2. Particle size distribution

Soil particle size distribution (PSD) pertains to the relative ratios of various particle sizes found in a soil sample, commonly categorized as sand, silt, and clay. This essential soil attribute plays a pivotal role in shaping key soil features like water retention capacity, nutrient accessibility, and soil composition [48–50].

3. Structure and texture

Soil's physical characteristics are defined by two key components: texture and structure. Soil texture is the mix of sand, silt, and clay particles, which affects the soil's ability to hold water, drain excess moisture, and support plant growth through its fertility. Soil structure, in contrast, describes how these particles are organized into stable clusters, influencing the soil's capacity to absorb water, exchange air, and allow roots to grow [51–53].

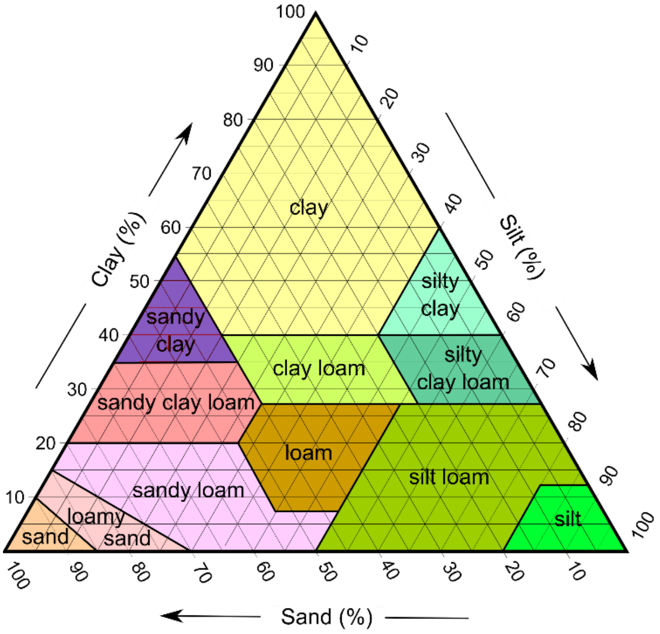


Figure 5. Soil triangle texture

3.1. Uniformity coefficient Cu

The uniformity coefficient (Cu) is a dimensionless ratio that describes the range of particle sizes in soil.

It is calculated by dividing the diameter of grains corresponding to 60% of the material passing through a sieve D_{60} by the diameter of grains corresponding to 10% passing D_{10}:

$$Cu = \frac{D_{60}}{D_{10}}$$

Soils are classified based on their Cu value:

- Well-graded soils have a Cu greater than 4 to 6, indicating a wide range of particle sizes.
- Poorly graded soils have a Cu less than 4, meaning the particle sizes are concentrated in a narrower range.
- Uniformly graded soils have a Cu around 1, with an extremely limited range of particle sizes.

3.2. Coefficient of curvature Cc

The curvature coefficient (Cc) is measure of the fineness or coarseness of soil particles, it provides information about the uniformity and gradation of particle sizes within a soil sample. The formula is:

$$Cc = \frac{D_{30}^2}{D_{60} \times D_{10}}$$

Where: D_{60}, D_{10}, D_{30} = soil diameters at which 60%, 10%, and 30% of the soil weight is finer.

4. Cation exchange capacity

Soil cation exchange capacity (CEC) is a key soil characteristic that assesses the soil's capacity to retain positively charged ions, or cations, by utilizing electrostatic interactions with negatively charged soil components such as clay and organic matter. CEC plays a vital role in determining soil fertility, nutrient accessibility, soil pH levels, and the soil's reaction to fertilizers and other soil treatments [54–57].

- Determination of soil CEC using methylene blue [58]
  - Preparation of a MB solution with a concentration of 4g/L with deionized water.
  - Preparation of the suspension of 1g in 10mL of deionized water, added to the sample in small quantities in the solution to avoid the formation of agglomerations, while maintaining agitation.
  - Add 1mL of MB to the suspension every 5min.
  - Using a glass rod, remove a drop of the suspension which is placed on filter paper before each addition of MB.
  - The manipulation process is completed once a blue halo appears around the suspension, which remains centered. At this stage, we note the total volume being poured, then perform the necessary calculations based on the observed volume.

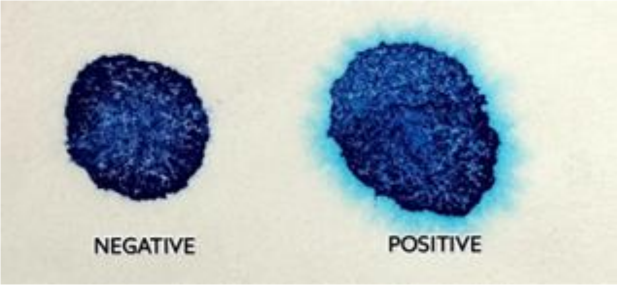


Figure 6. Representation of the spots (with and without blue halo) on filter paper as found in MB spot test for soil's CEC estimation

Results:

$$CEC = \frac{100}{Ws} \times V_{mb} \times \frac{W_{mb}}{320} \times \frac{100-X}{100} \quad \dots\dots\dots\dots\dots\dots [58]$$

Where : CEC = the cation exchange capacity (meq.100 g^{-1} soil), W_S = weight of the soil sample (g), V_{mb} = volume of the MB solution consumed (mL), W_{mb}= weight of methylene blue (g), X = the moisture content (%) of the MB substance.

5. Specific surface area

The specific surface area (SSA) of soil refers to the total surface area of soil particles per unit mass or volume. This fundamental soil property is directly influenced by the size and shape of the soil particles themselves [59]. The SSA of a soil is a crucial factor in determining its chemical and physical behavior, as it affects the soil's ability to adsorb and retain water, nutrients, and other substances [60].

To determine the samples specific area we used ***Malvern Mastersizer 3000 AERO S***, the results are shown in table 1.

6. Soil density

Soil density is the weight per unit volume of soil, a critical characteristic that impacts soil composition, nutrient accessibility, and plant development. It can be assessed through various methods like bulk density and particle density [61]. Comprehending soil density is vital for evaluating soil physical attributes, compaction issues, water flow dynamics, and root system expansion, underscoring its significance in appraising soil quality and guiding agricultural practices [62,63].

Soil density was determined using the graduated cylinder method:

- Pour water into the graduated cylinder and record volume V_1
- Prepare a sample of dry aggregates of mass M.
- Pour the sample into the cylinder using a funnel and cause the voids (air) to leave by stirring the mixture with the agitator rod.
- Note the new volume of water in the test tube V_2
- Empty the aggregates into a plastic bin and throw away its contents
- Repeat the operation at least twice

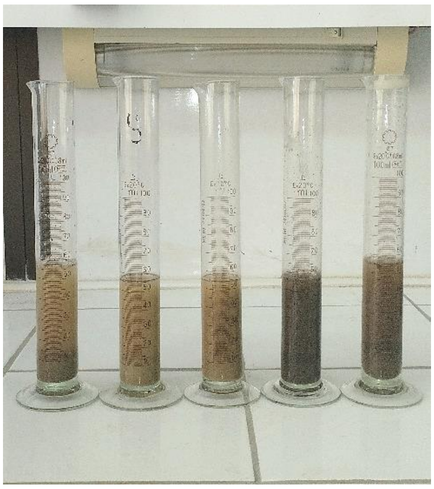


Figure 7. Cylinder method for determining soil density

7. Organic matter

Soil organic matter (SOM) is a critical element within soil composition, encompassing plant and animal remains at different decomposition stages. This organic material plays a key role in enhancing soil productivity and fertility by comprising plant residues, living microbial biomass, active soil organic matter (detritus), and stable soil organic matter (humus) [64–66].

Procedure

- Heat beakers or crucibles in a muffle furnace at 400°C for 2 hours.
- Cool the beakers or crucibles and determine the tare weight to 0.1 mg.
- Add 1 to 3 g of air-dried soil, ground to less than 0.4 mm, to the tared beaker or crucible.
- Heat the sample at 105°C for 24 hours.
- Cool the beaker or crucible in a desiccator over $CaCl_2$ and determine the weight of the beaker or crucible plus the sample to 0.1 mg.

- Obtain the weight of the oven-dried sample by subtraction W_{105}.
- Ignite the samples in a muffle furnace at 400°C for 16 hours.
- Cool the beakers or crucibles in a desiccator over $CaCl_2$ and determine the weight of the beaker or crucible plus the ignited sample to 0.1 mg.
- Calculate the weight of the ignited sample by subtraction W_{400}.

$$SOM = \frac{W_{105} - W_{400}}{W_{105}} \times 100 \text{ ………………..} [67]$$

8. Organic carbon

Soil organic carbon (SOC) is a vital constituent of soils, serving a pivotal role in governing soil health, ecosystem functions, and the global carbon cycle [68,69].

Organic carbon was estimated using the following formula:

Organic matter (%) = .35 + 1.80 x (% Organic C) ………………. [70]

9. Total organic carbon

Total organic carbon (TOC) is the measure of the carbon contained within soil organic matter (SOM). TOC is an important indicator of soil color, health and quality [71].

Organic matter (%) = Total organic carbon (%) x 1.72

10. Atterberg Limits

The Atterberg limits represent a series of soil characteristics that delineate the transitions between solid, semi-solid, plastic, and liquid states in fine-grained soils, particularly clays and silts [72]. The primary Atterberg limits are:

Liquid Limit (LL): This limit defines the maximum moisture content at which a soil exhibits liquid behavior. It is determined using either the Casagrande cup method or the cone penetrometer technique [73].

Plastic Limit (PL): The plastic limit represents the minimum moisture content at which a soil displays plastic properties. It is measured by rolling a soil thread and identifying the moisture content at which the thread first crumbles [74].

The plasticity index (PI) of soil is a key factor that defines the extent of water content within which soil maintains its plasticity. It is the difference between the liquid limit and plastic limit: $PI = LL - PL$ …………………………. [75].

The liquidity index (LI) is a crucial parameter employed in the field of soil mechanics to evaluate the consistency and physical condition of fine-grained soils [76]. It is mathematically defined as the quotient obtained by dividing the difference between the natural water content (wn) and the plastic limit (PL) by the plasticity index (PI):

$$LI = \frac{Wn - PL}{PI}$$

Procedure

10.1. Liquid limit (Casagrande method)

1- Begin by air drying a soil sample and sieving it through a 400 µm sieve to isolate fine-grained soil particles such as silt and clay.

2- Take approximately 120 g of the sieved soil and thoroughly mix it with distilled water until a consistent paste is formed.

3- Place the prepared soil paste into the brass cup of the Casagrande apparatus, ensuring it is leveled to a depth of 10 mm.

4- Use a standard grooving tool to create a precise, clean groove along the diameter of the soil sample within the cup.

5- Rotate the crank of the apparatus at a steady rate of 2 revolutions per second, allowing the cup to drop until the groove closes over a length of 12 mm. Record the number of drops required for closure.

6- Extract a sample from the closed section of the groove to determine the moisture content accurately.

7- Repeat steps 3 to 6 a minimum of 3 additional times (total at least 4 trials) with the soil paste, adjusting the water content each time to vary the consistency.

8- Plot the number of drops against the corresponding moisture contents on a semi-log graph, with moisture content on the y-axis and number of blows on the x-axis.

9- Draw a best-fit straight line (flow curve) through the data points. The moisture content value corresponding to 25 drops on the flow curve represents the liquid limit of the soil sample.

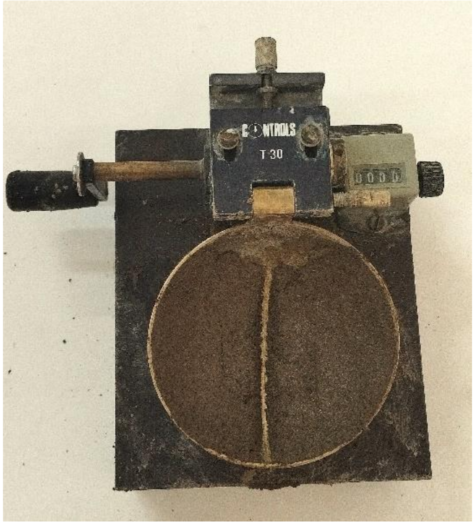


Figure 8. Liquid limit test of soil using Casagrande apparatus

10.2. Plastic limit

The plastic limit of soil is typically determined using a method known as the "rolling method". This method involves the following steps:

1- A soil sample is taken and rolled into a thread on a flat surface.
2- The soil thread is rolled until it reaches a diameter of 3 mm.
3- The plastic limit is the water content at which the soil thread just begins to crumble when it reaches the specified diameter of 3 mm.

Figure 9. Plastic limit test using the rolling method

11.Loss On Ignition

Loss on Ignition (LOI) is an analytical method widely employed in inorganic chemistry and soil science to quantify the volatile components present in a sample. This test determines the volatile content by measuring the change in the sample's weight after subjecting it to high-temperature heating [77,78].

12.XRF

X-ray Fluorescence (XRF) is a method of analysis that relies on the interaction between X-rays and a substance to establish its elemental constitution. When subjected to intense X-rays, a material's atoms can become ionized, leading to the expulsion of inner electrons. Subsequent to this, outer electrons occupy these spaces, releasing fluorescent X-rays with energies that are indicative of the particular elements within.

These emitted fluorescent X-rays are then captured and assessed to measure the elements present in the specimen. XRF is adept at examining solids, liquids, and powders, and is commonly non-destructive [79–81].

13.XRD

X-ray diffraction (XRD) stands as a versatile and non-destructive analytical method that unveils the chemical composition and crystallographic structure of materials. This technique operates by directing a focused X-ray beam onto a sample and scrutinizing the resulting diffraction pattern arising from the interaction of X-rays with the atoms within the sample [82,83].

When X-rays encounter a crystalline substance, they undergo scattering due to the atoms arranged in the crystal lattice. Constructive interference of the scattered X-rays leads to the formation of distinct diffraction peaks. The angles at which these peaks manifest are contingent upon the spacing between the atomic planes within the crystal lattice, a relationship elucidated by Bragg's law [84]:

$$\mathbf{n\lambda = 2d\,sin\theta}$$

Where:

- n represents an integer

- λ signifies the wavelength of the X-rays
- d denotes the spacing between atomic planes
- θ indicates the angle of incidence of the X-rays

14.FTIR

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique that excels in identifying organic, polymeric, and certain inorganic materials. This method operates by passing infrared radiation through a sample and measuring the resulting absorption spectrum [85].

The underlying principle of FTIR is that molecules possess the unique ability to absorb specific frequencies of infrared radiation, which are characteristic of their structural makeup. When infrared radiation interacts with a sample, it excites the chemical bonds within the molecules, causing them to vibrate, stretch, contract, and bend [86].

The absorption spectrum generated by this process represents the molecular absorption and transmission, effectively creating a molecular fingerprint of the sample. This fingerprint serves as a distinctive signature, allowing for the identification of unknown materials, assessment of sample quality or consistency, and determination of component quantities in mixtures [87,88].

FTIR stands out as a fast, accurate, and non-destructive technique that requires minimal sample preparation. Its versatility has made it an indispensable tool in various fields, including chemistry, materials science, forensics, and pharmaceuticals [89,90].

15.ICP-OES

ICP-OES, short for Inductively Coupled Plasma Optical Emission Spectroscopy, is an analytical method utilized to ascertain the elemental composition of a sample by gauging the light intensity emitted by the elements within the sample at specific wavelengths [91].

This technique entails passing the sample through an argon plasma, prompting the atoms to emit distinctive light that is subsequently scrutinized to determine and quantify the elements within the sample [92].

Widely employed for analyzing trace elements in diverse samples like water, soil, sediment, and biological materials, ICP-OES is favored for its exceptional sensitivity, broad linear dynamic range, and proficiency in analyzing intricate matrices [93].

16. Acid digestion

Acid digestion is a chemical process utilized to dissolve solid samples such as sediments, sludges, soils, and solid wastes in preparation for elemental analysis. This method involves subjecting the samples to the action of potent acids, such as nitric acid and hydrogen peroxide, to disintegrate the matrix and liberate the elements of interest for subsequent analysis using techniques like Flame Atomic Absorption Spectrometry (FLAA) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) [94]…

In environmental analysis, acid digestion plays a vital role by guaranteeing the precise assessment of heavy metals and other elements within samples, essential for meeting regulatory standards and conducting effective environmental monitoring [95].

16.1. Soil digestion [96]

- Accurately measure out a quantity of ground soil ranging from 0.2 g to 0.5 g into 50mL beaker.
- Proceed by adding 7.5 to 10 mL of 37% HCl and 2.5 to 5 mL of 65% HNO_3.
- Boil for 2-5 hours (95-105°C), while covering with watch glass.
- Remove the latter and dry.
- Add 25mL of 5% HCl, and maintain the heat for about 10min.
- Cool down at room temperature, filter then transfer into volumetric flask and adjust with pure water.

16.2. Sludge digestion [97]

- In a 50mL PTFE beaker, add 0.2g-0.5g of sludge sample.
- Introduce 1.0 (± 0.1) mL of water to moisten the sample.
- Sequentially add a mixture of HCl-HNO_3-HF (3:1:1) down the beaker's side.
- Position the beaker in the heating plate, ensuring gentle reflux of the sample.
- After 10 (± 2) minutes, rinse the beaker's sides with approximately 5 mL of water.

- Reflux for an additional 5 (± 1) minutes, then remove the beaker.
- Allow it to cool and adjust the volume with water, and transfer the digested sample to an appropriately sized volumetric flask for dilution to the mark with water.

16.3. Water digestion (Thermo scientific Sample preparation techniques for AAS, ICP-OES and ICP-MS for regulated testing laboratories)

- Introduce 25 mL of the water sample to a PTFE beaker, acidify the sample by adding 2.0 mL of concentrated nitric acid (HNO_3) and 6.0 mL of concentrated hydrochloric acid (HCl).
- Place the beaker on a hot plate located in a fume extraction hood, and heat the sample until it is just below boiling.
- Continue heating until the solution becomes clear and transparent.
- Allow the sample to cool down to room temperature, then transfer to 50mL volumetric flask, and bring the sample up to the mark using ultrapure water.

17.Soil washing

Soil washing with EDTA (ethylenediaminetetraacetic acid) is an effective technique for removing heavy metals from contaminated soils [98,99].

About 20g of each dry sample were extracted with 250mL of 0.1M EDTA.

The recipient containing the soil and extractant agent were shaken for 4 h and then filtered through a 0.45 µm Whatman filter.

Samples of the filtrate and filter cake (residue) from each run were taken for analysis for Cr, Pb, and Fe.

After the final run of each sample, the soil was air-dried and saved for ICP-OES analysis.

Figure 10. Sample washing process

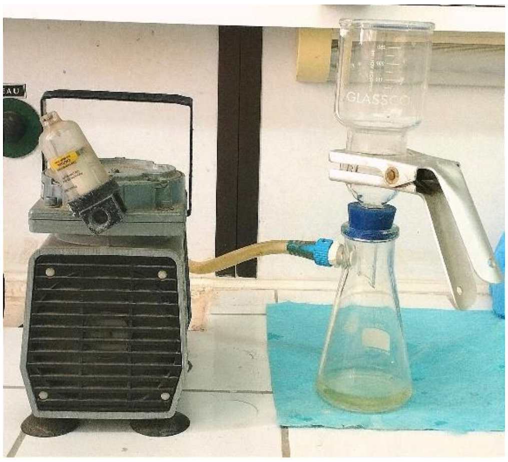


Figure 11. Sample filtration

The reactions happening within for lead, iron, chromium, are successively:

$$Pb^{2+}_{(aq)} + Y^{4-}_{(aq)} \rightleftharpoons PbY^{2-}_{(aq)}$$

$$Fe^{2+}_{(aq)} + Y^{4-}_{(aq)} \rightleftharpoons FeY^{2-}_{(aq)}$$

$$Cr^{2+}_{(aq)} + Y^{4-}_{(aq)} \rightleftharpoons CrY^{2-}_{(aq)}$$

Whereas: Y^{4-} is the shorthand notation for the fully deprotonated form of EDTA.

CHAPTER III

Results and discussion

I. Introduction

In this chapter, the study's findings are outlined and analyzed in relation to the study's objective, which was to characterize the soil and sludge samples, quantify the presence of heavy metals, and extract them using a chelating method.

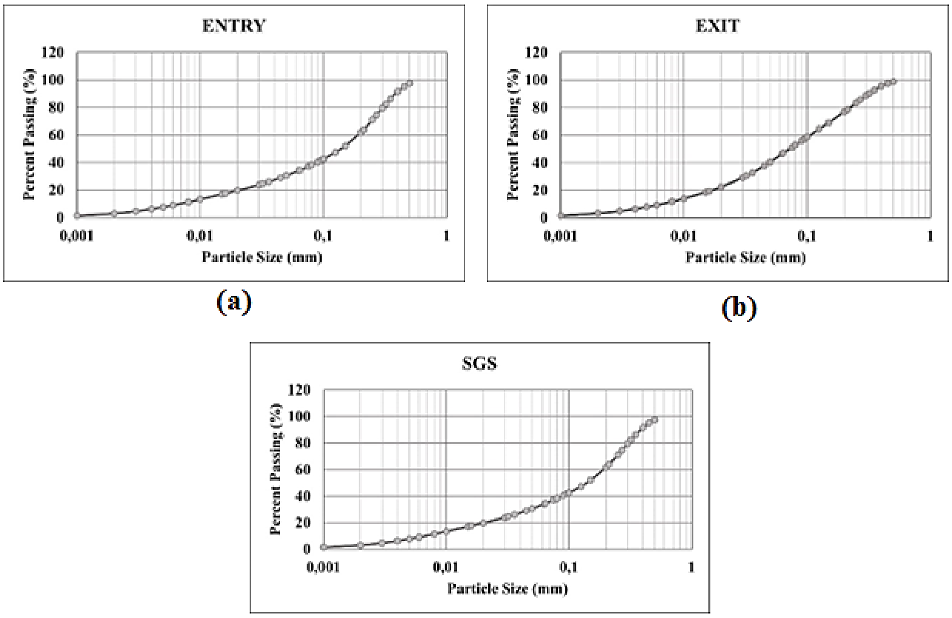
II. Samples characteristics

1. Particle size distribution

This experiment consists of determining the texture of the soil through several sieves in which we place various samples and leave them to sift for a certain period. Then we determine the quantity that passed through each sieve and draw the curve representing the passing quantity as a function of the size of the sieve.

In the current experiment, ***Malvern Mastersizer 3000 AERO S*** apparatus was used. It can determine directly the size of the sieve and quantity of soil passed through, without weighing the samples.

According to the obtained curves (Figure 12), and following the order of the MIT soil classification system, we find the percentage of clay, silt and sand present in the soil, and we conclude with the determination of the texture using the texture triangle mentioned previously in the second chapter. The results are summarized in (Table 1).

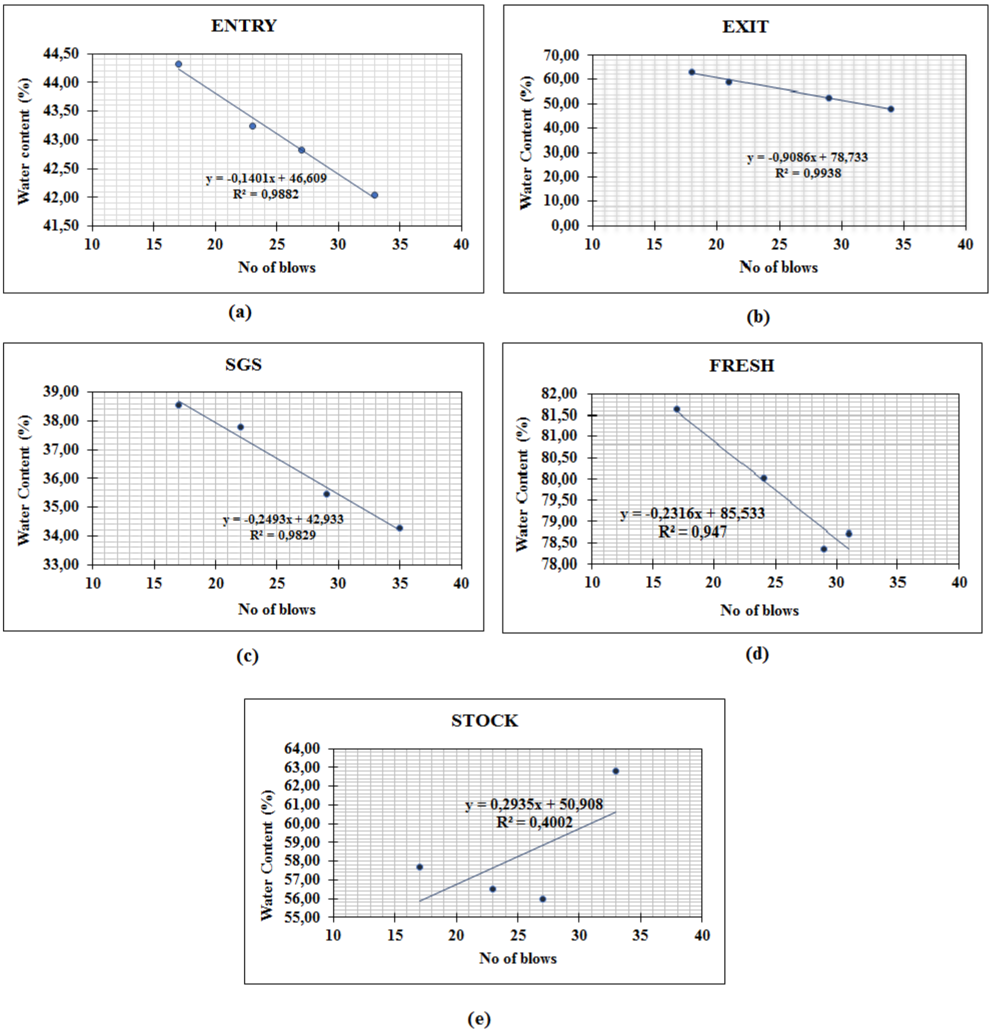


(a) (b) (c)

Figure 12. Soil samples PSD, (a) Entry, (b) Exit, (c) Sludge soil

2. Atterberg limits

In this experiment, we would like to estimate the amount of fluidity or plasticity of the soil by following the method mentioned previously in the second chapter. We have drawn the curve that shows the percentage of water in the soil as a function of the number of blows. At the blow number 25, we can determine the liquid limit. The results obtained are attached to (Table 1).



(a) (b) (c) (d) (e)

Figure 13. Atterberg limits of samples, (a) Entry, (b) Exit, (c) SGS, (d) Fresh, (e) Stock

3. Physicochemical characteristics

The obtained results for selected physic-chemical properties of soil samples were summarized in (Table 1).

Table 1. physicochemical characteristics of the samples

	ENTRY	EXIT	SGS	FRESH	STOCK
pH	7,96	8,35	7,91	7,50	6,87
T (°C)	27,00	26,20	26,10	24,90	25,00
EC (µS/cm)	1707	1231	1059	3990	2630
T(°C)	25,80	25,70	26,20	25,70	25,10
SOM (%)	5,35	4,85	3,38	33,32	19,63
OC (%)	2,78	2,50	1,68	18,32	10,71
TOC (%)	3,11	2,82	1,96	19,37	11,42
SSA (m2/Kg)	142,60	159,50	45,61	52,66	40,15
SWC (%)	2,78	3,44	2,47	2,10	2,22
Clay (%)	1,60	1,68	0,27	-	-
Sand (%)	67,25	55,12	67,60	-	-
Silt (%)	31,15	43,20	32,13	-	-
Texture	Sandy Loam	Sandy Loam	Sandy Loam	-	-
Cu	28,10	16,16	6,23	10,33	8,21
Cc	1,80	1,41	1,22	1,35	1,46
LL	43,11	56,02	36,70	79,74	43,57
PL	24,30	27,55	18,00	57,21	41,58
PI	18,81	28,47	18,70	22,53	1,99
CEC (cmol/Kg)	15,01	10,00	8,75	2,50	1,25
Density (g/cm3)	2,00	1,82	2,50	2,50	2,00
LOI at 950°C (%)	26,33	22,07	26,63	54,75	37,91

In fact, pH in samples was in slightly alkaline condition and ranged from 7.50 to 8.35. The exception to this finding was at sewage sludge sample (STOCK), where the soil pH was a bit acidic (pH 6.87).

The cation exchange capacity of soil depends on the amount and type of soil colloids present, the soil pH, and the organic matter content of the soil. The soil CEC ranged from 8.75 to 15.01 cmol/Kg indicating a slightly low nutrients holding capacity, confirming a loamy mineral soil. Values for TOC ranged from 1.96% to 3.11% for soil, 11.42% and 19.37% for sludges.

The uniformity coefficient Cu, shows that the samples are well graded.

4. Statistical analysis

The correlation test is introduced using Pearson. It is an association and relationship of values to each other, ranging from 1 to -1. If the value is 1 or closer, we say that it is positively correlated, and if it is minus, then vice versa.

Tables 2 and 3, shows the correlation between samples parameters, and between the latter and HMs.

Table 2. The Pearson Correlation coefficient analysis between samples parameters

Variables	pH	EC	SOM	OC	TOC	SSA	CEC	Density	LOI
pH	**1**	-0,628	-0,648	-0,648	-0,649	0,757	0,788	-0,179	-0,627
EC	-0,628	**1**	0,988	0,988	0,988	-0,470	-0,701	0,368	0,975
SOM	-0,648	0,988	**1**	1,000	1,000	-0,541	-0,792	0,401	0,983
OC	-0,648	0,988	1,000	**1**	1,000	-0,541	-0,792	0,401	0,983
TOC	-0,649	0,988	1,000	1,000	**1**	-0,541	-0,792	0,401	0,983
SSA	0,757	-0,470	-0,541	-0,541	-0,541	**1**	0,771	-0,709	-0,613
CEC	0,788	-0,701	-0,792	-0,792	-0,792	0,771	**1**	-0,326	-0,750
Density	-0,179	0,368	0,401	0,401	0,401	-0,709	-0,326	**1**	0,552
LOI	-0,627	0,975	0,983	0,983	0,983	-0,613	-0,750	0,552	**1**

The correlation matrix of all parameters studied reveals that soil organic matter is positively and strongly correlated to soil organic carbon, total organic carbon, and loss on ignition, which is the same case with the electrical conductivity.

On the other hand, we analyzed the correlation between samples characteristics and heavy metals within (Table 3).

Table 3. The Pearson Correlation coefficient analysis between soil parameters and heavy metals

Variables	pH	EC	SSA	CEC	Pb	Fe	Cr
pH	**1**	-0,628	0,757	0,788	0,175	-0,840	-0,835
EC	-0,628	**1**	-0,470	-0,701	0,277	0,349	0,928
SSA	0,757	-0,470	**1**	0,771	0,404	-0,347	-0,640
CEC	0,788	-0,701	0,771	**1**	0,479	-0,582	-0,890
Pb	0,175	0,277	0,404	0,479	**1**	-0,234	-0,033
Fe	-0,840	0,349	-0,347	-0,582	-0,234	**1**	0,613
Cr	-0,835	0,928	-0,640	-0,890	-0,033	0,613	**1**

Where pH is negatively correlated to iron and chromium metals, while there's a positive significative correlation between chromium and electrical conductivity, and a negative one between the former and cation exchange capacity.

5. XRD

For this part of experiments, we used two different kinds of DRX. The results obtained are reported for the first apparatus in the global figure (Figure 14):

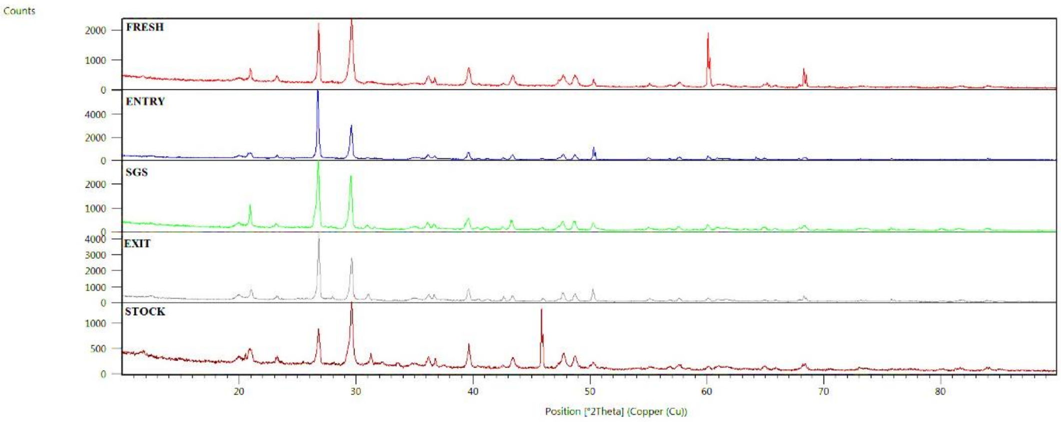


Figure 14. XRD combined spectra of samples analyzed

Whereas for the second data using (BRUKER D4 ENDEAVOR) are depicted in the table below (Table 4):

Table 4. XRD analysis results

Sample	Calcite	Dolomite	Quartz	Illite	Kaolinite	Chlorite	Pyrophyllite	Albite	Microcline	Diaspore	Topaz	Fluorite
----------	%	%	%	%	%	%	%	%	%	%	%	%
ENTRY	40,43	2,83	28,09	9,92	6,00	2,21	2,75	1,09	4,79	0,34	0,01	1,55
EXIT	30,67	6,67	24,37	14,92	9,93	0,05	5,28	2,62	4,00	0,37	0,00	1,11
SGS	33,36	8,86	25,43	12,15	8,54	0,19	4,47	1,53	3,33	0,64	0,40	1,10
FRESH	50,88	3,69	17,63	5,59	4,49	0,00	8,32	1,43	4,76	1,95	0,92	0,33
STOCK	35,88	6,03	30,32	5,84	5,30	0,12	4,97	0,98	9,15	0,25	0,29	0,87

6. XRF

At the beginning of the quantitative analysis, and in order to obtain preliminary results, we used XRF method that initially give the list of minerals in our soil samples, results are shown in the table below (Table 4):

Table 5. XRF results for minerals in samples

Sample	Ba	Zr	Sr	Pb	As	Zn	Cu	Fe	Mn	Cr	Ti
ENTRY	319,1	130,6	471,6	234,0	14,8	198,2	28,1	22665,9	241,1	117,8	3237,6
EXIT	357,1	156,6	534,4	<LOD	7,0	46,7	26,8	24247,5	283,3	<LOD	2685,0
SGS	360,7	189,9	616,3	<LOD	<LOD	36,9	17,2	20257,7	243,7	<LOD	1977,2
FRESH	<LOD	61,5	1707,1	157,0	<LOD	816,7	138,7	9480,3	97,0	309,9	3816,2
STOCK	68,4	104,1	1346,0	53,9	<LOD	543,3	71,2	13314,1	122,5	299,9	2614,2

We also used another device that allowed us to determine the proportions of the oxides (Table 6). Where we notice that the biggest percentage is that of silicate.

Table 6. XRF results for oxides in samples

	ENTRY	EXIT	SGS	FRESH	STOCK
SiO_2 (%)	36.17	40.04	38.24	14.97	26.22
Al_2O_3 (%)	6.49	8.95	6.53	2.89	4.48
Fe_2O_3 (%)	3.36	4.05	3.29	1.51	2.14
CaO (%)	22.81	18.61	19.97	16.99	18.01
MgO (%)	1.59	2.60	2.21	1.64	1.67
P_2O_5 (%)	0.49	0.28	0.25	3.95	4.59
TiO_2 (%)	0.36	0.49	0.39	0.21	0.264
Cr_2O_3 (%)	0.014	0.014	0.010	0.052	0.054
Mn_2O_3 (%)	0.038	0.045	0.039	0.02	0.027
ZnO (%)	0.023	0.009	0.006	0.044	0.06
SrO (%)	0.054	0.066	0.066	0.178	0.147

These data were very useful for the remaining steps of our work and it is used for the optimization of the processes and methods.

7. FTIR

In common practices, the FTIR spectroscopy is a supplementary and an alternative technique to the traditional wet methods. It is useful in the estimation and monitoring of the contamination level in soils. In our experiments, the FTIR analyses of the soil samples were carried out in order to consolidate our quantitative analysis.

The soil is a very complex media. It contains both inorganic and organic components. For the former components, we found silicates, alumina, and lime, as shown in XRF results.

The analysis results are depicted in the (figure 2) as the variation of transmittance as a function of wavenumber, using the "**IRAffinity-Is SHIMADZU**".

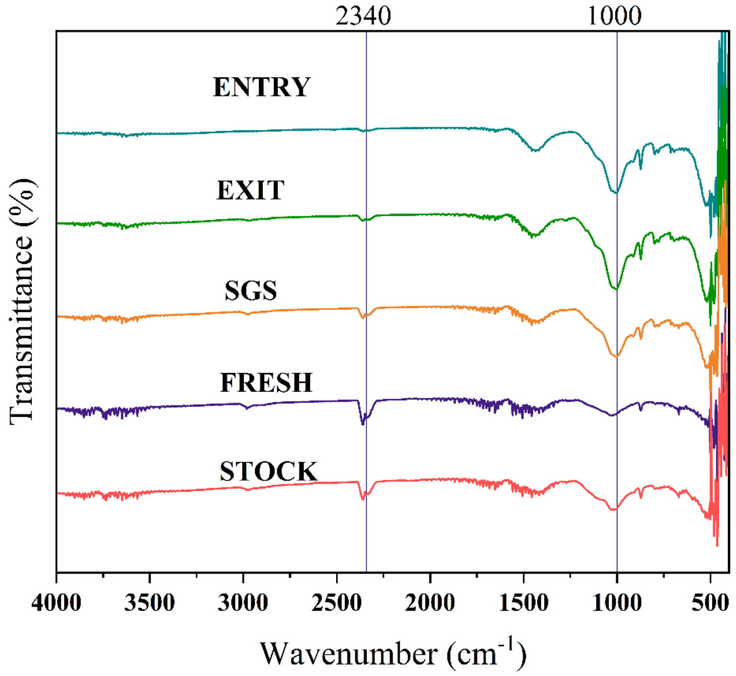


Figure 15. FTIR-ATR spectrum of analyzed samples

Generally, Bands related to various functional groups, such as phenolic, carbonyl, carboxylic, anhydrides, and nitrogen-containing groups, are expected in the infrared spectrum of a soil sample [100].

The strong band between 1150 and 1000 cm^{-1} of FTIR spectra taken from soils is usually due to the C–OH stretching of polysaccharides. However, this band overlaps with the Si–O–Si stretching of silicate bands (1200-970 cm^{-1}) in soil, and may undermine the identification of the polysaccharide peak position, as well as the quantification of this functional group from the peak intensity.

Whereas, the peak at 2340cm^{-1} is due to amine salts, phosphorus, and sulfur compounds in soils.

III. Soil Washing

The washing phase of soil is conducted with EDTA, and after 04 hours of treatment we observed good results and we obtained a net and excellent yield. The recovery rates for the analysed elements are shown in the following table (Table 6):

Table 7. Heavy metals concentrations in samples before and after washing

Sample		Pb (mg/Kg)	Fe (mg/Kg)	Cr (mg/Kg)	Removed Pb (%)	Removed Fe (%)	Removed Cr (%)
ENTRY	Contaminated	310,553	26213,248	644,081	78,93	97,96	97,69
	Washed	65,431	533,794	14,900			
EXIT	Contaminated	100,250	25848,329	600,365	47,30	97,46	97,20
	Washed	52,837	656,288	16,789			
SGS	Contaminated	73,469	25077,639	588,399	68,06	97,64	97,88
	Washed	23,464	591,205	12,468			
FRESH	Contaminated	212,750	26098,160	2464,482	81,08	99,56	99,27
	Washed	40,261	115,112	17,948			
STOCK	Contaminated	77,023	29961,267	2259,773	77,28	99,71	98,94
	Washed	17,500	87,905	23,986			

To observe the washing phase, we quantify the content of metals in the EDTA solution and in order to track the process, we report the diminution of concentration which represents the metal desorption. The experiment results are shown below (Figure 16)

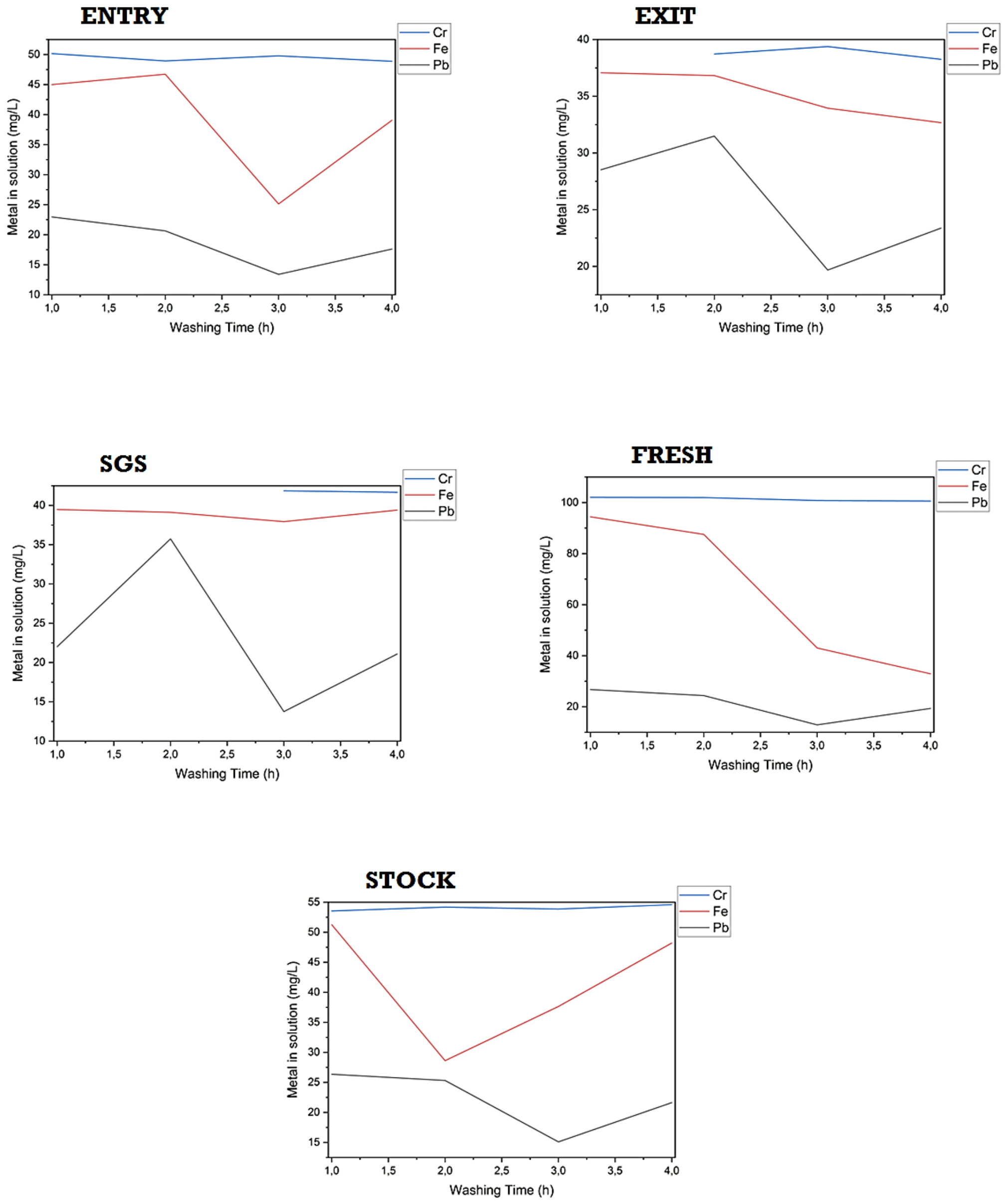


Figure 16. variation of the metal concentration in solution over time, (a) Entry, (b) Exit, (c) SGS, (d) Fresh, (e) Stock.

For further confirmation, water samples from the entrance and exit of the station were analyzed for the same metals, and the results are as follow (Table 8):

Table 8. Heavy metals concentrations in water samples

Sample	pH	EC (µs/cm)	Pb (mg/L)	Fe (mg/L)	Cr (mg/L)
Water Entrance	6,93	3481	27,554	55,355	10,372
Water Exit	7,17	3486	25,674	47,239	9,688

The results showed us that the HM concentrations in entrance water has decreased, which means that the WWTP treatment process is effective.

CONCLUSION

Conclusion

The analyses of soil’s chemical and physical characterization revealed and confirmed the presence of certain heavy metals in varying proportions and their relation to some chemical and physical properties, alongside a notable organic matter content.

Utilizing EDTA for cleansing heavy metal-contaminated soil has proven to be a successful approach in eliminating these pollutants. The study indicates that EDTA effectively enhances the leaching of heavy metals like lead, chromium, and iron from polluted soils, including those in sewage sludge.

Although this technique is especially beneficial for alleviating the environmental repercussions of heavy metal contamination, which can detrimentally affect soil fertility, plant development, and the quality of groundwater, its efficiency was only tested on laboratory scale, and needs to be studied on field, but as the title says this work is only a contribution to the study of soil pollution by HM.

In a nutshell, these results lead us to the idea that the WWTP does an efficient job of purifying and cleaning water from various contaminants, including heavy metals. This is particularly noteworthy, as these heavy metals are known to be highly toxic and can have severe adverse effects on both human health and the environment if not properly removed from the water.

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