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PREPARATION OF CHITOSAN-GEOPOLYMER COMPOSITES, THEIR CHARACTERIZATION AND APPLICATION IN HEAVY METALS ADSORPTION FROM MINE EFFLUENTS

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ABSTRACT

One of the main elements of the **European Green Deal** is Transforming the **EU**'s **Economy** for A Sustainable Future and this is going to be through designing a set of deeply transformative policies. New measures alone will not be enough to achieve the **European Green Deal's objectives**. Hence, mobilizing the industry for a clean and circular economy is demanded by applying an action plan that will include a 'sustainable products' policy to support the circular design of all products based on a common methodology and principles. In this study, Chitosan-Geopolymer Composites (Alkali-activated material) as a **SMARTech Material** studied for the removal of heavy metals Nickel, Zinc and Manganese (Ni, Zn, Mg). Some of the advantages of geopolymer are low energy consumption and low carbon dioxide emissions. The mine water was applied to it as adsorbents for the removal of heavy metals.

The application of heavy metals from mine effluent is adsorption that is stimulated from the tertiary treatment stage in a Wastewater Treatment Plant (**WWTP**) as a large-scale treatment. These metals are considered contaminants and toxic materials. Therefore, Chitosan-Geopolymer composites have been studied to protect the environment from harmful impacts as a friendly environment, low-cost and sustainable product. The findings are divided into two parts; the first part is related to the heavy metals showed a high removal efficiency for (Ni, Zn, Mn) in adsorption experiments with different variables including adsorbent dosage, initial concentrations, contact time and pH. Also, a good removal efficiency for Arsenic (As). In addition, the second part is for adsorbents containing chitosan, X-ray photoelectron spectroscopy (XPS) surface analysis results for adsorbents containing chitin, chitosan

This study may highlight the great potential of these alkali-activated, geopolymer-based adsorbents for efficiently removing heavy metals from mine water.

FOREWORD

First and foremost, my deepest gratitude to my supervisor and mentor **Dr Fatone Francesco** (Full Professor, Chemical-Environmental Engineering) who gave me this chance to be in exchange through the **Erasmus + Training Program**. Without his acceptance, following up, and teaching in Wastewater treatment plants & circular economy and guidance through studying as well as later during the Optimization of Chemical Environmental Plants, I would not have reached this stage. The support I received from the Water and Waste Environmental Engineering Lab (**WWEELAB**) which is coordinated by my supervisor and all the practical visits and seminars such as **ECOMONDO** that is held yearly in Rimini, Jesi WWTP, etc. at **Univesita Politecnica Delle Marche (UNIVPM)** I want to express my sincere gratitude to **Dr Tero Luukkonen**, my supervisor and mentor (Associate Professor, Geopolymer and Water Treatment Technology), for all his advice, inspiration, and support while I was working on my master´s thesis at the **University of Oulu (UNIOULU)** in Oulu, Finland. Without his recommendations and suggestions, this project would not have been completed, I will always be grateful for this. I am thankful to my co-supervisor, **Mohammad Amzad Hossain Bhuyan** (PhD) for his invaluable assistance during the process. I am thankful also to Nusrat Binte Kabir, a lab colleague, for her assistance and availability.

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The German Libraries and services that I have spent a time for studying there and writing.

No one is perfect, and I make every efforts to ensure no errors in the text. However, mistakes do occur. If you find an error I would be graetful for your feedback, as Thaer Roomi humbly said on his lectures on Numerical Weather Prediction.

Oulu, 28.09.2023,

Author

Abdallah Alrefaie

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LIST OF ABBREVIATIONS

AAMs **Alkali-activated materials**

AMD **Acid mine drainage**

CS **Chitosan**

DI water **Deionized water**

ISO **International Organization for Standardization**

MK **Metakaolin**

XPS **X-ray Photoelectron Spectroscopy**

1 INTRODUCTION

In 1985, **Joseph Davidovits** proposed Geopolymer, and it has been widely used for the purpose of describing a class of amorphous to semi-crystalline three-dimensional silica-alumina inorganic materials. As a new green cementitious material, geopolymer has received considerable attention recently. Describing the preparation process of geopolymer, starting by adding an alkali activator into silica-alumina raw materials, $(SiO_4)^{-2}$ tetrahedrons and $(AlO_4)^{-2}$ tetrahedrons can then be staggered and overlapped to form the geopolymer with three-dimensional network structure through the process of "solution-monomer-reconstruction-poly-condensation". Some distinguished advantages of geopolymer formed by geopolymerization compared with the commonly used Ordinary Portland Cement such as low carbon dioxide emissions and low energy consumption. In addition, other properties have been mentioned recently, such as good fire resistance, excellent acid resistance, desirable impermeability, rapid development of early strength and high compressive strength. However, before it can be widely used as a building material, its high brittleness and poor toughness are not negligible disadvantages **(Qin et al., 2020)**.

The shortcoming (low ratio of flexural strength to compressive strength) restricts seriously the applications of geopolymer in modern concrete engineering, which has higher and stricter requirements for flexural and tensile strength, stiffness, ductility, toughness, and crack resistance ability. To reinforce geopolymer as well as to cope with the poor flexural toughness, **(Qin et al., 2020) found that Dias et al., Lin et al., and Sun et al.,** used fibers, such as basalt fibers, carbon fibers, and polyvinyl alcohol fibers (PVA). Indeed, it was found that the addition of fibers had a toughening effect on geopolymer to a certain degree. Moreover, organic polymer with functional groups has also been applied to toughen geopolymer.

Organic polymers could improve the structure of geopolymers at both molecular and submicroscopic levels. Chitosan is a long-chain organic polymer, which can be obtained by deacetylation of chitin, i.e., the main component of the cell wall in the exoskeleton. It is rich in sources and has good biocompatibility, desirable biodegradability, and nontoxicity. It is noted that the modulus ratio and concentration of alkali activator are key

factors affecting the mechanical properties of geopolymer **(Qin et al., 2020). Chitosan is soluble in aqueous acidic media via primary amine protonation (Aranaz et al., 2021).**

The applications of alkali-activated materials (AAMs) in waste treatment are the separation, elimination, or immobilization of inorganic or organic pollutants present in wastewater, gas, or solid waste streams **(LUUKKONEN, 2020).** One of the subcategories of environmental technology is waste treatment or (so-called end-of-pipe treatment) **(Kuehr, 2007).** "Natural processes can cause contamination, such as in the case of groundwater dissolving igneous and sedimentary rocks to release arsenic and other potentially toxic elements" **(LUUKKONEN, 2020).** The UN Sustainable Development Goals, especially **SDG6 (Clean Water and Sanitation) and SDG12 (responsible consumption and production)** are all strongly connected to pollution control and waste treatment. As **(LUUKKONEN, 2020)** AAMs are needed because they provide interesting or even unique prospects due to their simple, low-energy and flexible preparation processes combined with promising technical performance in pollution control when compared to some of the currently used materials (such as synthetic zeolites or conventional ceramics).

By treating wastewater better, there may be more health benefits. Almost 1 billion individuals still engage in open defecation worldwide, even though 2.1 billion people have had access to better sanitation facilities since 1990. **The 2017 World Water Development Report from the United Nations (PDF). The Untapped Resource: Wastewater.**

The term alkali activation (also called alkaline activation) refers to a series of reactions taking place between a solid silicate or aluminosilicate precursor and an alkali activator (or alkali source) at high pH, which include dissolution, coagulation, polycondensation, and, ultimately, a formation of hardened new mineral phase at relatively low temperature (< 100°C) **(Duxson et al., 2007; Provis, 2014, 2018).**

Some individuals consider geopolymers to be a subset of AAMs **(Provis, 2014).** The sodium-aluminium-silicate-hydrate gel (or N-A-S-H in the cement chemist nomenclature), with $SiQ4(2Al)$ as the predominate silicon microenvironment, makes up the nanoscale structure of low-calcium AAMs (i.e., geopolymers).
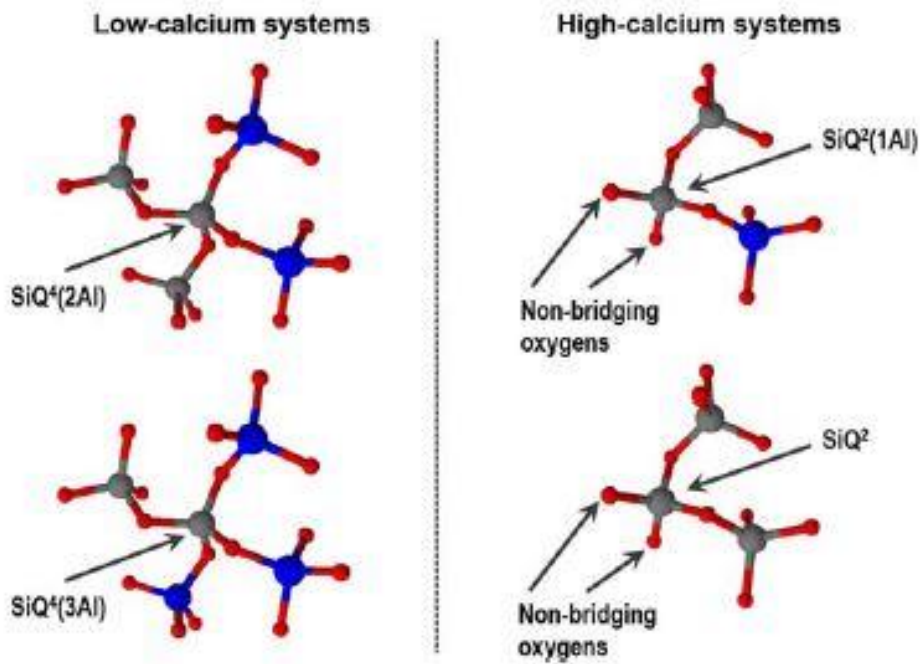
Fig. 1. The predominant silicon environments in low-calcium alkali-activated materials (geopolymers) and high-calcium alkali-activated materials according to Lecomte et al. (2006). The grey atoms in the figure represent silicon, red atoms oxygen, and blue atoms aluminum.

It should be noted that the term "geopolymer" is occasionally used in the literature to refer to aluminosilicate materials made with acids, such as phosphoric acid, rather than alkali activator **(He et al., 2016, p. 4; Lin et al., 2021; Wang et al., 2019; Zhang et al., 2020)**. In addition, there are some similarities between alkali- and acid-activated materials such as the fact that both harden at (near) ambient temperature **(kinnunen et al., 2018).**

1.1 Water Balance Management System Components

In general, the mine-site water cycles can be divided into three categories:

- Both process waters and the process effluent waters to be discharged after treatment.
- Clean waters category, which includes groundwaters, surface waters, as well as rainfall, snowfall, and water evaporation. Mine the watering waters basically represent groundwaters but due to their possible salinity, high concentrations of

metals and metalloids as well as the amount of N-compounds, water treatment is usually required.

- Wastewaters and/or utilized waters that may or may not need treatment are contained in tailings, dams, ponds, seepage waters, etc., the treatment facilities are also included here.
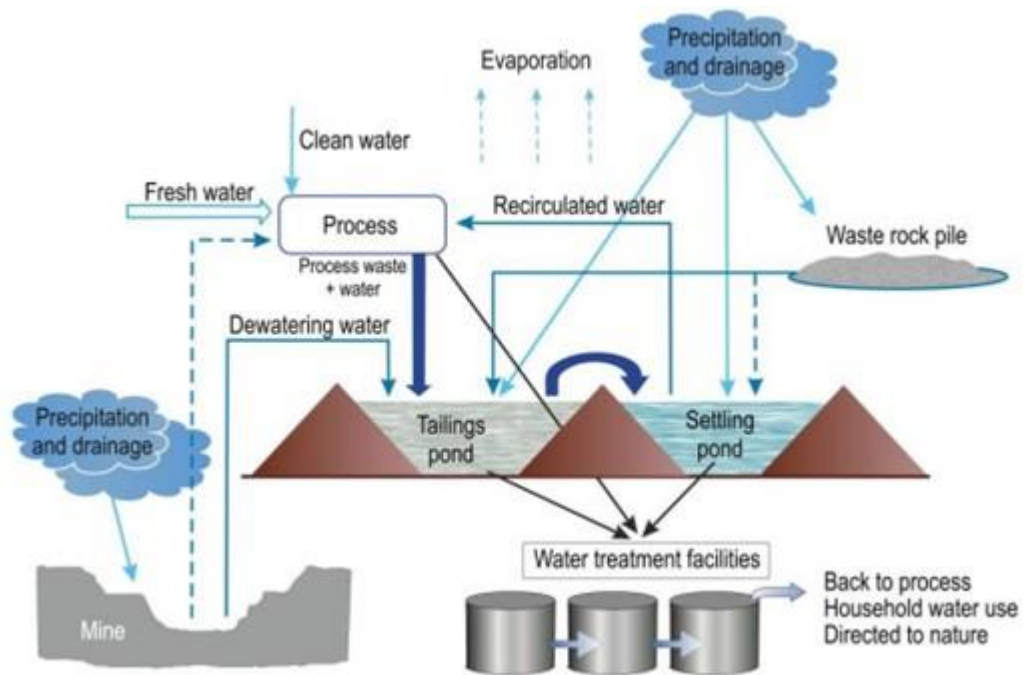
Fig. 2. Example of different mine water sources and streams (modified from Kauppila et al. 2011)

Characteristics affecting mine water balance in Finland

The water balances in Finnish mines; are typically net positive **(Haanpää, 2013).** According to **Salonen et al. (2014),** the typical overbalance varies from 40% to 60%. The following table clarifies the net water in Finland.

Table 1. Average amounts of precipitation, runoff, and evaporation in Finland (Karhu, 2005).

	Amount, mm/a	Comments
Precipitation	500-750	August is the rainiest, March is the driest
Overall runoff	200-400	Share of spring runoff is around 30-50%
Evaporation	300-400	In Northern Finland, the evaporation rate is only ~25-50% of the average

The main problems that can be found during the mining process are as follows:

Acid mine drainage

The contact time between ore and water should be as limited as possible to prevent the creation of acid mine drainage and other harmful effects of dissolution. **(Khanyisa Thisani et al., 2021)** in this study for the remediation solution for Acid Mine Drainage showed that chemical desalination the greatest potential with high quality treated water and operational costs.

Soil pollution

Heavy metals present in the soil cause risks to the whole biosphere and are ingested directly by plants, which can be hazardous for both the plant and the food chain that consumes the plant. They also change the soil´s properties, such as pH, colour, porosity, and natural chemistry, which affect the soil´s quality and contaminates the water **(Briffa et al., 2020)**.

Water pollution

By the runoffs, the metals are brought from villages, towns, cities, and industries which accumulate in the sediments of water bodies. The toxicity of heavy metals depends on many factors such as the nature of the metal. They are found in high concentrations in raw sewage, and they are not degraded in sewage treatment. They are removed either in the final effluent or in the sludge produced **(Briffa et al., 2020).**

Air pollution

The division of the atmosphere is into five layers, the essential layers are the troposphere and stratosphere for pollutant migration. The closest layer to the Earth is the troposphere and above it is the stratosphere where at the top the ozone layer lies. Pollutants enter the atmosphere as particles, droplets, or in the gaseous form, or in association with particles and droplets. One example of the sources of atmospheric pollution is the particulate matter (PMs) that can precipitate severe health problems, the formation of acid rain, corrosion, eutrophication due to particulate matters failing in the water when it rains, and it can cause haze **(Briffa et al., 2020).**

The mining sector has largely ignored the economic consequences of clean air, water, and soil. As a result, the scale of mining increases exponentially, as do its detrimental effects (Margarete Kalin, 2004)

1.2 Treatment Methods for Mine Water

The selection between active and passive water treatment is essential for the success of the treatment. The selection of the active or passive treatment depends on some factors such as sufficient space, chemistry, flow rates once they are expected to do not change with time, then in this case, the passive treatment can be appropriate as active mines. In the long term in terms of cost, passive treatment is more economic than active treatment. **(Trumm, 2010)**.

Typical active systems require continuous dosing with chemicals, power consumed and required regular operation and maintenance. On top of the advantages, they are effective at removing contaminants from mine drainage, have precise process control and could be accommodated in locations where only a small land area is available. Some of the disadvantages of active treatment are the high capital cost and high ongoing operation costs **(Trumm, 2010).**

The reliability of the passive systems depends on natural physical, geochemical, and biological processes **(Skousen et al., 200)**. Also, most passive treatment systems rely on the dissolution of a neutralizing material (usually limestone). Typical passive systems require large land areas and are more suited to complement active systems or closed mine sites. Several factors can influence the decision whether to use active or passive treatment.
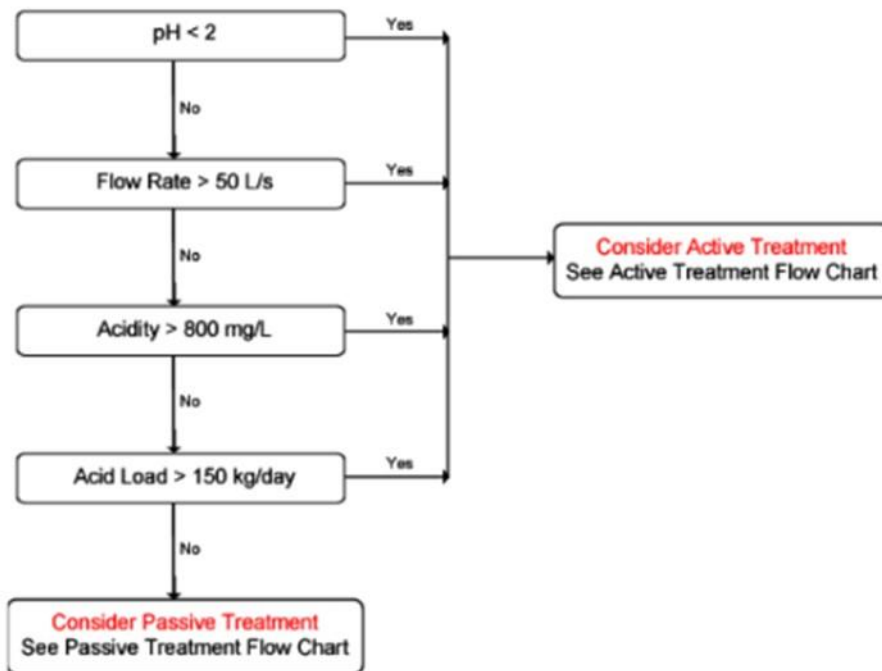

Fig. 3. Flow chart to select between active and passive treatment for AMD, (Modified from Waters et al., 2003)

For the selection of the appropriate chemical is primarily dependent on the concentration of dissolved Mn and Fe and the flow rate of the AMD, although other factors will influence chemical selection. Such as chemical cost, neutralizing efficiency, maximum pH potential and therefore the ability to remove metals such as Mn, the dispensing

mechanism required, mixing mechanism required, health and safety issues, sludge settling rates and therefore the requirement for flocculants or coagulants; and resulting sludge volume and density **(Skousen et al., 2000; Waters et al., 2003; Means, 2006).**

1.3 Passive Mine Water Treatment

The passive system was first documented in the early 1980s during studies conducted by Hunstman et al. and Wieder and Lang; natural Sphagnum mosses wetlands that received acid mine drainage resulted in the amelioration of water quality.

For the development of the most applied passive treatment schemes, anaerobic processes were found to be important in metals removal and ecosystems are not needed. The main processes encountered in passive treatment systems for the removal contaminants are summarized:

- Oxidation and hydrolysis
- Metal removal by plants algae and organic substrates
- Reduction
- Limestone addition

There are also other methods that have been considered in other countries as stated in a European Commission report in mining waste. The Swedish technique is a text-based, qualitative decision-support system that uses the information that is currently available, maybe including sample analysis from the contaminated areas but not always. The Swedish method evaluates four criteria: potential for contaminant spread, level of contamination, hazard of contamination, and sensitivity of the site's environment (e.g., soil, groundwater). Based on the investigator's reading of the data, a chart is used to determine the risk class. There are four risk classes: 1 (very high risk) to 4 (low risk).

The German technique, in comparison, employs a quantitative way to evaluate the air, soil, surface water, and groundwater at contaminated locations. It is a model-based decision-support system. Points are given, for example, to represent the usage, state, and degree of contamination of groundwater. Sites are automatically categorised into one of

three risk classes based on the total amount of points for each of the four environmental compartments, with the compartment with the highest score receiving the greatest weight.

1.4 Adsorption Method

To describe the adsorption processes that are used for drinking water, industrial water, and wastewater. Adsorption and/or ion-exchange processes with natural zeolites or activated carbon can be applied for various tertiary treatments, for example, nutrients or organic micropollutants removal in municipal wastewater treatment **(Tchobanoglous et al., 2004)**.

1.5 Alkali-Activated Material

Since the original work of **Li et al. (2006)** and to date, the majority of studies evaluated the use of powdered AAMs as adsorbent, possibly due to expected higher specific surface area (SSA) compared to the use of bulk-type (not powders) bodies ultimately inducing higher pollutants sorption. The common route involves crushing, grinding, and sieving steps to obtain micrometer-sized powders with the required size. The recommended sorbent particle size is **(63 <d<125) μm (Luukkonen et al., 2016**). Nevertheless, this size has been applied to laboratory experiments.

The use of bulk-type AAMs in wastewater treatment is much less explored, despite the increasing interest in this avenue possibly connected with their easier recovery after sorption compared to their powdered counterparts. Granules are mostly irregular. Monolithic bodies (e.g., membranes) are a subset of bulk-type AAMs and their use in wastewater treatment applications is recent.

AAMs have been evaluated as adsorbents for various pollutants typically found in industrial wastewaters, mostly considering the extraction of heavy metals and dyes, but

other relevant pollutants have also been considered at a lower degree, including surfactants, radioisotopes-bearing elements, and ammonium.

The presence of heavy metals in industrial wastewaters **(Rasaki et al., 2019)** and drinking waters **(Pieper et al., 2018; Roy et al., 2019)** is a serious and long-lasting problem. Concerns about their presence, even at trace levels, in water sources and their severe impact on human health **(Siyal et al., 2018)** help to explain the high number of studies that have addressed the use of AAMs as heavy metals adsorbents. Heavy metals such as cadmium, chromium, copper, nickel, lead, and zinc have been studied (detailed reviews can be found in **Luukkonen et al., 2019; Novais et al., 2020b; Rasaki et al., 2019; Siyal et al., 2018**).

Lead is one of the most toxic and common heavy metals in industrial effluents, and as a result, it has been frequently employed as a model heavy metal in studies dealing with adsorption by using pulverized or bulk-type AAMs. Compared to Cu (II), AAMs usually show higher affinity for Pb (II) ions regardless of the adsorbents' shape which relates to the smaller size of the hydrated Pb21 ions, and their lower free energy of hydration compared to the Cu21 **(Cheng et al., 2012; Tang et al., 2019a).** All these studies corroborate the higher selectivity of the AAMs sorbents toward lead ions. The selectivity of AAMs is a key point that will ultimately dictate their behavior as adsorbents when dealing with real effluents where the presence of other heavy metals or contaminants is to be expected. The synthesis of sorbents requires a thermal treatment at 45 °C for 6 hr to eliminate the silica oil, increasing the sorbent´.

Adsorption of dyes using AAMs has been a subject of study over the years, but to a lower degree compared to works studying the removal of heavy metals from wastewater, as can be repeated from the analysis of recent reviews.
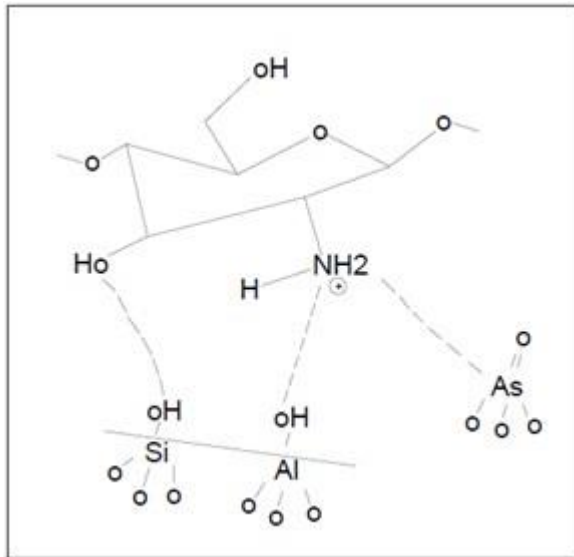
Fig. 4. Schematic representation of a possible bonding formation between chitosan (CS), geopolymer and arsenic (As5) from lab experiments

2 MATERIALS& METHODS

The preparation of acid-dissolved chitosan-based geopolymer composite, its characterization, and its application for adsorption of heavy metals will be discussed in this chapter.

2.1 Raw materials

Acid-dissolved chitosan solution preparation:

To prepare the acid-dissolved chitosan solution, 0.5 g of chitosan was added to a 15.5 mL solution containing 2% acetic acid. The mixture was then stirred overnight using a magnetic stirrer. To aid in the dissolution of chitosan, the solution was shortly heated in an oven at 60 °C.

Alkali-solution preparation:

After that, measuring the amount required 19.63 g of Na-metasilicate and measuring 4.04 g of Silica fume and mix them with 17 mL of DI water for the overnight and heated it for the mixing and dissolving purposes at 60 °C.

Preparation of Metakaolin (MK) and Chitosan (Cs) composite based geopolymer (acid-dissolved chitosan):

Bring metakaolin and measure the amount to be 84.4 g in a mixing vessel. Then, add 2% acetic acid-dissolved chitosan solution and alkali-activator solution. After that, mix them in a vessel homogeneously by using high speed shear mixer at 1500 – 2000 rpm for 5 minutes. After mixing, pour the paste in the silicon mold and keep them in a plastic bag. After 7 days, demolding the samples and pulverized them by using vibrating disc mill (**RS-150**).

Preparation of the adsorbents:

Move forward after the pulverization of the chitosan-based geopolymer, sieve analysis has been completed with a size (63-125 µm), the main reason that we have taken this range size 63<d<125 µm (**Luukkonen et al., 2016**) in our lab experiments is to reach to the optimum range of our sample.
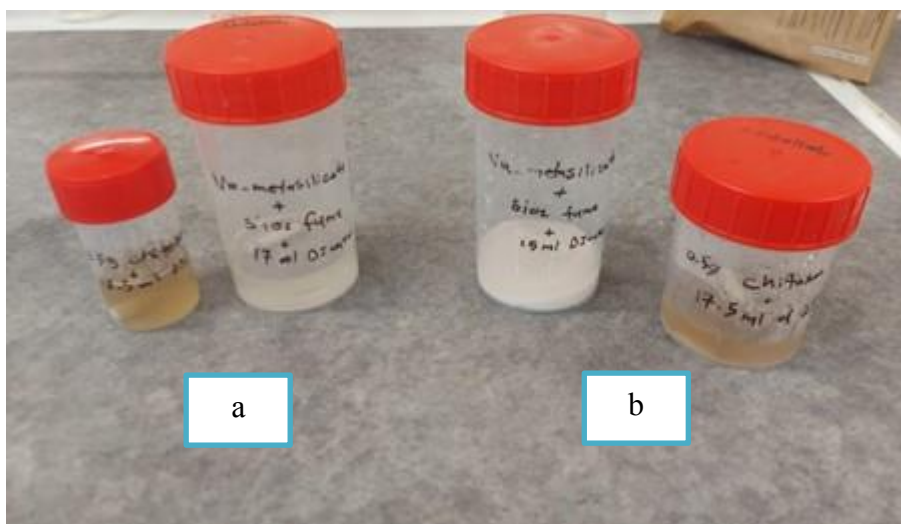
Fig. 5. The optimum amount of the mixture for the CS adsorbent: (a) Mixture 1, (b) Mixture 2.

2.2 Neutralization of the adsorbents

Neutralization of the adsorbent by using 0.1M acetic acid (CH_3COOH). The preparation of the 0.1M acetic acid is by taking 5.7 mL glacial acetic acid (100%, VWR Merck) in little amount of DI water in 1 L volumetric flask. Pour the glacial acetic acid quantity and then the DI water till reach to 1 L. Neutralization of the adsorbents (pH to be around 7) by using 0.1M acetic acid. The pH of the filtrate liquid was measured whether it was in the pH range or not (6.5-7.5). The mixture was filtered through filter paper with pore sizes of 0.45 μm 50 mm because it is a typical size of bacteria, the standard.

Furthermore, another mixture was poured through the adsorbent powder on the filter paper with different size. This process was repeated for every batch of adsorbents until the targeted pH was reached for another mixture. After that, the drying of the sample in the oven at 60 °C for 24 hr. completed. After drying, the final prepared adsorbents were preserved in separate plastic containers at room temperature (~22°C) to avoid contamination.

2.3 Methods for Characterization and Adsorption Experiment of The Adsorbents

2.3.1 Characterization Method for Adsorbents Containing Chitin/Chitosan

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is an analysis technique that allows the determination of the oxidation state, the nearest adjacent atoms, the type of bond, and the surface (approximately 1-10 nm) **(kanuchova et al., 2015).** The **ESCALAB 250Xi system** was used to perform the XPS analysis at the Centre for Material Analysis of the University of Oulu. In this study, the surface atomic percentages of oxygen, silicon, sodium, aluminum, carbon, and nitrogen adsorbents were determined.

2.3.2 Adsorption Method

One of the serious and long-lasting problems is the presence of heavy metals in industrial wastewaters **(Rasaki et al., 2019)** and drinking waters **(Pieper et al., 2018; Roy et al., 2019).** AAMs have been examined as an adsorbent for a variety of pollutants normally present in industrial wastewater, with the extraction of heavy metals and dyes receiving most of the focus. However, other pertinent contaminants, such as Ammonium, radioisotopes-bearing elements, and surfactants **Siyal et al., (2018)** employed the AAMs as heavy metals adsorbents on their work. Heavy metals such as copper, nickel, lead, and zinc have been studied **(Luukkonen et al., 2019; Novais et al., 2020b; Rasaki et al., 2019; Siyal et al., 2018**).

2.4 Experimental Work

2.4.1 Adsorption Test with Adsorbents Containing Chitin/Chitosan

Preparation of model water

The preparation of the stock solution (c) was by adding $MnCl_2.4H_2O$ ($\geq$ 98%, Sigma-Aldrich), $ZnCl_2$ ($\geq$ 98%, Sigma-Aldrich) and $NiCl_2.6H_2O$ according to the table in 100 mL of DI water (each metal concentration 1 g/L). As for arsenic, a separate stock solution

(d) with NaOH was prepared as arsenic is not soluble in DI water. This solution was prepared by adding 0.132g of As_2O_3 in 100 mL of 6 M NaOH so that the As concentration remains 1 g/L. Both stock solutions (c& d) were shaken in a reciprocal shaker for 24 hours. Model water (a) was prepared by diluting stock solution (c) with DI water (as 10 mL/L respectively) in a method that detains the concentration of Ni, Zn, and Mn as 10 mg/L. Since stock solution (d) was made with NaOH, it has a high pH range, and it was affecting the other the disassociation of other metal salts used in model water (a). Model water (b) was prepared by diluting stock solution (d) with DI water (as 10 mL/L respectively). Both model water (a& b) were stirred on a magnetic stirrer and the pH range was adjusted to 4.00 using HCL acid (37%, Sigma-Aldrich), if the pH is above 4, then it can precipitate.

Table 2. Amount of salts needed for the preparation of stock solution (c)

Salt used	The required amount of salt in DI water for 100 mL stock solution (c), g
$MnCl_2.4H_2O$	0.36
$ZnCl_2$	0.21
$NiCl2.6H_2O$	0.41

The procedure of batch adsorption test

Each experiment was carried out in triplicate using model water (a& b). First, 40 mL of model water (a) or model water (b) and 0.04 g of adsorbent were weighed into a 50 mL tube. Using a reciprocal shaker, the tubes were shaken for 24 hours at a speed of 220 rpm. After that, a pH meter and probe were used to measure the pH of the solutions. Following

that, each solution was filtered through a 0.45 µm filter paper. The filtrate solutions were collected.

Furthermore, all the solutions were sent to the **Feasib Oy lab** to determine the concentration of Ni, Zn, and Mn (using the FAAS method) and to the **Eurofins** external laboratory to determine the concentration of As (**using SFS-EN ISO 17294-2:2016 method**). The removal capacity (%) of the adsorbents is determined by the following equation:

$$Rn = \frac{(Co - Cn) \times 100}{Co}\%$$

Where **R_n** is the removal percentage of metals (%)

Co is the initial concentration of metal in model water (mg/L)

Cn is the remaining concentration of metal in the treated water (mg/L)

n = 1, 2, 3 as experiments were conducted thrice and the average of the three results were taken for each batch of adsorbents.

3 RESULTS& DISCUSSION

3.1 Results for Heavy Metals

To evaluate the ability of adsorption of (Ni, Zn, Mn), the variables such as concentrations, contact time and pH were studied. These effets of different experimental factors such as pH, reaction time, and initial concentration usually studied **(Panda L et al., 2020)** for the purpose of optimizaton the removal efficiency.

3.1.1 Adsorption Experiment with Variable Adsorbent Dosage for Heavy Metals (Ni, Zn, Mn)

Firstly, the adsorption of Ni, Zn, and Mn was investigated by determining the effect of variable adsorbent dosage. The figure below illustrates the efficiency of heavy metals removal with different dosages varying from 5 to 30 mg for Ni, Zn, and Mn. Results show that the adsorption rate of materials towards all the tested heavy metals is comparable. It can be noticed that Ni& Mn have a higher percentage of removal compared to Zn. However, the peak value where the highest removal is happening is when using 20mg of adsorbent.
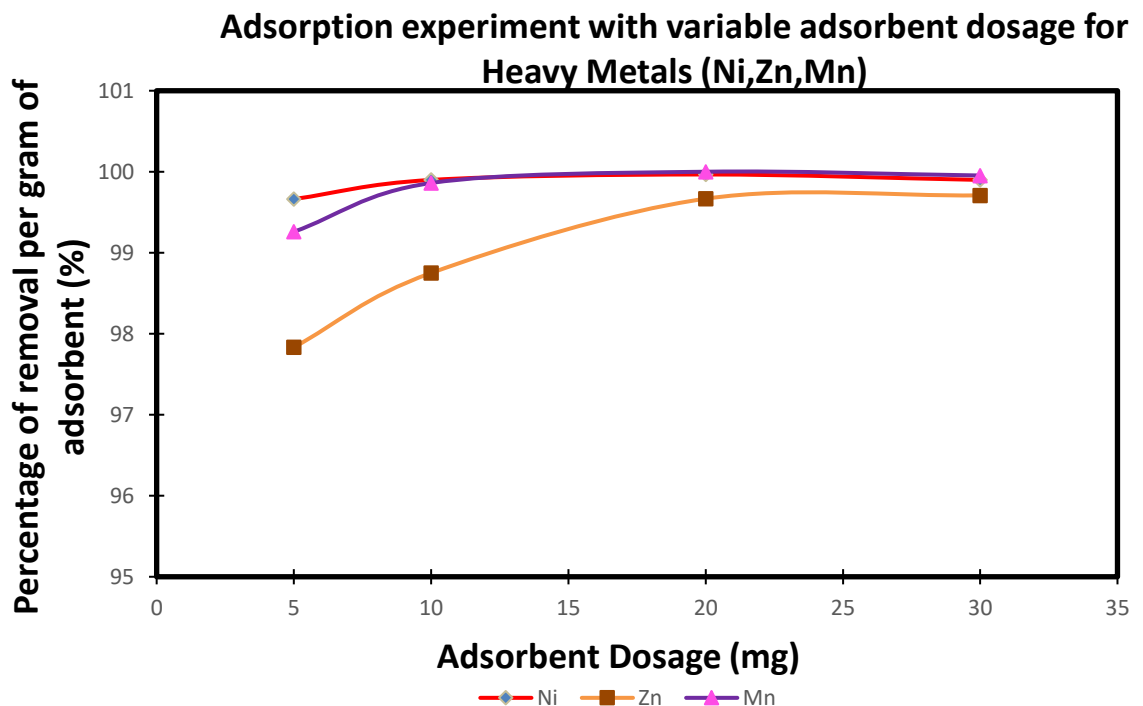
Fig. 6. Adsorption experiment with variable adsorbent dosage (mg) for Heavy Metals (Ni, Zn, Mn).

(Jaafarzadeh et al., 2014) studied in their research the effect of adsorbent dosage and their study showed that the removal efficiency of ZN (II) increased with the increase of adsorbent dosage.

3.1.2 Adsorption experiment with variable contact time for Heavy Metals (Ni, Zn, Mn)

In the beginning, the adsorption of Ni, Zn, and Mn was investigated by determining the effect of contact time. The figure below illustrates the efficiency of heavy metals removal with different time varying in this range (24hr, 9hr, 6hr, 3hr, 2hr, 1hr, 30 min, 15min, 5min) for Ni, Zn, Mn. Results show that the adsorption rate of materials towards all the tested heavy metals is comparable. It can be noticed that the lowest removal is once the experiment was conducted at 30 min so the precipitation achieved. Furthermore, the materials have almost the same percentage in removal.

Fig. 7. Adsorption experiment with variable contact time (min) for Heavy Metals (Ni, Zn, Mn).

(Boulaiche et al., 2019) in their research, for the removal of heavy metals: the adsorption equilibrium occurs within 30 min of all metals in the effect of contact time.

3.1.3 Adsorption experiment with variable pH for Heavy Metals (Ni, Zn, Mn)

The adsorption of Ni, Zn, Mn was investigated by determining the effect of variable pH. In the experiment, the examination was completed with different pH ranges (2,3,5), and triplicate samples for each range of all materials. It is noted from the graph that the Manganese has the highest removal compared to Nickel and Zinc. The pH of the water containing adsorbents was recorded for each batch after the adsorption experiment. It was increased for all ranges. The results for all materials were, the average of **pH2** was (3.74),

the average of **pH3** was (6.35) and the average of **pH5** was (7.
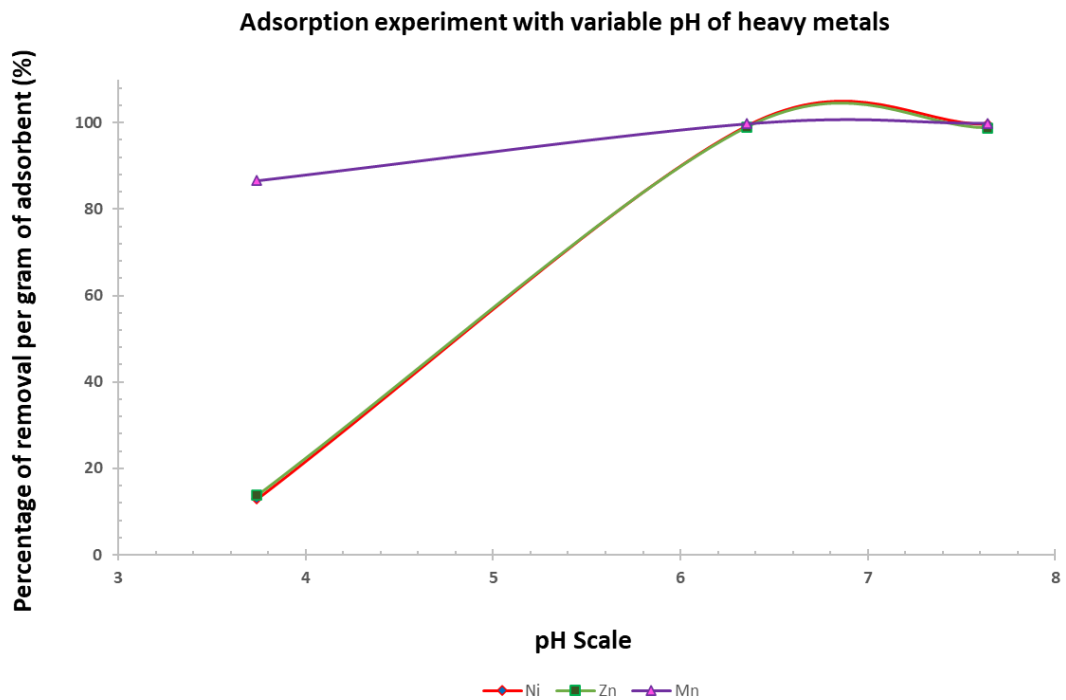
Fig. 8. Adsorption experiment with variable pH for Heavy Metals (Ni, Zn, Mn).

3.1.4 Adsorption experiment with variable initial concentration for Heavy Metals (Ni, Zn, Mn)

The adsorption of Ni, Zn, Mn was investigated by determining the effect of variable initial concentrations after sending them to the Feasib lab. In the experiment, the concentrations were (12 mg/l, 15 mg/l, 20 mg/l, 25 mg/l, 50 mg/l, 100 mg/l, 150 mg/l). In total, there were 21 samples, tripled for each concentration. It is noted from the graph that 12 mg/l and 15 mg/l have the highest removal percentage. The peak value was with a concentration of 100 mg/l. There was a slightly decrease with the highest concentration (150 mg/l)
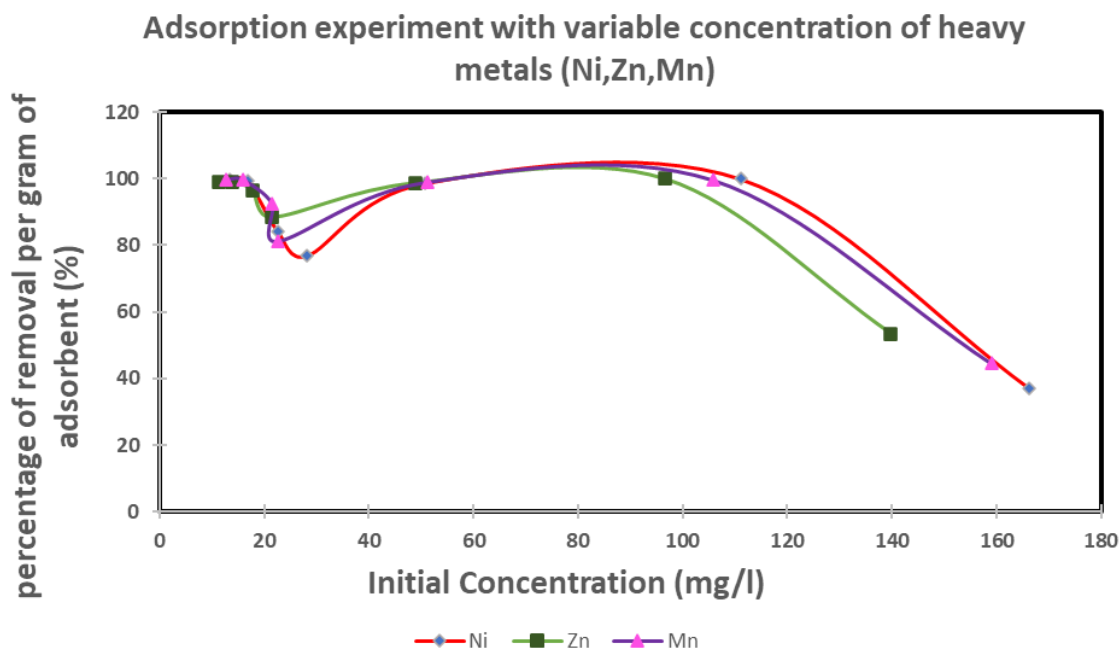
Fig. 9. Adsorption experiment with variable initial concentration for Heavy Metals (Ni, Zn, Mn).

One study showed a good efficiency removal of nitrate in the presence of Zn at initial concentration 40 mg Zn/L with a range of 17-50 and 9-26% **(Kyriaki et al, 2017)** and this is with different microbial cultures.

3.1.5 Adsorption experiment with variable concentration of Arsenic (As)

Table 3. First batch of the Arsenic experiment with variable concentration

Variable Concentration (As)		
Fixed dose	40	Mg/L

	Volume of water	40 mL								
	Initial Concentration	**Concentration after treatment**			**Average**	**Std. Dev**	**Removal Concentration**		**Average**	**Std. Dev**
mg/L	µg/L, R. S	As S1	As S2	As S3						
1.2	1200	1200	1100	1100	1133.33	57.74	0 100 100		66.67	57.74

As S1 = Arsenic sample no. 1, As S2 = Arsenic sample no.2, As S3 = Arsenic sample no.3, R. S = Reference Sample

Arsenic concentrations were determined by sending the samples to the external lab (Eurofins) in Oulu, by doing the atomic emission spectroscopy by parallel action inductively coupled plasma spectrometer ICP.

These samples were analyzed on 14th July 2023 from Eurofins lab. It is noticeable from the second and third samples that the percentage of removal is 100%, as an average, the removal was 66.67 %.

As for the second batch of the experiment, we received results in the following schedule. No removal has happened.

Table 4. Second batch of the Arsenic experiment

Analysis	Test Code	Unit	Outcome	Outcome	Outcome	Outcome	Outcome
Elemental Analysis							
Arsenic (As)	YB0XG	Mg/L	1.5	1.5	1.5	1.5	1.5

*The method is accredited.

3.2 Results for adsorbents containing chitin/chitosan

Table 5. Peak table results of X-ray photoelectron spectroscopy (XPS)

	Peak Table	
Name	**Peak BE**	**Atomic %**
Al2p	73.09	10.00
C1s	284.83	3.63
N1s	399.15	0.43
Na1s	1074.62	10.24
O1s	530.98	58.25
Si2p	101.22	17.46

X-ray photoelectron spectroscopy (**XPS**) is an analysis technique that allows the determination of the oxidation state, the nearest adjacent atoms, the type of bond, and the surface (approximately 1-10 nm) **(kanuchova et al., 2015).** The **ESCALAB 250Xi system** was used to perform the XPS analysis at the Centre for Material Analysis of the University of Oulu. XPS characterised materials to get information on how the chitosan was integrated into the structure.

Binding Energy **(BE)** = Final energy of Ion – Initial energy of an atom

The energy of incident photon = **hv**

The kinetic energy of the scattered electron **(KE) = hv - BE**

From (Table 5) sodium (Na1s) has the highest binding energy with a value of 1074.62 ev.

XPS is a team activity with the knowledge of the overall analysis procedure. Data treatment is often shared between a material scientist and the instrument expert, all rely to a greater or lesser extent, on the support of others (researchers, students, interns etc.) within their research field, the instrument vendors, and designers of data analysis software. (N. Fairley et al., 2021)

However, in the XPS surface analysis results, the following elements were measured: Silicon (Si2p), Oygen (Ols), Sodium (Nals), Nitrogen (Nls), Carbon (Cls), Aluminum (Al2p).

3.2.1 Silicon (Si2p)
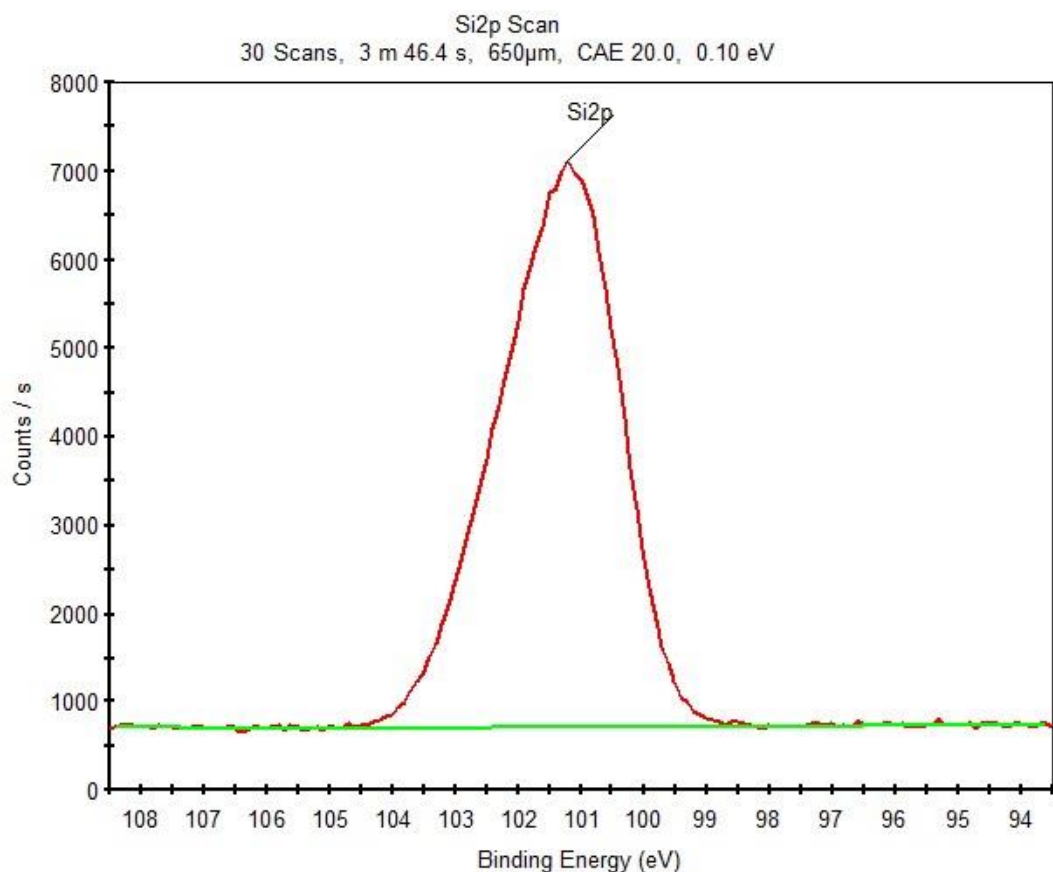
Fig. 10. XPS graph of Si2p silicon spectrum with peak BE

There is always uncertainty regarding the accuracy of XPS quantities, this uncertainty in sensitivity factors and other unknowns such the true background created by the inelastic scattering of electrons. To enhance analysis by peak models, quantification of a sample based on survey measurements was achieved.

3.2.2 Oxygen (O1s):
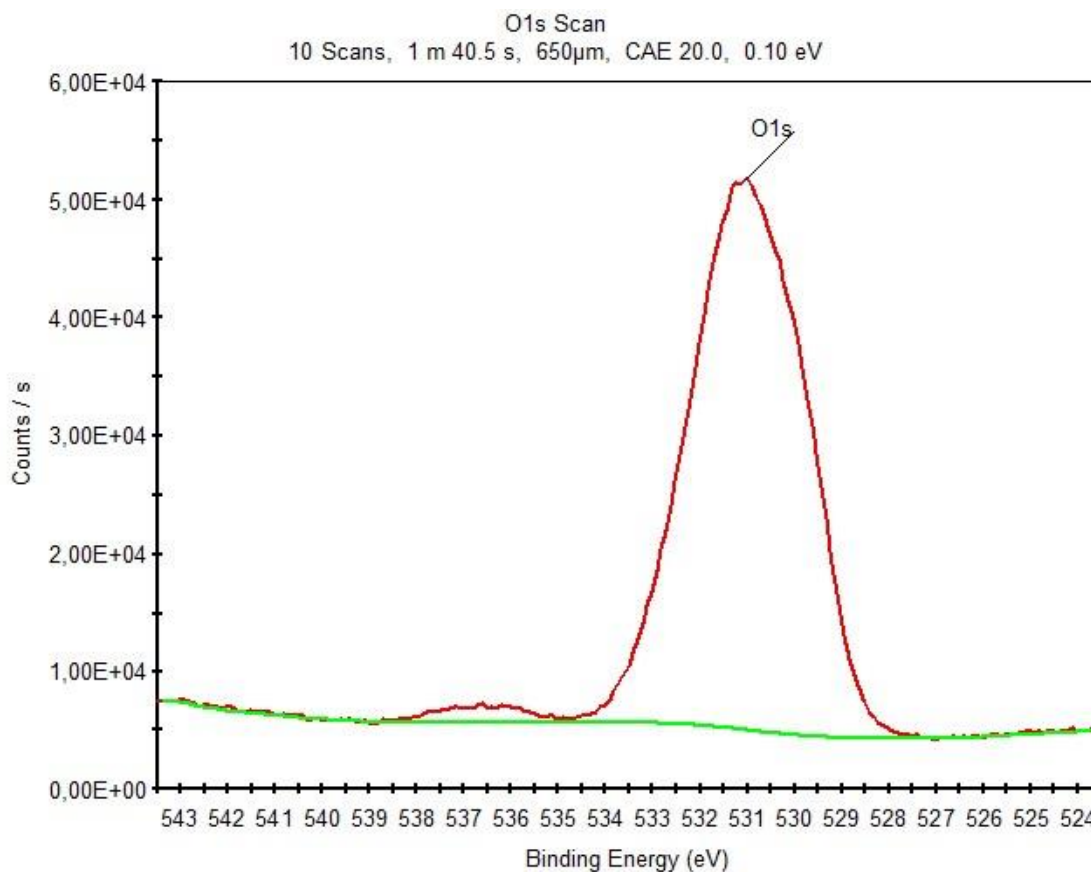
Fig. 11. XPS graph of Ols Oxygen spectrum with peak BE

3.2.3 Sodium (Na1s):
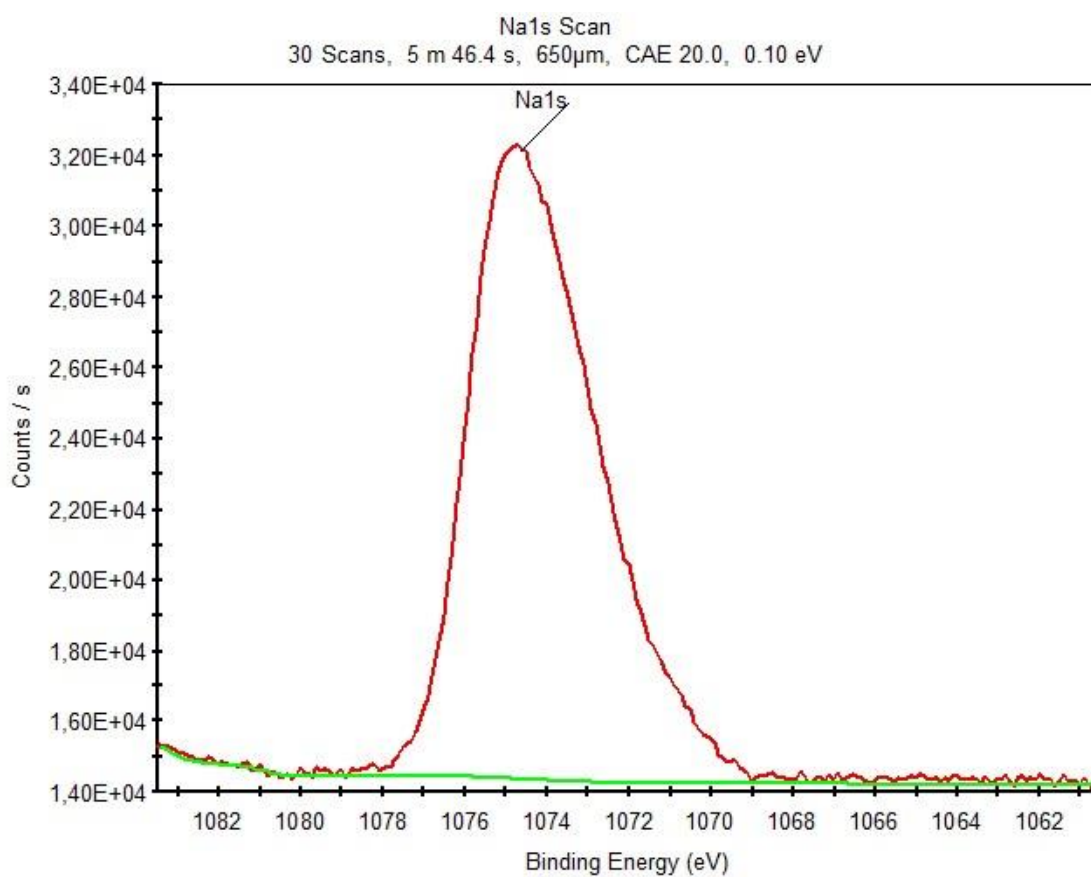
Fig. 12. XPS graph of Na1s Sodium spectrum with peak BE

3.2.4 Nitrogen (N1s):
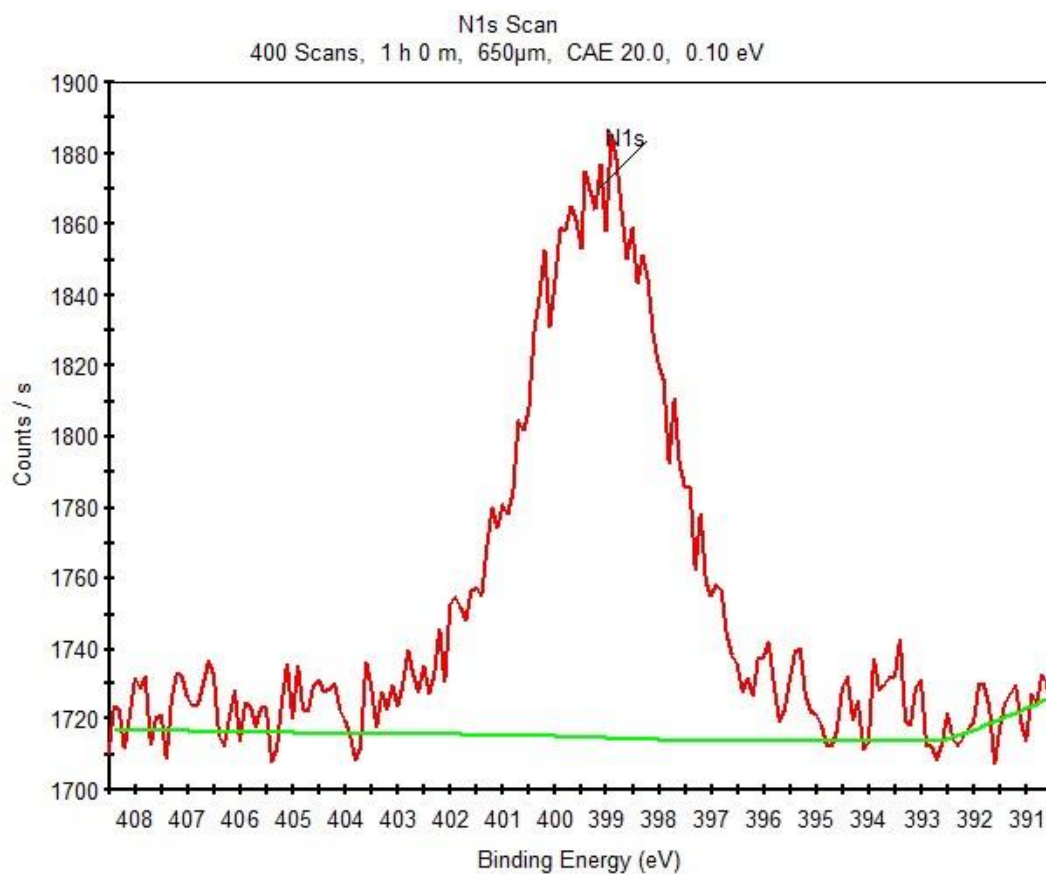
Fig. 13. XPS graph of N1s Nitrogen spectrum with peak BE

3.2.5 Carbon (C1s)
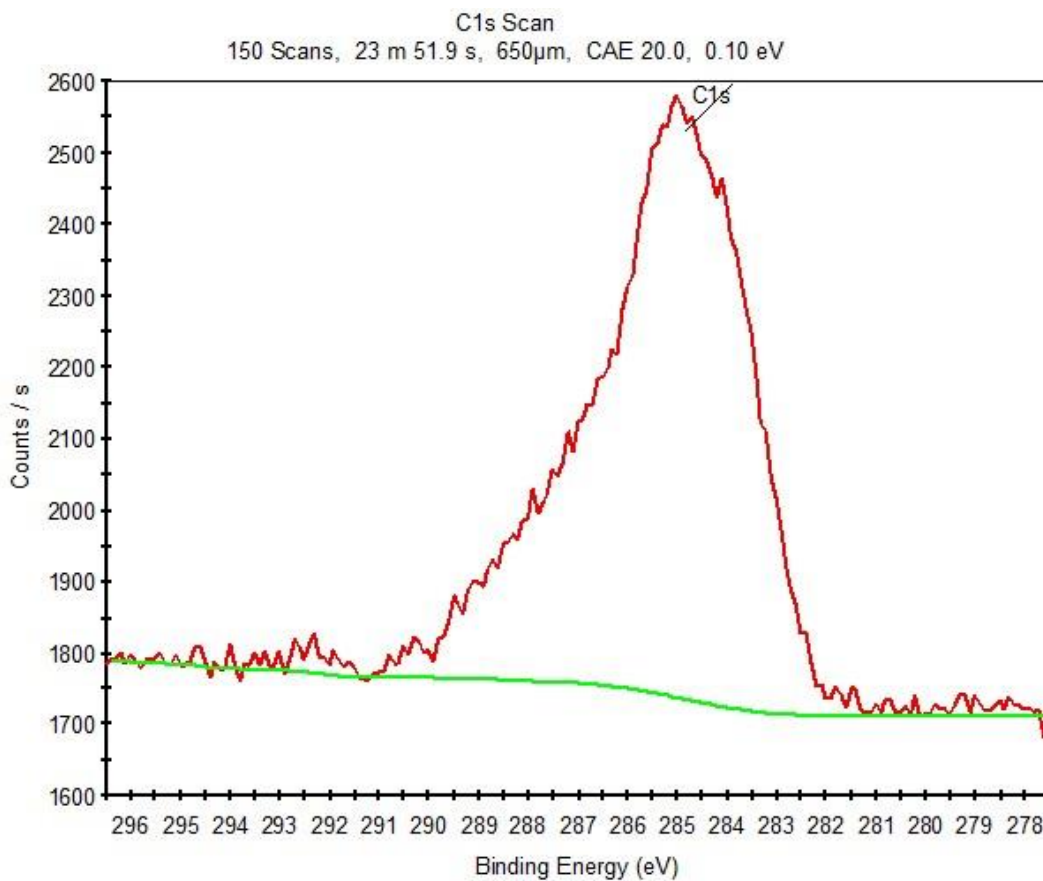
Fig. 14. XPS graph of C1s Carbon spectrum with peak BE

3.2.6 Aluminum (Al2p)
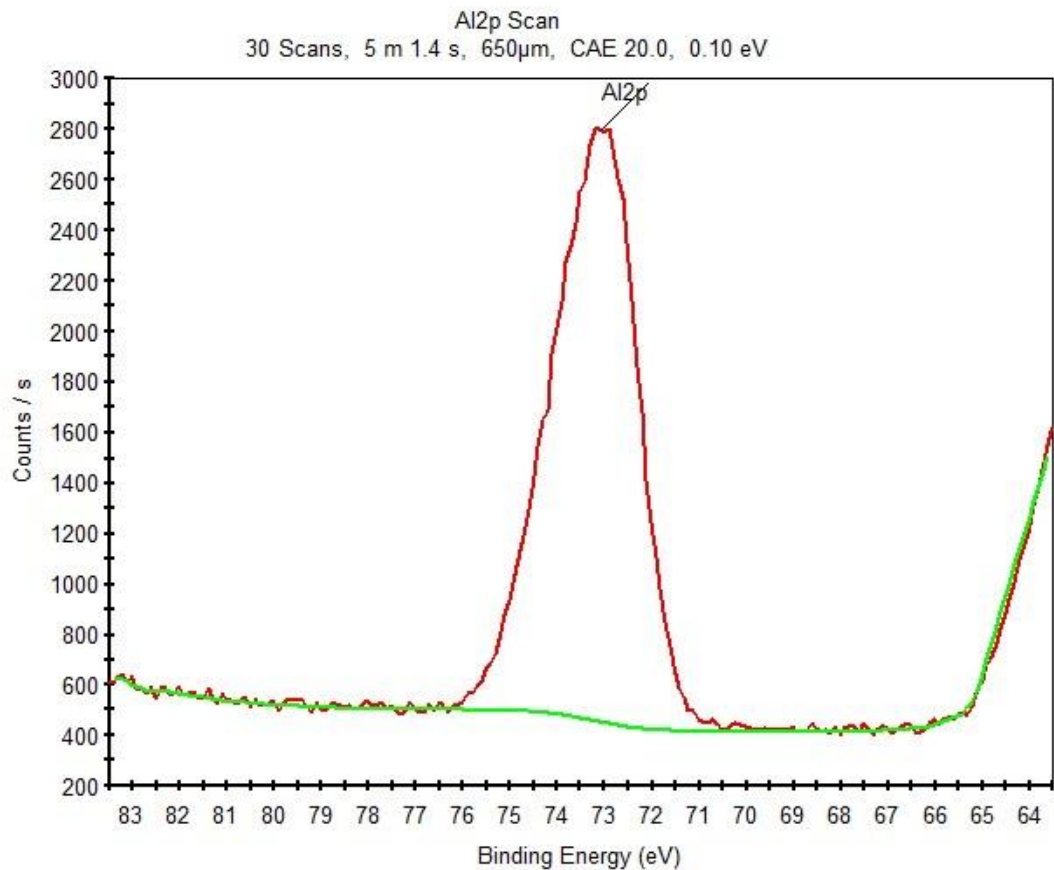
Fig. 15. XPS graph of Al2p Aluminum spectrum with peak BE

Consequently, a wide variety of different materials can be used as precursors, including, but not limited to, clay minerals, natural pozzolans, fly and bottom ashes from the combustion of solid fuels, metallurgical slags, mine tailings, sludges from water treatment, waste glass, and certain construction and demolition waste fractions **(Criado et al., 2017; Dadsetan et al., 2019; De Carvalho Gomes et al., 2019; Firdous et al., 2018; Khalifa et al., 2020; Kiventer¨a et al., 2020; Zhuang et al., 2016).**

4 CONCLUSIONS AND RECOMMENDATIONS

Overall, the toxicity in heavy metals while doing some work related to the mining industry affects our Earth's water resources which suggests precautions should be taken whenever mining activities are close to water streams. In a medium scale, laboratory manual must be studied and tested for a researcher before entering a lab. Lab tour is performed with scientists. Lab visits are performed gradually with experts before working on a project or a suggested protocol. However, this study presents the high-potential of geopolymer-based alkali activated adsorbents for heavy metal removal and the future possibility of recovering and reusing these removed metals.

In chemistry, pH is a logarithmic measure for the acidity of an aqueous solution like in our study. Logarithms are commonplace in scientific formulae, and in measurements of the complexity of algorithms. The adsorption experiment of independent variable pH for the removal of heavy metals (Ni, Zn, Mn) showed an increment of pH range for all pH ranges applied (2,3,5) to be between 3-7 in a pH scale, direct proportional with removal efficiency.

In mathematics, the average is the ratio of summation of all the data to the number of units present. In the adsorption experiment for the removal of (As), the average (66.67 %) showed a good removal efficiency because of chitosan addition. In statistics, the standard deviation is a measure of the amount of variation or dispersion of a set of values. The standard deviation of a sample like in our case in arsenic was 57.74 and it is to indicate how the values are close to the mean or spread out. Moreover, the arsenic used successfully was (As3) Arsenite, or trivalent arsenic. The separation of cationic transition metals and arsenic from water was evaluated by varying the adsorption conditions in the adsorption experiments.

Analysis of XPS data is best performed to get information of how the chitosan was integrated into the structure. Between the elements, (Na1s) showed highest peak BE and (O1s) showed highest atomic %.

Finally, if chitin/chitosan-based composites can be utilized, their removal efficiency can be compared with the existing toxic metal removal efficiency of powder adsorbents. One recommendation could be to purchase machines and provide them in labs for 3D printing for optimization for instance and check the manuals for external labs for the economic purposes.

Summary

The major goal of the research was to utilize chitosan-geopolymer composites and evaluate their ability to remove harmful metals from mine water/metal-concentrated model water. The objective has been accomplished since the study showed that the adsorbents have promising potential for further development in in mine water treatment. Adjusting the pH in the preparation of stock solution and model water, the solubility of chitin/chitosan in alkali-activator solution, checking the availability of materials in a plan before performing experiments and inform about the lack when it is occurred were some of the difficulties this study had to overcome.

Additionally, precipitation in some samples upon the completion of the adsorption experiments for heavy metals removal was clarified, and the high pH grade of As5 was noticed. These minor issues were not considered due to the short timeframe of the activity. However, there is still an opportunity in the advancement of this work for regeneration of adsorbent as well as by addressing the difficulties mentioned earlier.

ANNEX

Cost of the Technology

The case study that is considered for the cost Technology is Sewage Sludge Management at District Level: Reduction and Nutrients Recovery via Hydrothermal Carbonization in Trento WWTP

Each process and material has a cost, whether in situ and/or in the lab. Transport cost, disposal cost, new technology, maintenance cost, taxes, etc.

As **(D. Scrinzi et al., 2022)** consider nutrients recovery, all the phosphorus and nitrogen present in the HTCL, could be used for struvite precipitation with an average yearly gain of 1 million euros. Moreover, the introduction of **HTC** in the **Trento 3 WWTP** could allow a reduction in the sludge management costs of up to 2 M€/year.
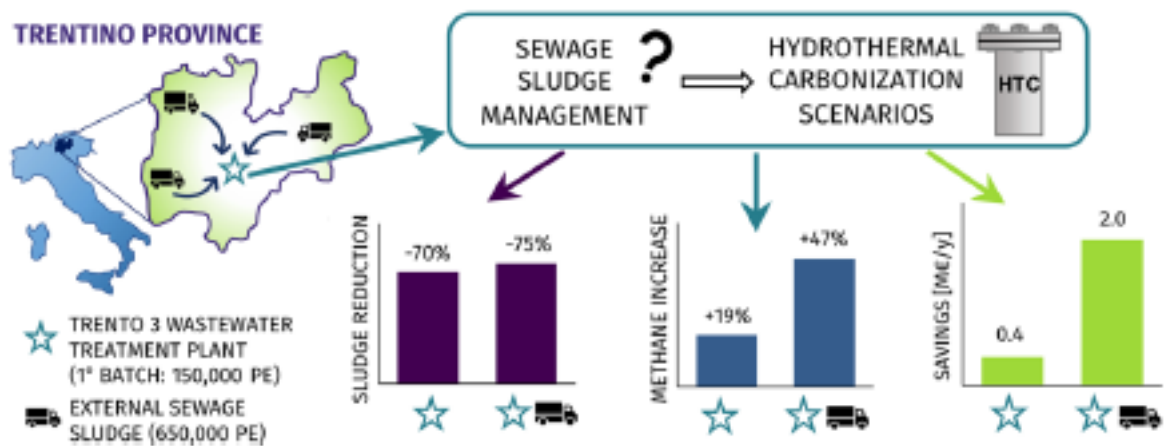
Figure 1A (D.scrinzi et al., 2022) showed in this graph a reduction in the sludge management costs

The cost of HTC treatment is €31 per tons of sewage sludge treated. The energy consumption had taken into account in the calculation, the management, and maintenance

costs of the process excluding taxes, costs for property and patent license application, expenses and wastewater treatment **(D.scrinizi et al., 2022)**.

The cost for disposal considering the average price for the sludge disposal of 150 €/tons. In Trento 3 WWTP, there were two scenarios; the first one of the dewatered sludge produced by the plant, and the second scenario was with the sum of the sludge produced from the plant and surroundings, the second scenario had obviously a large cost. However, the implementation of the HTC treatment, according to 1st scenario allows a 69% reduction in solid waste disposal costs. In addition, the surroundings WWTPs generate an amount of dewatered sludge of 24,500 tons/year which accounts for 5,512,500 €/year for the sludge disposal. Comparing the result with that of the HTC configuration according to scenario 2, a reduction of 75% with that of HTC configuration according to scenario 2. **(D.scrinizi et al., 2022)**.

Lower disposal costs could be achieved if the wet hydrochar is the thermal treatment by using the dewatered sludge dryer available within the PAT territory as the average cost of this treatment is 57€/tons.

The plant is designed to treat an influent of 96,000 m^3/d, corresponding to 300,000 PE, mainly coming from the city of Trento and the Surrounding municipalities. There are three parallel lines with grit trap and grease separation in the water line of the Trento 3 WWTP, 12 lines with primary clarification and chemical phosphorus removal, 4 lines with biological reactors alternating oxic/anoxic phases for the implementation of nitrification and denitrification processes, 24 lines with secondary clarifiers with sludge recirculation and purge followed by tertiary treatments such as flocculation/dephosphorisation, filtration, energy recovery and disinfection. There are 2 lines static and 4 lines of dynamic pre-thickening units in the sludge line, ultrasonic treatment, an AD treatment with a post-thickening system and, finally, a mechanical dewatering unit. The entire plant includes the biogas treatment and recovery with a gasometer and a cogeneration unit.

The following figure (2-A) shows the division in percentage for the sectors as well as the cost for the disposal of dewatered sewage sludge of the PAT in 2019, including thermal

treatment, use in agriculture, landfilling and third company. The highest disposal cost (160 €/ton) is incurred for landfill. Also, the third companies act as intermediaries between the disposal service and the other companies that dispose of sewage sludge through composting, direct agricultural application and other processes.

Figure 2-A Disposal solution for dewatered sewage sludge in 2019, (D.scrinzi et al., 2022)

Laboratory Safety and Chemical Materials

Safety in labs is essential while working, dealing with chemicals, external labs, manufacturers, and colleagues. The following table clarifies the chemicals that should and should not be mixed with each other

Table 1-A. Chemicals that should not be mixed with each other with reference to the Ankara University Laboratory Manual

Chemical	Chemicals not to be mixed with
Acetic Acid	Chromic acid, nitric acid, hydroxyl-containing compounds, ethylene glycol, perchloric acid, peroxides, permanganates

Acetone	Concentrated nitric acid, concentrated sulfuric acid
Acetylene	Fluorine, chlorine, bromine, copper, mercury, silver
Activated carbon	Calcium hypochlorite, oxidants
Alkali metals (Na, K, etc.)	Hydrocarbons and their aqueous solutions, water
Ammonia	Mercury, chlorine, iodine, bromine, calcium
Ammonium nitrate	Powdered metals, flammable liquids, sulphur, chlorates, all acids, nitrites
Aniline	Hydrogen peroxide, nitric acid
Bromine	Ammonia, acetylene, butane and other petroleum gases, turpentine
Calcium oxide	Water
Chlorates	Ammonia, powdered metals
Chlorine	**Ammonia**, acetylene, butane and other petroleum gases, turpentine
Chromic acid	Acetic acid, glycerine, some alcohols, flammable liquids, turpentine
Copper	Acetylene, hydrogen peroxide

Flammable liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, halogens
Fluorine	All chemical substances

During the experiments, the Acetic Acid (CH3COOH) which is an acidic, colorless liquid and organic compound prepared through two methods. The first one was by adding 98% of MQ Water to 2ml of CH_3COOH (2%). The second one was by adding 99% of MQ water to 1 ml of CH_3CO_2H (1%). It is essential to dispose the acids with very low pH (<2) safely with a specific container. However, If the acid does not have heavy metals or other toxic substances dissolved in it, the neutralization of pH to a less acidic level (Ph 6.6 – 7.4) allows you to dispose of the substance in the standard sewer system.

Table 2-A. Chemicals that should not be mixed with each other-cont. with reference to the Ankara University Laboratory Manual

Chemical	Chemicals not to be mixed with
Hydrocarbons	Fluorine, Chlorine, bromine, chromic acid, sodium peroxide (benzene, other)
Hydrocyanic acid	Nitric acid, alkalis
Hydrofluoric acid	Ammonia
Hydrogen peroxide	Copper, chrome, iron, metal and metal salts, flammable liquids, aniline, nitromethane
Hydrogen sulphide	Nitric acid, oxidants
Iodine	Acetylene, ammonia
Mercury	Acetylene, ammonia
Nitric acid	**Acetic acid,** aniline, chromic acid, hydrocyanic acid, hydrogen sulphide, flammable liquids and gases
Oxalic acid	Silver, mercury
Oxygen	Oils, grease, hydrogen, flammable fluids, gases and solids

Per chloric acid	Acetic anhydride, alcohols, carbon tetrachloride, carbon dioxide
Potassium permanganate	Glycerine, ethylene glycol, benzaldehyde, sulphuric acid
Silver	Acetylene, oxalic acid, tartaric acid, ammonia, carbon dioxide
Sodium nitrate	Ammonium nitrate, other ammonium salts
Sulphuric acid	Chlorates, perchlorates, permanganates
Sulphurous hydrogen	Nitric acid, oxidant gases

Nitric acid could be used in case of necessity in our experiments. However, it is important to point out that it is forbidden to mix it with acetic acid.

A **GHS pictogram** indicate the potential hazards associated with a chemical's physical properties, such as flammability, explosiveness, and more, this definition from Smith Corona a Guide to GHS Pictograms. It is important that when dealing with chemicals and once doing the disposal to label the material with the GHS Pictogram. Wearing gloves, respiratory masks, lab coats, turn on the fume hoods and make sure that they are working well before starting the experiments, etc. If the case is dangerous or there is an unexpected fire, turning on the fire extinguishers from their locations. The following table clarifies GHS pictogram with its code and meaning.

Table 3-A. Chemical Inventory for some materials used in labs

GHS Pictogram	Code and meaning	GHS Pictogram	Code and meaning	GHS Pictogram	Code and meaning
	(C) Corrosive		(N) Nature Polluting		(XM) Harmful
	(E) Explosive		(O) Oxidizing		Non-Flammable Gas
	(F) Flammable		(T) Toxic		Hazardous to health

The effects of the codes:

(C) Corrosive; Skin corrosion/ Burns, Eye Damage, Corrosive to metals

(E) Explosive; Explosives, Self-Reactives, Organic Peroxides

(F) Flame; Flammables, Pyrophorics, Self-Heating, Emits Flammable Gas, Self-Reactives, Organic Peroxides

(N) Nature Polluting; Aquatic Toxicity

(O) Oxidizing; oxidizers

(T) Toxic; Acute toxicity (fatal or toxic)

(XM) Harmful; Iritant (skin and eye), skin sensitizer, Acute Toxicity, Narcotic effects, Respiratory Tract Irritant, Hazardous to Ozone Layer (Non-Mandatory)

Non-Flammable Gas; Gases Under Pressure

Hazardous to Health; Carcinogen, mutagenicity, reproductive toxicity, respiratory sensitizer, Target Organ Toxicity, Aspiration Toxicity

The following table shows the details of some chemical materials used during the experiments.

Table 4-A. Chemical Inventory for some materials used in labs

Lab	Cabinet	Shelf	CHEMICAL	CAS No.	☣☢☠ ☠!☣ ☢☣	Product No.	Retailer/Manufacturer	Unit Size
PR196	K12	1	Chitosan	9012-76-4		448869	Sigma-Aldrich	50g
PR196	K12	1	Chitosan	9012-76-4		448877	Sigma-Aldrich	50g
PR162	K1	4	Silica fumed 0.07μm	112945-52-5	non-toxic	S5130	Sigma-Aldrich	500g
PR196	K5	2	Sodim Hydroxide	1310-73-2	☣	1.06498.1000	VWR Prolabo	2.5 Kg
PH	K5	2	Sodium Hydroxide	1310-73-2	☣	1.06462.5000	VWR Merck	1 KG
PR196	K5	2	Sodium Hydroxide	1310-73-2	☣	28244.295	VWR Merck	5000 g
PR196	K5	2	Sodium Hydroxide	1310-73-2	☣	S5881	VWR Merck	1 Kg
PR162	K1	4	Sodium Hydroxide	1310-73-2	☣	655104	Sigma - Aldrich	1 Kg

PH	K5	3	Sodium Hydroxide	1310-73-2	⬦	451130050	VWR Honeywell	2.5 Kg, 2.5 Kg
PR162	K1	5	Sodium Hydroxide	1310-73-2	⬦	28245.367	VWR Acros	5 Kg, 5Kg
PR162	K1	5	Sodium Hydroxide	1310-73-2	⬦	28245.46	VWR	5 Kg
PR196	K5	3	Sodium Hydroxide 0,1M	EY 215-185-5 1310-73-2	non-toxic	FF103	VWR	25 Kg * 3 3*1l
PR196	K5	3	Sodium Hydroxide 0.25M	EY 215-185-5 1310-73-2	⬦	FF109	VWR FF-Chemicals	2*1l
PR196	K5	3	Sodium Hydroxide 0.5M	EY 215-185-5 1310-73-2	⬦	FF111	VWR FF-Chemicals	1l
PR196	K5	3	Sodium Hydroxide 1M	EY 215-185-5 1310-73-2	⬦	FF124	VWR FF-Chemicals	2*1l

The following figure shows the paste of the preparation of the acid-dissolved chitosan-based geopolymer composite.
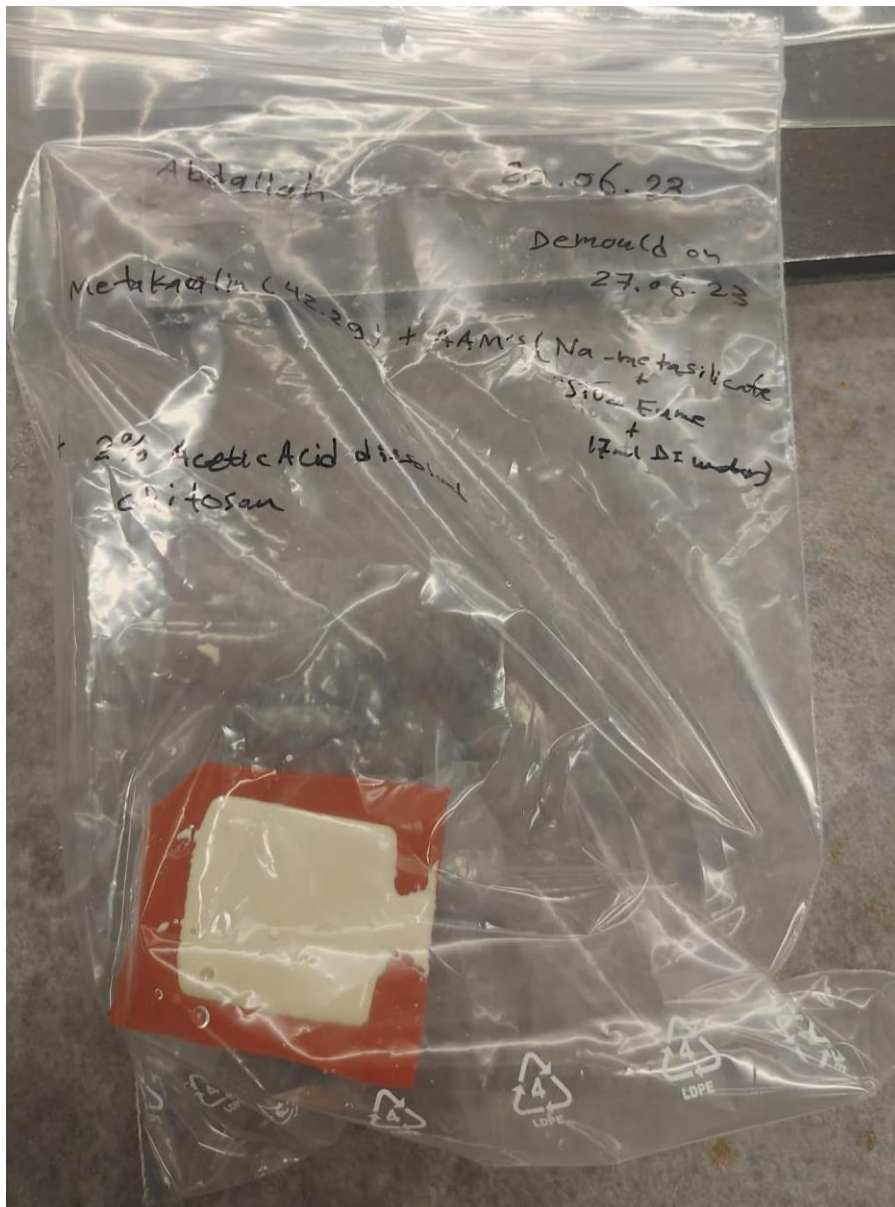
Figure 6-A An acid-dissolved chitosan-based geopolymer composite

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