The Thesis of the Doctoral (Ph. D.) dissertation

HEBA MUNEER NASER

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Hungarian University of Agricultural and Life Sciences

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INCORPORATION OF CELLULOSE-BASED ADSORBENT ASH WITH POTENTIALLY TOXIC ELEMENTS INTO MORTAR: A SUSTAINABLE APPROACH

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1. BACKGROUND OF THE WORK AND ITS AIMS

Since the 1980s, living or dead microorganisms and biological materials have been employed for wastewater treatment, targeting contaminants such as Potentially Toxic Elements (PTEs), ions, and dyes (Çolak et al., 2009). Bio-based adsorbents suggested as a viable approach for mitigating waterborne toxins (Hubbe, 2022), offer several advantages, including cost-effectiveness, potential metal recovery, biosorbent regeneration, and reduced chemical and biological sludge volume (Beni and Esmaeili, 2020). In recent years, cellulose-based adsorbents have gained attention as effective agents for removing PTEs from polluted water. Cellulose's desirable characteristics, such as high surface area, biocompatibility, and affordability, make it an attractive PTE adsorbent. The adsorption process involves physical and chemical interactions, encompassing ion exchange (Nata et al., 2022), electrostatic attractions, and complexation. Most cellulose-based adsorbents follow the pseudo-second-order kinetic model, emphasizing chemisorption as the rate-determining step (Syeda and Yap, 2022). Researchers have also explored techniques like chemical modification, physical treatment, and functional group grafting to enhance adsorption capacity and selectivity (De Quadros et al., 2016). While much research has focused on the efficacy of cellulose-based adsorbents in PTE removal, limited attention has been given to the fate of these loaded adsorbents. This oversight is significant due to the potential environmental implications, as biosorption can lead to secondary pollution when used adsorbents end up in landfills, contributing to PTE leaching into groundwater. Most of the research work focuses on adding the wastepaper ash and wood biomass ash to ordinary portland cement or partially substituting cement in mortars or concrete in terms of the mechanical properties of the mix (Ahmad et al. 2013; Monosi et al. 2012; Zmamou et al. 2021; Ayobami 2021; Martínez-Lage et al. 2016; Wong et al. 2015; Frías et al. 2015; Carević et al. 2019; Castrillón and Gil 2020). Only a few researchers have studied the leaching of PTEs of mortar incorporated with fly ash and bottom ash of paper and wood biomass. (Ismail et al. 2019) used wastepaper sludge ash in the cement matrix to stabilize water treatment sludge, while (Carević et al. 2020) conducted leaching tests of wood biomass ash cement replacement by 15% of the cement composite. Also, insufficient research has been done on the final fate of cellulose-based adsorbents loaded with contaminants. Contaminated cellulose adsorbents typically include a lot of water and PTEs; therefore, they will not be suitable for landfilling, raising concerns about the leaching of pollutants into groundwater. In this study, the proposed solution to this problem was investigated through a

procedure of compression and incineration of the contaminated cellulose adsorbent waste, followed by incorporating the resulting ash within a mortar matrix. Mortar is a workable paste used as a binding agent for masonry work units such as stones, bricks, and concrete masonry work units to fill and seal uneven spaces between them.
Recently, fly ash and bottom ash from industrial by-products have been widely used to replace Portland cement in cementitious composites like mortar (Sathonsaowaphak et al. 2009; Agrawal andSavoikar.2022; Omur et al. 2023). Other researchers studied the partial replacement of binder with waste wood ash and other cellulose-based materials ash. The results seem to indicate an auspicious pozzolanic material with no reduction in the mortar strength, enhanced durability of the sample, and significantly contributing to the sustainability of the construction industry with added environmental value where waste wood ash is utilized and the amount of discarded ash and its adverse effects on the environment can be diminished significantly, this also contributes to reducing the amount of waste sent to landfills (Martínez-García, et al. 2022). Other studies have proved that adding calcium carbonate to a cementitious composite positively affects early-age strength, the hydration process, and durability (Cao et al. 2019). Knowing that the main components of adsorbed paper ash (APA) and adsorbed mulch ash (AMA) are $CaCO_3$ and SiO_2 supports their suitability to be added to a mortar mix.
To assess the feasibility of using APA and AMA mortar composites in engineering applications while ensuring environmental suitability by utilizing the leaching test. This research included the preparation and the use of two kinds of adsorption process waste ash - adsorbed paper ash (APA) and adsorbed mulch ash (AMA)- as an additive to mortar, which added an environmental and economic value through energy recovery during the ashing process following the ideas of the waste to energy and circular economy, in addition to immobilizing the PTEs into a cement matrix aiming to close the loop of pollution. This study focused on investigating the leaching behavior of PTEs (Cd, Zn, Cu, and Pb) at five different artificial adsorption initial concentrations (0.5, 1, 5, 10, and 50) mg L^{-1} and three different mixing weight proportions of ash with cement, as well as their pH-dependent behavior, to ensure environmental safety ensuring their suitability for use in constructions covering a wide range of acidic environments by using the CEN/TS 14429:2015 (BSI 2005) test method. To detect the release of PTEs from the mortar ash mixes, the ICP-OES technique was used, and then the concentrations were compared to the permissible leaching value limits for the waste categories according to EU directive 1999/31/EC.

A literature review also showed that studies on cellulose-based materials ash in construction products are limited to mechanical strength, with only a few studies reporting on its microstructural characteristics. While no microstructural characterization study was reported on cellulose-based adsorbents ash loaded with PTEs, this research further investigated the elemental and microstructural characteristics of (APA) and (AMA) mortar composites by using an SEM device equipped with energy-dispersive X-ray spectroscopy (EDS) to ensure the development and improvement of materials, performance evaluations, and describe the immobilization and distribution of PTEs within a mortar composite.

1.2 Aim of the study

This research aimed to study the potential for paper and mulch waste previously used for the (PTEs) adsorption process and then ashed as an additive to mortar which added an environmental and economic value through energy recovery during the ashing process following the idea of the waste to energy, also reducing the quantity of waste landfilled ,in addition to immobilizing the PTEs into a cement matrix aiming to close the loop of pollution to achieve environmental safety and sustainability in addition to the circular economy.

1.3. Study objectives

Based on the problem statement, the following objectives were identified:

1- Determine the leaching values of (Cd, Pb, Zn, and Cu) by using the ICP-OES technique and describe the behavior of each element in addition to studying the influence of the (pH)on the AMA and APA in mortar leaching concentrations.
2- Assess leaching as a component of environmental safety after comparing the measured leaching values with the standard permissible leaching limits value for the waste categories according to EU directive 1999/31/EC.
3- Determine the optimum weight ratio for APA or AMA addition to the mortar mix based on the compared leaching values.
4- Study the microstructural and elemental characteristics of (APA) and (AMA) mortar composites by using an SEM device equipped with energy-dispersive X-ray spectroscopy (EDS).
5- Compare the two used adsorbents' ash suitability as a construction material based on leaching experiments and the microstructural and elemental testing of the prepared mortar.

2. Materials and methods

2.1 Batch adsorption method

Two cellulose-based adsorbents, depicted in Figure 1, were employed in this study. The first adsorbent is a wastepaper including cardboard and receipts obtained from a local store in Gödöllő, Hungary. The sample was washed several times with distilled water, dried, ground then kept in sterilized plastic bottles. The second adsorbent is mulch obtained from Oak trees. The sample was washed several times with distilled water, dried, ground then kept in sterilized plastic bottles. Chemical grade salts [$Pb(NO_3)_2$, $CdCl_2 \cdot 2.5H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(CH_3CO_2)_2 \cdot 2H_2O$] were used to prepare the concentrated stock solution 1000 mg L^{-1} of each of (Pb(II), Cu(II), Zn(II), Cd(II)) ions by dissolving 2.03 g of cadmium dichloride, 1.60 g of lead nitrate, 3.80 of Copper (II) nitrate and 3.36 of Zinc acetate in the same solution. This stock solution was subsequently diluted to five different concentrations (0.5, 1, 5, 10, 50) mg L^{-1}. Each adsorbent was applied at a concentration of 1 g in 100 ml. The samples were shaken for four hours. The type and operating conditions of the shaker used: (Multi Rotator /PTR-60 Grant-bio, speed =24 rpm, vibration mode = 1°, reciprocal mode=2°). Triplicate repetition of the adsorption process was conducted at five different concentrations. After adsorption, samples were filtered using ashless MN 640m.Ø90mm filter paper. The total elemental content of PTEs filtrate was determined by a Horiba Jobin Yvon Activa M Inductively Coupled Plasma–Optical Emission Spectrometer (ICP-OES). The obtained data were used to calculate the adsorption capacity of PTEs in mg g^{-1} according to the equation (1):

$$q = [(C_o - C_e) /m] * V \qquad (1)$$

Where q is the uptake (mg g^{-1}), C_0 and C_e are the liquid phase concentrations of PTEs at initial and equilibrium (mg L^{-1}), V is the volume (L), and m is the amount of adsorbent (g).

Figure 1. Raw materials mulch and paper

2.2. Adsorbent ash preparation

The remaining adsorbents on filter paper were compressed to separate the adsorbed fraction; this procedure was followed by oven drying at 105°C. Finally, samples were burned in the furnace at 580°C for four hours.

2.3. Determination of adsorbents' moisture content (%)

The moisture content of 30 samples utilizing mulch and paper as adsorbents was assessed in accordance with (ISO 287:2017), This procedure was done in triplicate for each adsorption initial concentration sample.

2.4. Determination of the ash percentage (%)

The determination of the percentage of ash of mulch and paper adsorbents was performed on 30 samples according to the standard test method ASTM D1102-84 (2013).

2.5.X-Ray Diffraction (XRD) of adsorbents ash

The phase composition was studied by the X-ray diffraction (XRD) method (D4 Bruker, Germany). The obtained data confirmed that the predominant crystalline phase in the paper-contaminated ash samples was calcite $CaCO_3$, accompanied by smaller quantities of Quartz SiO_2, Talc $H_2Mg_3O_{12}Si_4$, and Dolomite $CaMg(CO_3)_2$. In the mulch-contaminated ash, the predominant crystalline phase was calcite $CaCO_3$, accompanied by smaller quantities of quartz SiO_2 and Muscovite $KAl_2(Si_3Al)O_{10}(OH,F)_2$.

2.6. Mortar adsorbent ash mixture preparation

Ash mortar mixture preparation involved weighing the various constituents of the mixture. Mix proportions are listed in Table 1. The preparation steps are summarized as follows: Sand was added to AMA or APA ash and mixed to improve the homogenization of the mortar. Cement was added with additional dry mixing. Finally, water addition had a fixed ratio of water/binder (w/b). The specimens were left for 28 days under temperature-controlled conditions in the laboratory at 20°C±2°C (Figure 2). The procedure also included the preparation of blank mortar samples. For each analyzed parameter, three repetitions were made to ensure the accuracy of the work.

Table 1. *Mix proportions of mortar ash specimen constituents based on weight. XP (1 % paper ash), XM (1 % Mulch ash), YP (2% paper ash), YM (2% mulch ash), ZP (3% paper ash), ZM (3% mulch ash), B0 (Blank)*

Set	Cement	Sand	w/b	Ash
PX	1	3	0.5	0.01
PY	1	3	0.5	0.02
PZ	1	3	0.5	0.03
MX	1	3	0.5	0.01
MY	1	3	0.5	0.02
MZ	1	3	0.5	0.03
BO	1	3	0.5	0

Figure2. Mortar-incorporated adsorbed ash composite

2.7. Leaching experimental testing

Experiments for the leaching of PTEs from the APA mortar composite and AMA mortar composite were carried out in accordance with the CEN/TS 14429:2015 test method.

2.8. Instrumental analysis

The total elemental content of PTEs leachate solutions was determined by a HORIBA Jobin Yvon ACTIVA M Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) using the operation parameters proposed by the manufacturer and yttrium internal standard.

2.9. Scanning electron microscopy (SEM)

The microstructure and elemental mapping study of the mortar ash composite samples were performed using scanning electron microscopy (SEM). SEM analysis investigated the structural differences between mortar before and after incorporating (APA) and (AMA) into mortar composites. The instrument used for SEM analysis was a Hitachi S-4700 field emission scanning electron microscope combined with a Bruker (former Röntec) QX2 energy dispersive X-ray fluorescence spectrometer before analysis to enable the user to gather high-quality information from SEM. An extra step involved coating the sample with an additional thin layer (~10 nm) of a conductive material; the sputter coater used to coat the samples were gold. The elemental mapping of the studied elements (Cu, Pb, Zn, Cd, Si, Ca, Al) was carried out at 20 kV acceleration voltage and 9 µA beam current. The acquisition time of the individual samples was at least 1 hour.

2.10. Image Analysis Procedure

The elemental mapping covered the adsorbed elements (Cd, Zn, Cu, Pb) and others (Si, Ca, and Al). The working method of image analysis of the elemental maps of each of the seven elements in AMA, APA, and blank mortar composites, was carried out using ImageJ software V 1.8.0. Several steps were performed to conduct an in-depth analysis of the elemental maps. Each image was cropped, filtered, adjusted, and transformed to 8-bit using Image J software V 1.8.0 (Zohar & Haruzi, 2021). The analyzed elemental maps provided information on the estimated area coverage percentage (%) for the adsorbed PTEs and other major elemental content in the studied mortar composites.

2.11. Statistical analysis

To achieve our objectives, we used various statistical methodologies for analyzing data collected from experimental trials. The recorded data, stored in Microsoft Excel spreadsheets, underwent initial handling for outlier and missing values using appropriate techniques, such as the interquartile range method (Vinutha et al., 2018). GenStat 12th edition software was utilized for subsequent statistical analysis. We assessed data distribution for normality, normalizing where possible, and applying relevant statistical tests based on distribution. The research employed a factorial design approach to investigate primary and interaction effects of four independent variables: initial concentration of PTEs, incorporated ash percentage %, molarity of HNO_3 used, and adsorbent type (Nordstokke & Colp, 2014). For comparing means among variables and dealing with multiple factors, appropriate forms of Analysis of Variance (ANOVA) were employed, including one-way, two-way, or multifactor ANOVA (Kim, 2014). The hypothesis focused on studying the factorial effects on leaching concentrations of PTEs. A factorial experimental design with ANOVA will determine if the combination of these independent variables has a statistically significant effect. If the p-value is below the chosen significance level ($\alpha = 0.05$), we will reject the null hypothesis, concluding a significant factorial effect on the leaching concentrations of PTEs.

3. RESULTS AND DISCUSSION

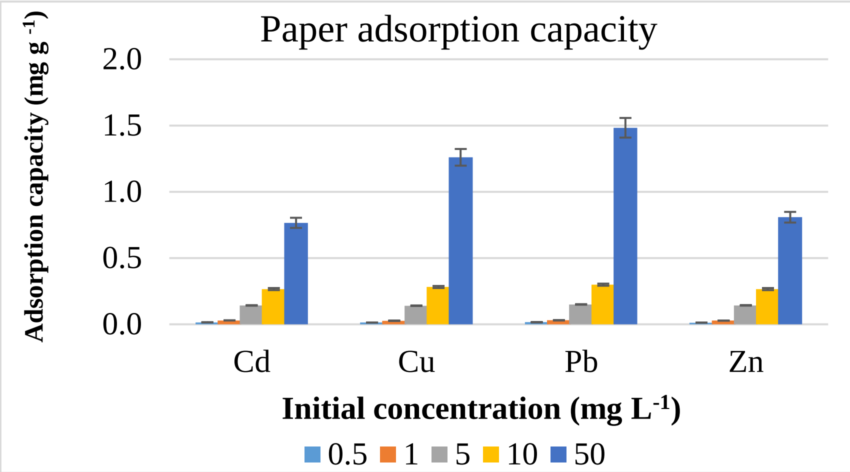
3.1. Adsorption

The study examined the adsorption capacities of potentially toxic elements (PTEs), specifically lead (Pb), copper (Cu), cadmium (Cd), and zinc (Zn), within mulch and paper substrates. These findings are graphically represented in Figure 3(a, b). The correlation analysis reveals a strong positive correlation between the initial concentration of all studied PTEs and the corresponding adsorption capacity of both adsorbent materials, this indicates that as the initial concentration of PTEs increases, the adsorption capacity also increases, suggesting a direct relationship between these two variables in the studied system.

In mulch samples, the competitive adsorption capacities among these metal cations exhibited a slightly descending order: Pb ≥ Cu ≥ Cd > Zn, with respective capacities of 0.496, 0.495, 0.491, and 0.482 mg g^{-1}. This trend is in accordance with prior findings reported by Chirenje *et al.* (2006), which suggested that wood ash effectively immobilized these four metals. The quantities of metals retained by the wood ash also followed the Pb > Cu > Cd > Zn sequence. Similarly, modified coated wood mulches follow the same order for pb, Cu, and Zn (Soleimanifar *et al*., 2016; Sidhu *et al*., 2021). Furthermore, an intriguing consistency emerged between adsorption affinity and electronegativity, suggesting that electronegativity provided a compelling explanation for our experimental observations.

In contrast, when examining the adsorption capacities of these same metal cations within the paper, the competitive adsorption capacities followed a descending order of Pb > Cu > Zn > Cd, with respective capacities of 1.48, 1.26, 0.81, and 0.76 mg g^{-1}. This outcome is consistent with the study by Ding *et al*. (2018), which looked at the adsorption capacity of carbonized paper packaging boxes for aqueous Pb, Zn, and Cd. Their study revealed high aqueous Pb, Zn, and Cd sorption capacities, with Langmuir maximum sorption capacities of 458, 146, and 10.7 mg g^{-1}, respectively. Notably, cadmium exhibited the lowest adsorption among these elements. Furthermore, it was observed that the paper showed a superior adsorption capacity compared to mulch for all the investigated PTEs.

a)



b)

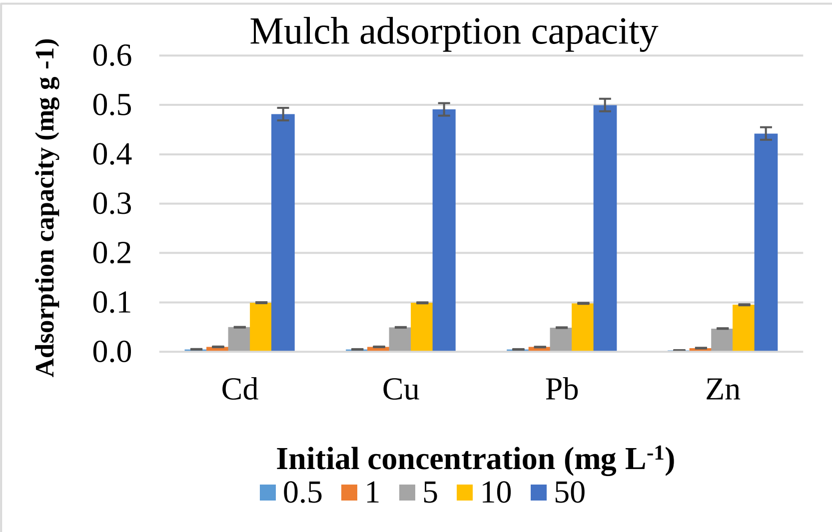


Figure 3. a) adsorption capacity of paper b) adsorption capacity of mulch

3.2. Moisture content % and ash percentage%

In the context of our investigation, we have quantified the increase in water content resulting from the adsorption process of PTEs; The calculations relied on wet-based moisture content. Specifically, the moisture content within Mulch adsorbents exhibited a range between 78.3 ± 0.27 (%) and 81.6 ± 0.21 (%), while paper-based adsorbents demonstrated moisture levels ranging from 51.3 ± 0.28

(%) to 56.4 ± 0.03 (%). These findings align with the observations made by Chen *et al.*(2014), where the moisture content of paper pulp ranged from 50% to 66.7% upon saturation with water adsorption. Additionally, a study conducted by Khazaei in 2008 exploring various wood sample species, indicated that the moisture reached an excess of 60% for most wood species. Mulch adsorbents exhibited ash percentages ranging from 6.10 ± 0.33 (%) to 7.88 ± 0.99 (%). These findings align with previous studies, indicating a wood ash percentage of 6.2% at 550°C (Steenari et al., 1999b; Al-Mefarrej et al., 2013). Paper adsorbent ash content ranged from 13.8 ± 0.26 (%) to 14.8 ± 0.25 (%). Notably, Wielgosiński et al. (2021) reported an average ash percentage of 12% for paper/cardboard, attributing the higher percentage in this study to incineration temperature variations. Hui et al. (2020) demonstrated that increasing incineration temperature resulted in decreased ash content in paper sludge, affecting particle characteristics and chemical composition.

3.3. Leaching of PTEs

Leaching test assessment on the crushed APA and AMA mortar samples was done by comparing the values of the tested samples with the leaching value limits for the waste categories according to EU directive 1999/31/EC. With reference to Figure 4, concentrations of Zn leached from the tested crushed mortar samples at the 0.43M HNO_3 trial come under the inert waste category.

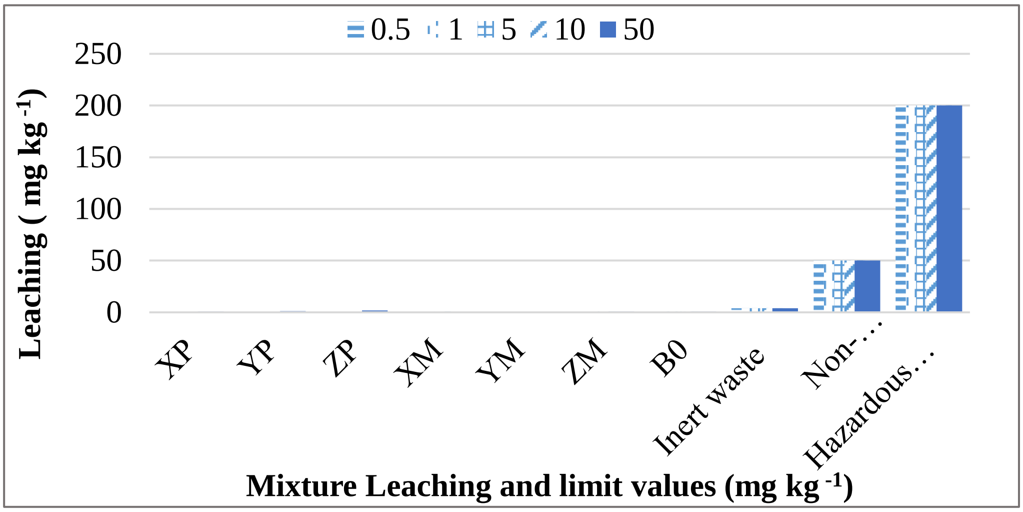


Figure 4. Zn leaching concentrations at 0.43M HNO_3 compared to limit values for the individual waste categories. XP (1 % paper ash), XM (1 % Mulch ash), YP (2% paper ash), YM (2% mulch ash), ZP (3% paper ash), ZM (3% mulch ash), B0 (Blank) mortar composites. five initial concentrations of PTEs (0.5, 1, 5, 10, 50) mg kg $^{-1}$.

The leaching results of Cu at 0.43M HNO_3 illustrated in Figure 5 also lie under the inert waste category in all composites.

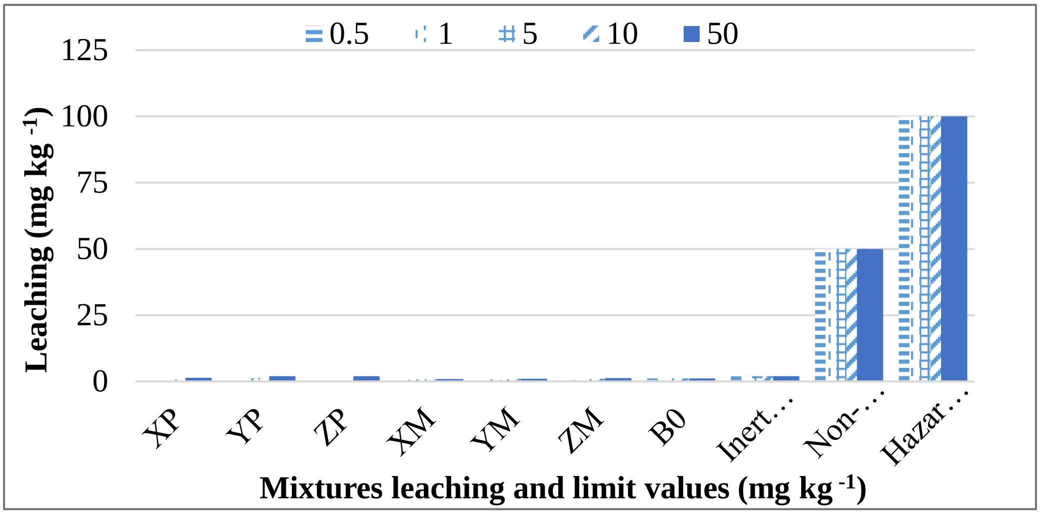


Figure 5. Cu leaching concentrations at 0.43M HNO_3 compared to limit values for the individual waste categories.

Pb concentration is slightly higher than that of the inert waste limit category in the case of APA mortar samples but inert in the AMA mortar samples according to Figure 6. The explanation for the different Pb leaching values is apparent when comparing the results of the Pb adsorption capacity in the mulch samples, which was 0.496 mg g^{-1} at 50 mg L^{-1} initial concentration of adsorption solution. In contrast, in the paper samples, the adsorption capacity reached 1.483 mg g^{-1} at the 50 mg L^{-1} initial concentration of Pb, in which the paper showed more affinity to adsorb Pb.

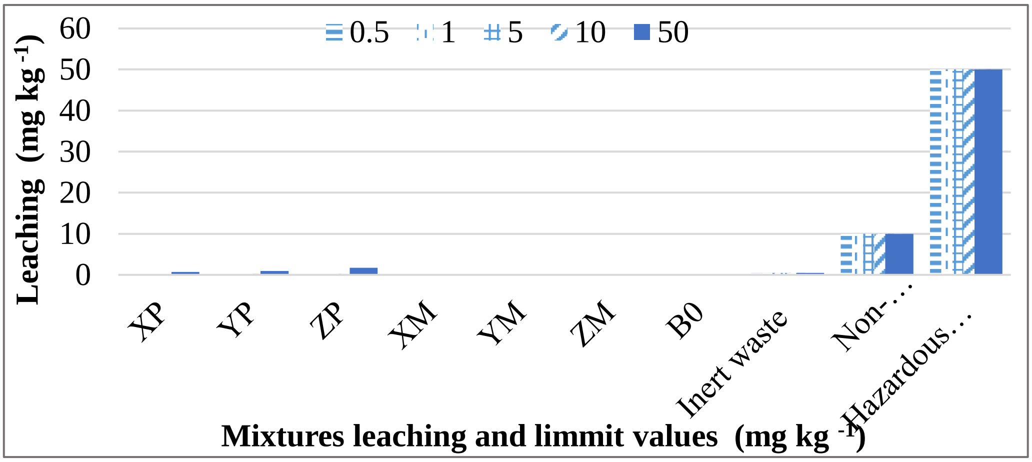


Figure 6. Pb leaching concentrations at 0.43M HNO_3 compared to limit values for the individual waste categories.

The Cd leached concentration at 0.43 M HNO_3 in Figure 7 was lower than the non-hazardous waste limit value.

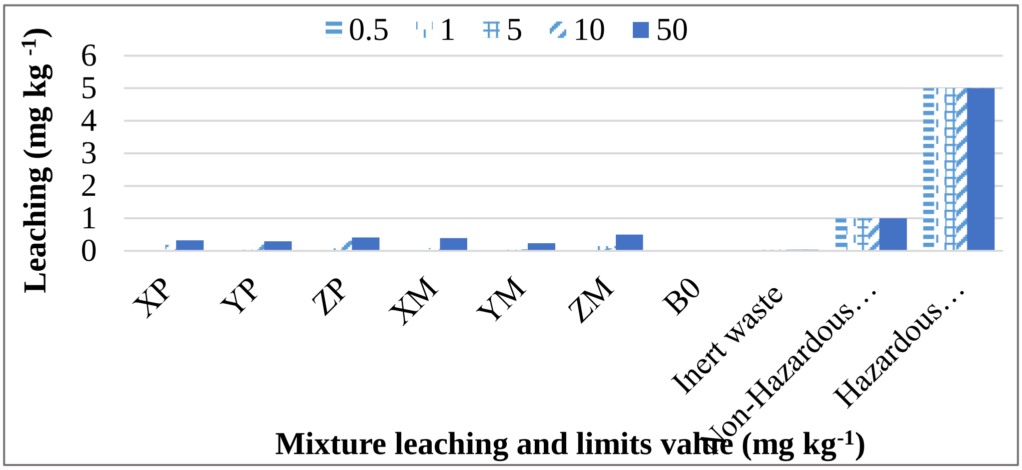


Figure 7. Cd leaching concentrations at 0.43M HNO_3 compared to limit values for the individual waste categories

Referring to Figure 8, the concentrations of Zn leached from the tested crushed mortar samples at the 4 M HNO_3 trial were within the safe limits under the non-hazardous waste category with higher leaching concentrations in the case of AMA mortar composites compared to APA leaching concentrations.

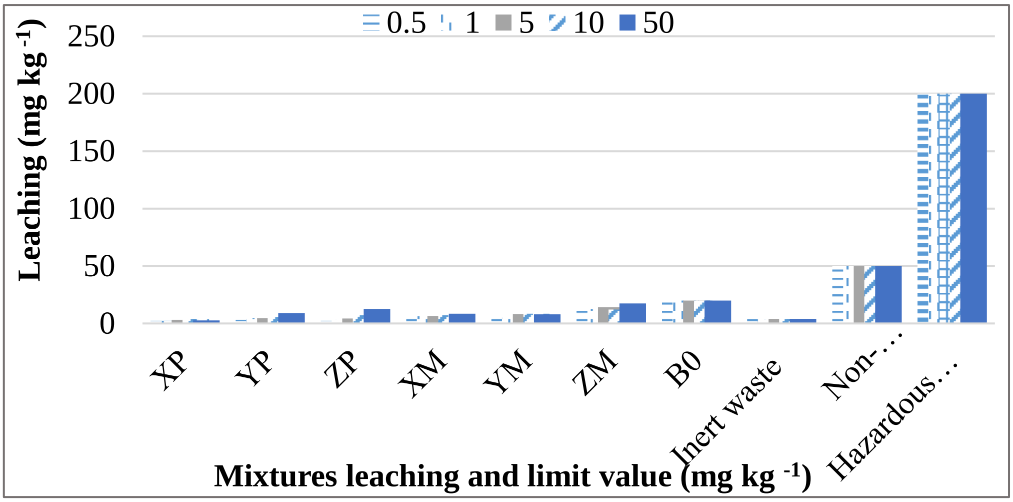


Figure 8. Zn leaching concentrations at 4 M HNO_3 compared to limit values for the individual waste categories.

The concentrations of Cu leached from the tested crushed mortar samples at the 4 M HNO_3 trial illustrated in (Figure 9), the results were within the safe limits under the non-hazardous waste category with higher leaching concentrations in the case of APA mortar composites compared to AMA leaching concentrations.

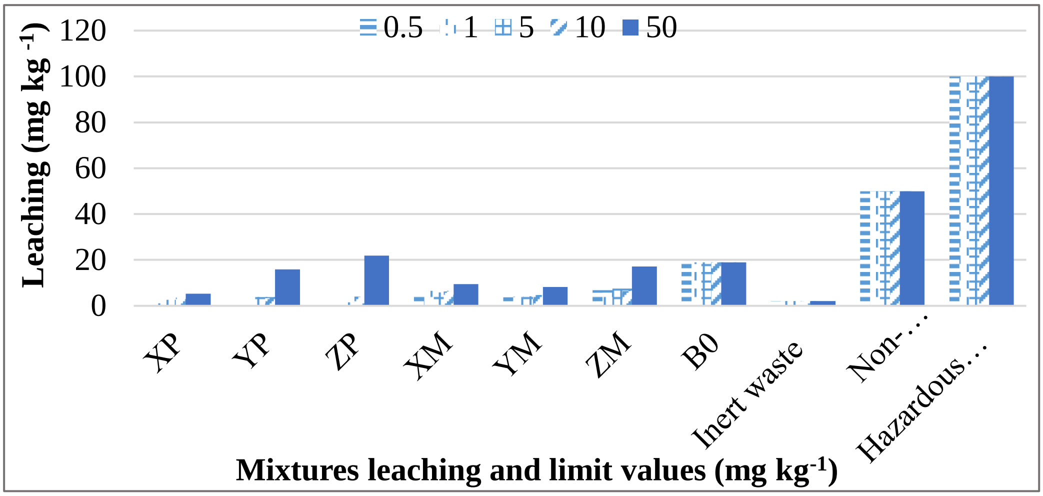


Figure9. Cu leaching concentrations at 4 M HNO_3 compared to limit values for the individual waste categories.

Pb leached from the tested crushed mortar samples at the 4 M HNO_3 trial were within the safe limits under the non-hazardous waste category with higher leaching concentrations from APA mortar composites compared to AMA mortar composites (Figure 10).

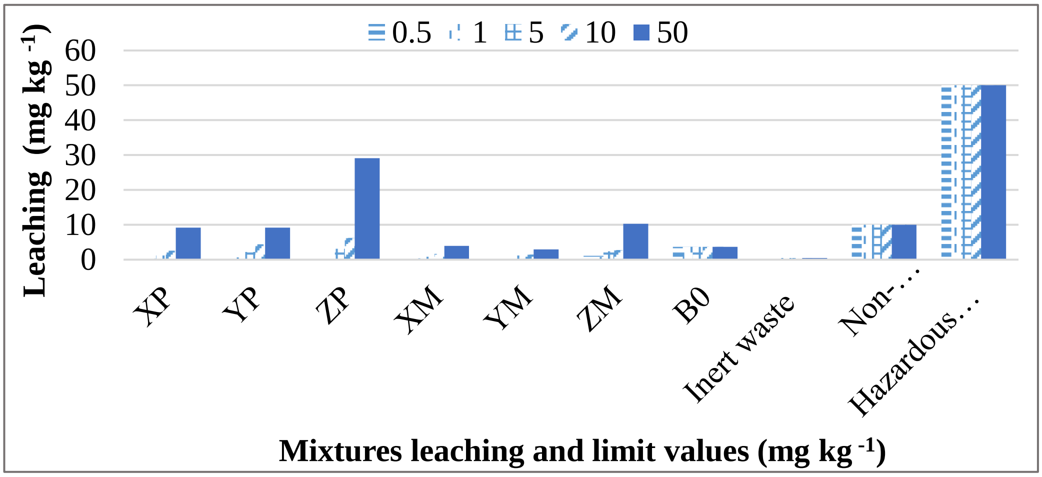


Figure10. Pb leaching concentrations at 4 M HNO_3 compared to limit values for the individual waste categories.

Only Cd leached above the regulatory limit (5 mg kg^{-1}) (Figure 11). This result corresponds to the findings of Yuan (2018); the author used the tank test, which showed that long-term exposure to cement concrete containing municipal solid waste incineration fly ash in a water environment might lead to Cd pollution. However, the Cd leached concentration was lower than the regulatory limit in the study conducted by Carević et al. (2020), in which crushed mortar samples of wood ash were incorporated into the cement mortar; this difference can be explained by the low Cd concentration in the wood ash used in their experiment.

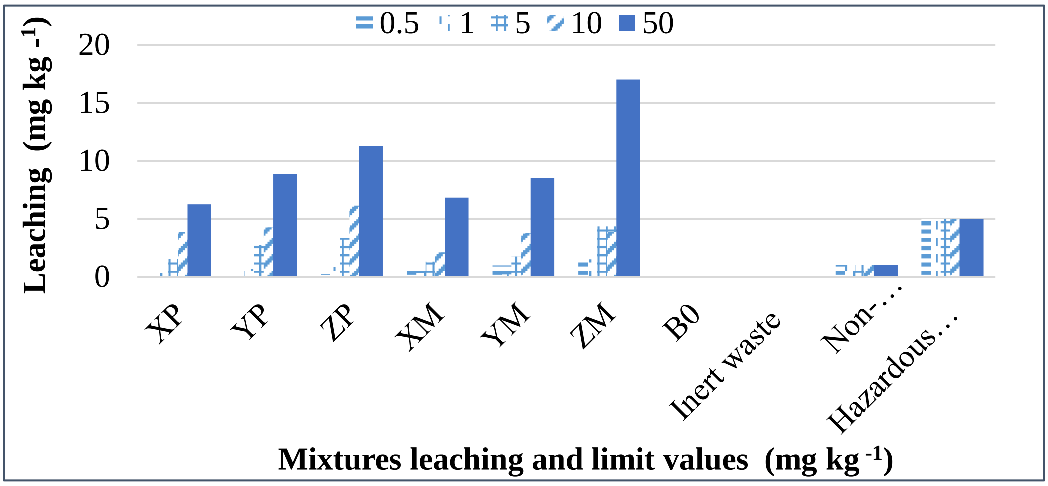


Figure11. Cd leaching concentrations at 4 M HNO_3 compared to limit values for the individual waste categories.

3.4. The pH effect on PTEs leaching

In this study, two trial tests with nitric acid concentrations of 0.43 M and 4 M were conducted on the crushed samples with a final leachate average pH of - 0.25 for (AMA) mortar - 0.07 for (APA)mortar samples at the 4M HNO_3 trial, and pH of 4.69 for (AMA) mortar 5.58 for (APA) mortar samples at 0.43 M HNO_3 trial. The results show that (AMA) mortar is more acidic than (APA) mortar, and the pH was lower than the simulated acid rains with pH of 3.0 and 2.5 (Kanazu *et al*., 2001). For (AMA) mortar mix samples, Figure 12(a-c) and (APA) Figure 12(b-d) show that the leached concentration of Pb, Cd, Cu, and Zn increased as the pH values of the solution decreased, which corresponds with (Udoeyo *et al*., 2006) findings. At the 0.43 M HNO_3 leaching test of (APA) samples, the highest leaching amount of Cu, Zn, Cd, and Pb was 1.96 mg kg^{-1}, 1.81 mg kg^{-1}, 0.41 mg kg^{-1}, and 1.69 mg kg^{-1} respectively, while at 4M leaching test the highest leaching amount of Cu, Zn, Cd, and Pb was 21.87 mg/kg, 12.72 mg/kg, 11.29

mg/kg, and 29.07 mg/kg respectively. Based on the findings of this study, future research involving more extensive analysis will aid in ensuring better use of this waste material; the future research work suggested must include the Study of leaching of non-crushed mortar samples for long-term exposure. Further studies should consider the mechanical strength and the durability of adsorbed paper ash mortar composite and the adsorbed mulch ash mortar composite to ensure that PTEs do not affect the properties of the mortar.

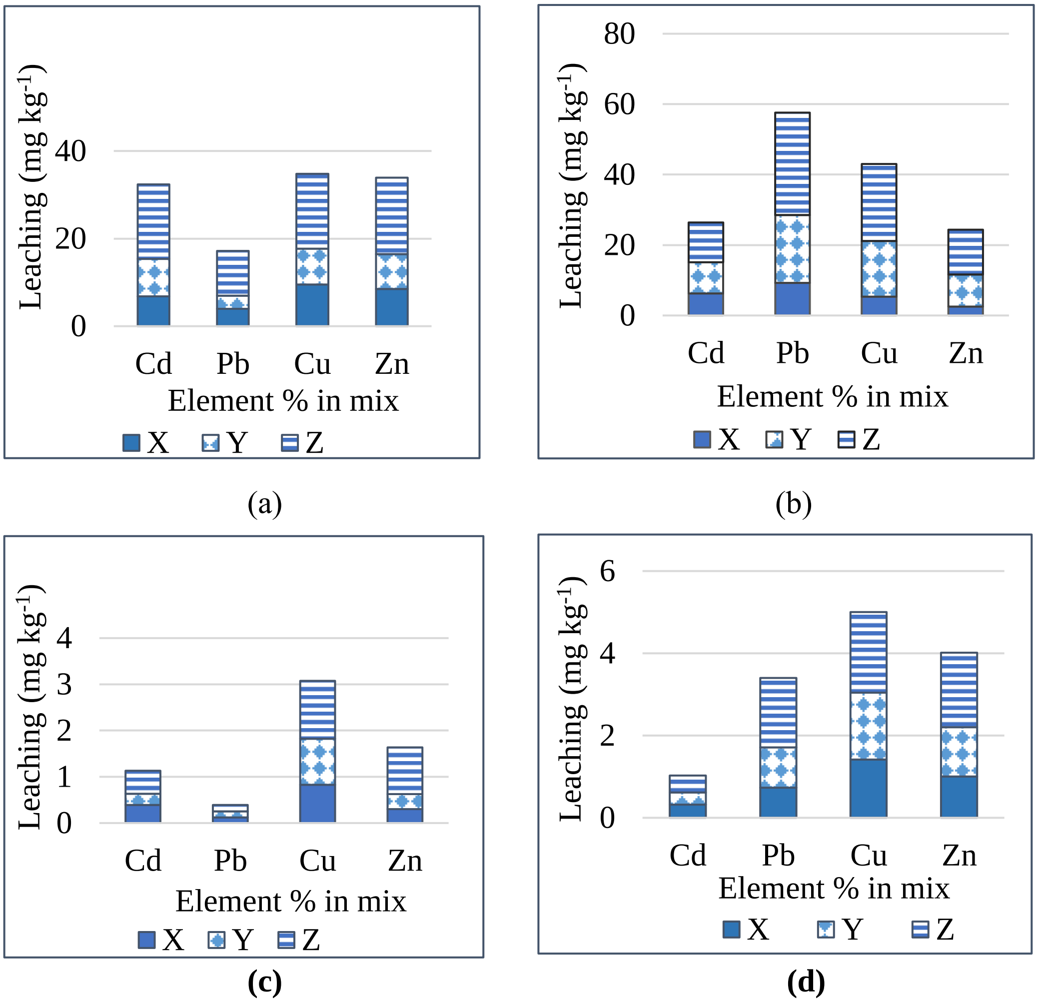


Figure12. (a) maximum leaching in mulch ash concrete mix (4M HNO_3), (b) maximum leaching in paper ash concrete mix (4M HNO_3), (c) maximum leaching in mulch 0.43M HNO_3, (d) maximum leaching in paper 0.43 M HNO_3.All results are based on average values of 3 replicates of 50 mgL^{-1} initial concentration of PTEs.

3.5. Adsorbent type combined effect on PTEs leaching and adsorption

Ash's elemental composition and structural characteristics can vary significantly depending on its source. When incorporating ash into mortars and concrete, it becomes challenging to predict how using a specific type of ash will impact the concrete's durability, as pointed out by Fava *et al*. (2018). Consequently, it is essential to conduct assessments on the final product using leaching tests. Hence, any new material must undergo a thorough technical and environmental analysis before it can be deemed suitable for practical applications.

The leaching results from the AMA mortar composite followed the order Cu >Zn > Cd>Pb, with respective values of 1.25, 1.01, 0.50, and 0.14 mg kg^{-1} at 0.43 M HNO_3 shown in Figure 12 (c) at Z =3% mulch ash composite. This observation could be attributed inversely to the ionic radius of PTEs, as indicated in Table 9. While APA leaching test results followed the order Cu >Zn>Pb> Cd with leaching amounts of 1.96, 1.81, 1.69, and 0.41 mg kg^{-1}, respectively shown in Figure 12 (d) at Z=3% of paper ash composite. Notably, cadmium was the metal with the least leached from APA mortar composites. These results highlight how adsorption affinity also played a pivotal role in determining the resulting leachate concentrations of PTEs. For instance, cadmium exhibited consistently low adsorption capacity when paper was used as the adsorbent. Additionally, pH, as noted by Hoang *et al*. (2022), is another influencing factor in the adsorption and leaching behavior of lignocellulosic biomass-activated carbon. After the leaching process with 0.43 M HNO_3, the measured pH values were 5.25 for (AMA) mortar and 7.22 for (APA) mortar at 50 mg L^{-1} initial concentration of PTE and 3% of ash content added in mortar. These results align with the idea that variations in pH contribute to the differing affinities for PTE adsorption, with (AMA) mortar being more acidic than (APA) mortar, which aligns with their respective adsorption preferences due to the pivotal role of acidity in this phenomenon.In this study the mulch and paper wastes were used as adsorbents showing different affinities to PTEs adsorption, which also influences the resultant APA and AMA mortar composites leachate concentration of PTEs.

3.6. PTEs immobilization efficiency of incorporated adsorbent ash

The immobilization efficiency (%) in APA mortar is higher than in AMA mortar, according to Table 2. The possible immobilization mechanisms of PTEs in concrete and mortar could be (1) sorption, (2) chemical incorporation (surface complexation, precipitation, co-precipitation, diodochy), and (3) micro-encapsulation or macro-encapsulation (Trussell and Spence 1994; Glasser, 1997). With reference to Figure 12 (a-b), PTEs show different leaching behaviors at 4M HNO_3 ; for example, Cd and Zn are more leached in the AMA mortar mix samples. Pb and Cu are more leached in the APA mortar mix. Furthermore, as the weight proportion of the contaminated ash added to the mortar increases, so does the content of PETs in the leachate. This result holds true for the AMA and APA mortar composites, as evidenced by the weight percentage addition of X =1%, Y =2%, and Z = 3% ash to the mortar. The leaching amount of the four PTEs at Z=3% of ash from the AMA mortar samples at 0.43 M HNO_3 follows the order Cu > Zn > Cd > Pb (Figure 12-c), and at 4 M HNO_3, the leaching order is Zn≈ Cd≈ Cu > Pb (Figure 12-a).

The order of leaching in the APA mortar samples at (Z=3% of ash 0.43 M HNO3) is Cu > Zn >Pb > Cd (Figure 12-d); at 4 M HNO_3, the order is Pb > Cu > Zn≈ Cd (Figure 12-b). These leaching results show that incorporating the APA and AMA into the mortar matrix confirms that the PTEs (Pb, Cu, Zn, and Cd) are successfully immobilized within the mortar matrix. Based on the obtained values, environmental safety can be ensured.

Table 2. *Immobilization efficiency % of PTEs encapsulated within the mortar. SD standard deviation.*

Element	AMA (Z)%	SD	APA (Z)%	SD
Cd	96.1	0.002	97.7	0.002
Pb	97.9	0.001	97.7	0.001
Cu	93.6	0.002	98.6	0.002
Zn	87.7	0.001	97.7	0.001

3.7. Microstructural characterization of incorporated adsorbent ash into the mortar

The SEM examination in this study revealed differences in the microstructure of APA, AMA, and blank samples, referring to Figure 13 of the SEM images. The results showed that, Unlike APA mortar, blank mortar has the most microcracks and porosity, while AMA mortar has the least. The microstructure of AMA mortar is significantly denser than that of APA and blank mortar. According to SEM examination, the inclusion of AMA and APA enhanced the microstructure of the mortar due to its micro-filling capabilities. The hydration phase was aluminate-ferrite, monosubstituted (AFm), a well-developed yet very thin hexagonal plate, indicating late formation for all composites. Another apparent color difference appeared in SEM images where both the adsorbed paper ash and adsorbed mulch ash, when incorporated in the mortar, led to a darker color compared to blank mortar this finding is consistent with the results of (Lessard *et al*., 2017) when using fly and bottom ash of paper waste in a concrete composite.

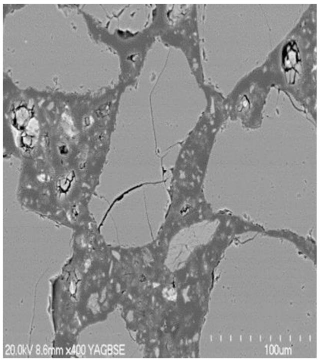
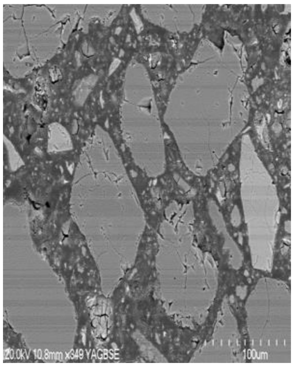
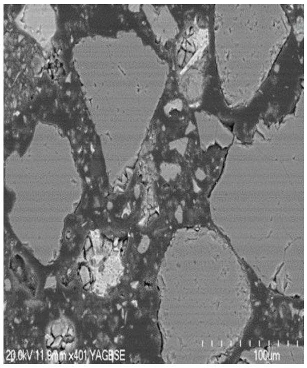
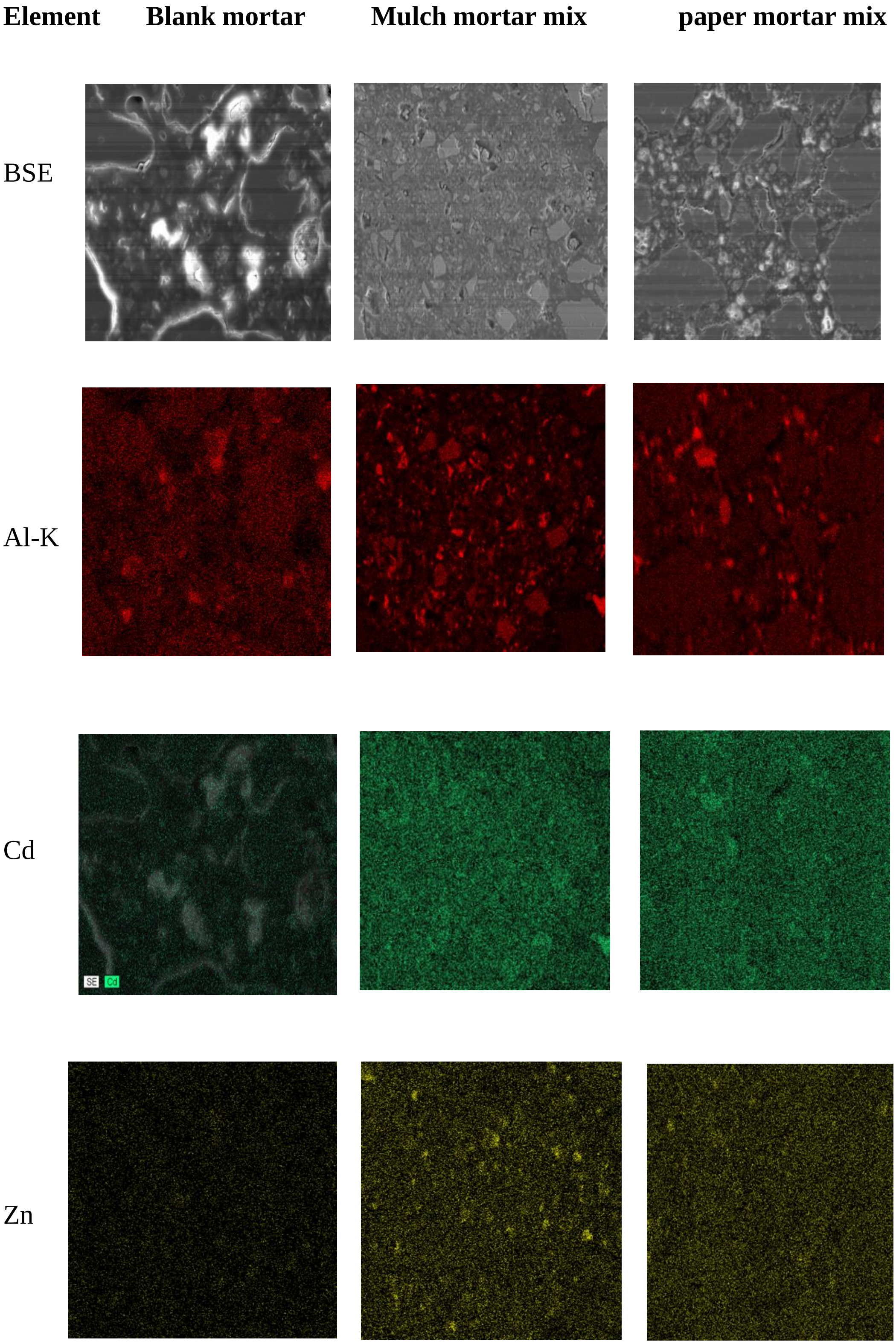
Blank mortar microstructure	APA mortar microstructure	AMA mortar microstructure
		

Figure 13. The microstructure of Blank, APA, and AMA mortar composites

3.8. Elemental mapping

Research findings on elemental mapping are presented in Figure 14. The elemental distribution of Al, Cd, Zn, Pb, Cu, Si, and Ca in the AMA, APA, and blank mortar composites was examined using SEM-EDS. The analysis revealed that the adsorbed potentially toxic elements - Cd, Zn, Cu, and Pb- exhibited a uniform distribution throughout the APA and AMA mortar matrix structure. However, their distribution intensity was higher than the blank mortar sample, indicating evidence of PTE immobilization.

Several steps were performed to conduct an in-depth analysis of the elemental maps. Each image was cropped, filtered, adjusted, and transformed to 8-bit using Image J software V 1.8.0 (Zohar & Haruzi, 2021).


Element
Blank mortar
Mulch mortar mix
paper mortar mix
BSE
Al-K
Cd
SE
Cd
Zn

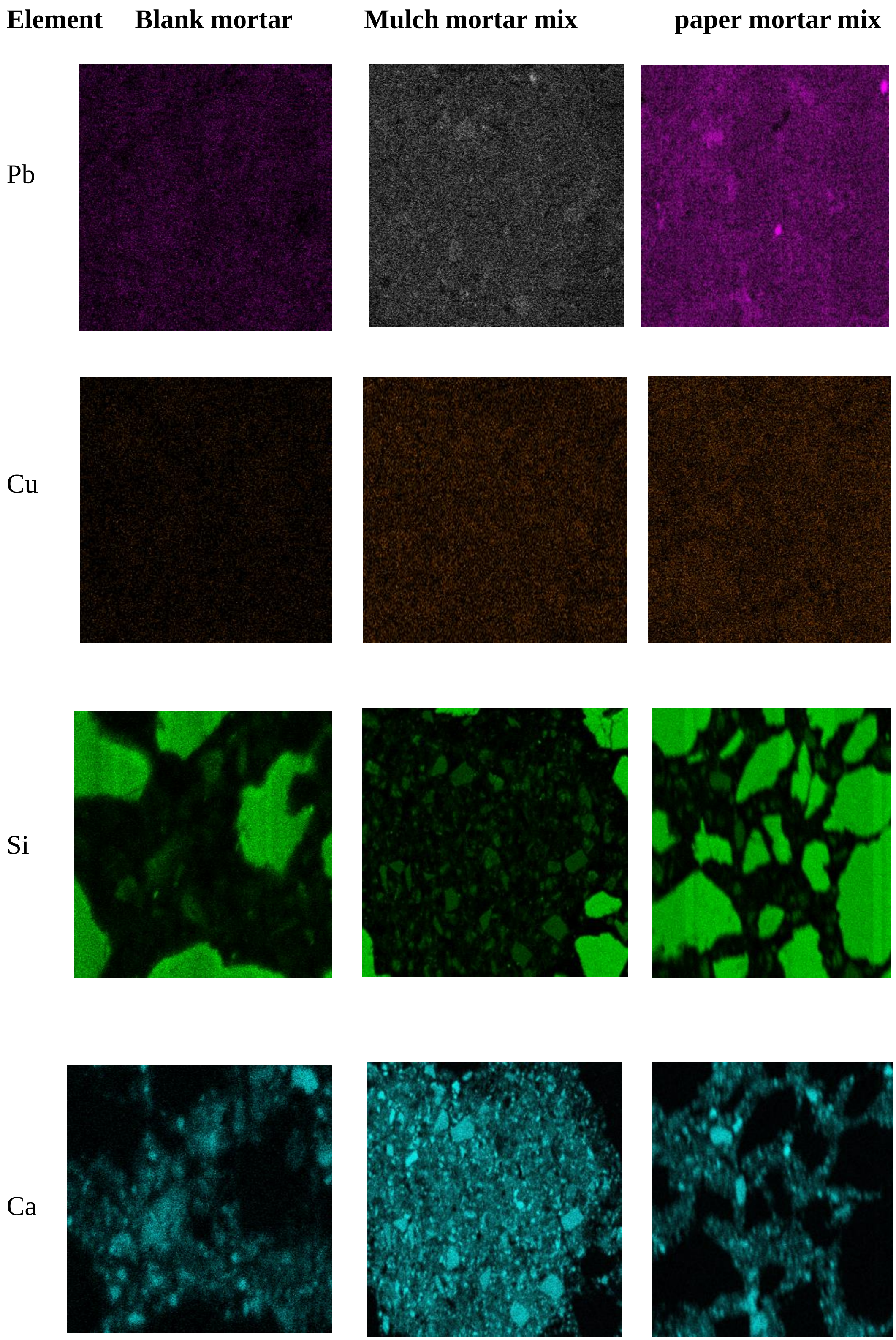


Figure14. Elemental mapping of APA, AMA, and blank mortar samples

The analyzed elemental maps provided information on the estimated area coverage percentage (%) for the adsorbed PTEs and other major elemental content in the studied mortar composites. Figure 15 displays the estimated percentage of the area coverage for each element of the adsorbed PTEs within AMA, APA, and blank mortar composites. The percentage of area coverage of PTEs within AMA mortar composites followed the following order: Pb > Cd>Zn>Cu, accounting for 32.1, 28.6, 13.8, and 12.4%, respectively. This order was also followed by the blank mortar composite, accounting for 12.5, 8.6, 4.5, and 4.2%, respectively.

In the APA mortar composite, the percentage of area coverage followed the following order: Cd>Pb>Zn>Cu, accounting for 27.7%, 26.6%, 14.5%, and 14.1%, respectively. The highest percentage of area coverage was observed for Pb, accounting for 32.1%, followed by Cd at 28.6% within the AMA mortar composite. In contrast, the APA mortar composite exhibited slightly lower percentages of area coverage for Pb and Cd, with values of 26.6% and 27.7%, respectively.

An inverse correlation between the estimated percentage of area coverage for adsorbed PTEs and the leaching results from the mortar composites was observed, suggesting valuable insights into the immobilization mechanisms for these PTEs. Specifically, the immobilization mechanisms for Pb, Cd, and Zn in cementitious materials can be explained as follows:

Lead (Pb): The predominant immobilization mechanism for Pb in cementitious materials involves precipitation as insoluble lead silicates (e.g., $PbSiO_3$, Pb_2SiO_4, Pb_3SiO_5, and Pb_4SiO_6) (Grubb *et al*.,2009; Liu *et al*., 2023). Cadmium (Cd): In cement hydration systems, Cd is primarily immobilized through the precipitation of hydroxides. These insoluble phases are subsequently adsorbed onto the C-S-H surface or fill the pore structure of cement pastes (Wang *et al*., 2018; Wang *et al*., 2022). Zinc (Zn): precipitation as hydroxides or carbonates may be the major mechanism for immobilizing Zn in solidification/stabilization systems (Liu *et al*., 2020). Zinc, being amphoteric, is soluble in a highly alkaline environment provided by cement hydration and exists as hydroxyl complexes ($[Zn(OH)_4]^{2-}$ and $[Zn(OH)_3]^{-}$). These hydroxyl complexes are less prone to adsorption onto the surface of C-S-H due to their negative charge (Liu *et al.*, 2023). Zn immobilized less than Pb and Cd because of its mechanism of immobilization. It is an amphoteric metal that is soluble in highly alkaline environments and hardly adsorbs onto C-S-H, while Pb and Cd precipitate as hydroxides, filling the pore structure of cement pastes.

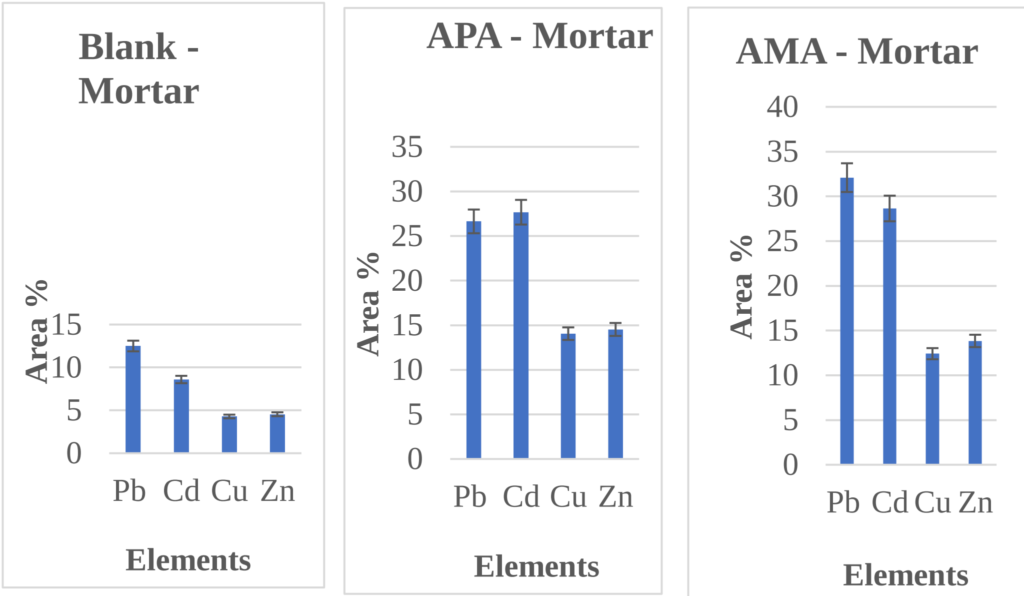


Figure15. Area coverage percentage (%) for adsorbed elements estimated using ImageJ software V 1.8.0 for AMA, APA, and blank mortar composites.

The percentage of area coverage of the major elements within AMA, APA, and blank mortar composites compared are presented in Figure 16.

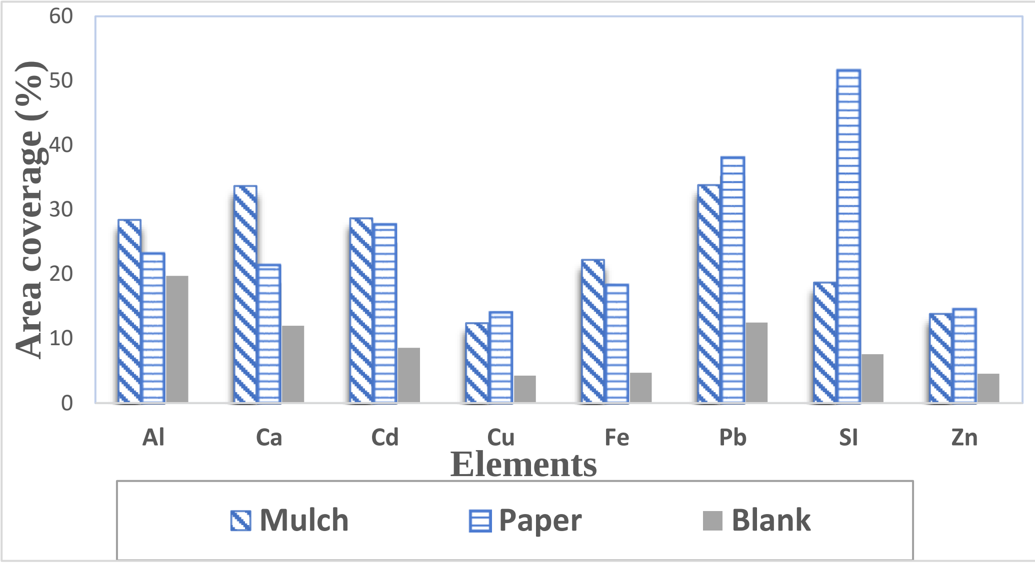


Figure16. Compared Area coverage percentage (%) for major elements estimated using ImageJ software V 1.8.0

3.9.Statistical analysis

This study investigated the effect of incorporating AMA and APA into the mortar on the leaching concentration of PTEs. The dependent variable is the leaching concentration of PTEs, also measured in mg kg^{-1}. The research hypotheses for this study are as follows: Null Hypothesis (H0): There is no significant factorial effect of the initial concentration of PTEs, the incorporated ash percentage %, the molarity of the used HNO_3, and the adsorbent type on the leaching concentrations of PTEs.

Alternative Hypothesis (Ha): There is a significant factorial effect of at least one of the independent variables on the leaching concentrations of PTEs. In other words, the factors have a statistically significant impact on the leaching concentrations of PTEs.

3.9.1.Molarity factor

The primary goal of this analysis is to determine if there are statistically significant differences in PTE leaching concentrations associated with varying eluant molarity levels. The data underwent statistical analysis, including mean calculation, determination of p-values, and computation of the least significant difference (LSD) for each element. A p-value of less than or equal to 0.05 indicates statistical significance, suggesting that molarity substantially influences PTE concentrations. As illustrated in Figure 17, which shows the AMA samples' statistical analysis results. The results unequivocally establish that molarity significantly influences the concentrations of Cd, Cu, Pb, and Zn. In all cases, elevating the molarity from 0.43 M to 4 M substantially increases PTE concentrations. These findings have important implications for understanding the behavior of these elements within different chemical environments.

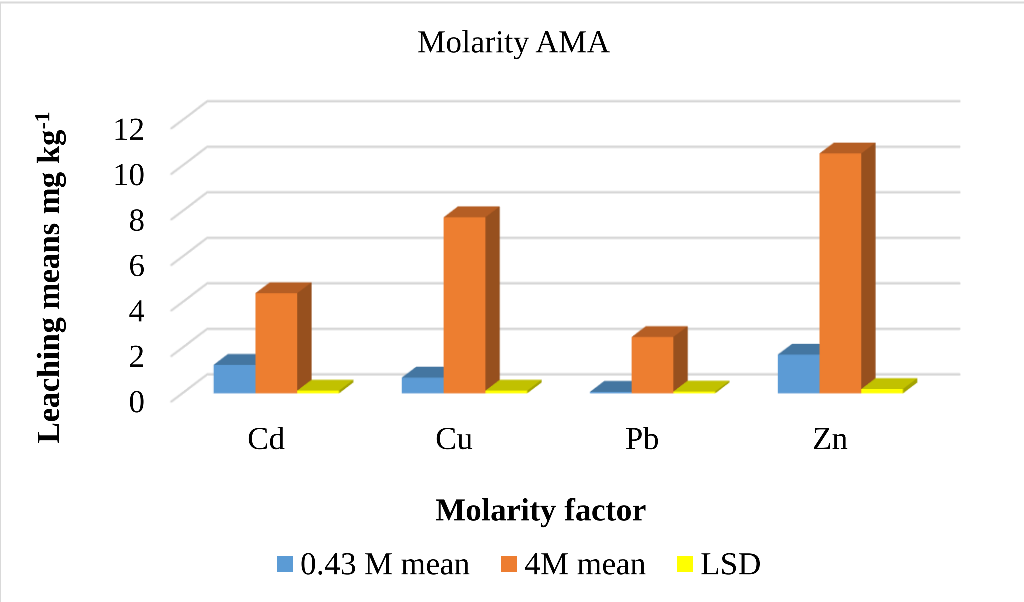


Figure17. AMA molarity factor statistical analysis

This statistical analysis confirms that molarity substantially influences the leaching concentrations of Cadmium, Copper, Lead, and Zinc. The marked increases in PTE concentrations at higher molarity levels underscore the necessity of considering molarity when studying the behavior of these elements. This insight is valuable for further research and environmental assessments, ensuring accurate characterizations of PTE concentrations.

In the case of the APA Samples, the statistical analysis illustrated in Figure 18 revealed that the p-values for all four elements (Cd, Cu, Pb, Zn) are less than 0.05. This means there is strong evidence to reject the null hypothesis (H0) for each element. The LSD values for each element represent the smallest difference between means that is statistically significant. The LSD values are smaller than the differences between the means for each element at the two molarity levels (0.43 M and 4 M). Therefore, we can conclude that the molarity of the eluant (M) has a significant factorial effect on the leaching concentrations of Cd, Cu, Pb, and Zn. The alternative hypothesis (Ha) is supported. The molarity of the eluant (M) has a statistically significant impact on the PTEs (Cd, Cu, Pb, Zn) leaching concentrations.

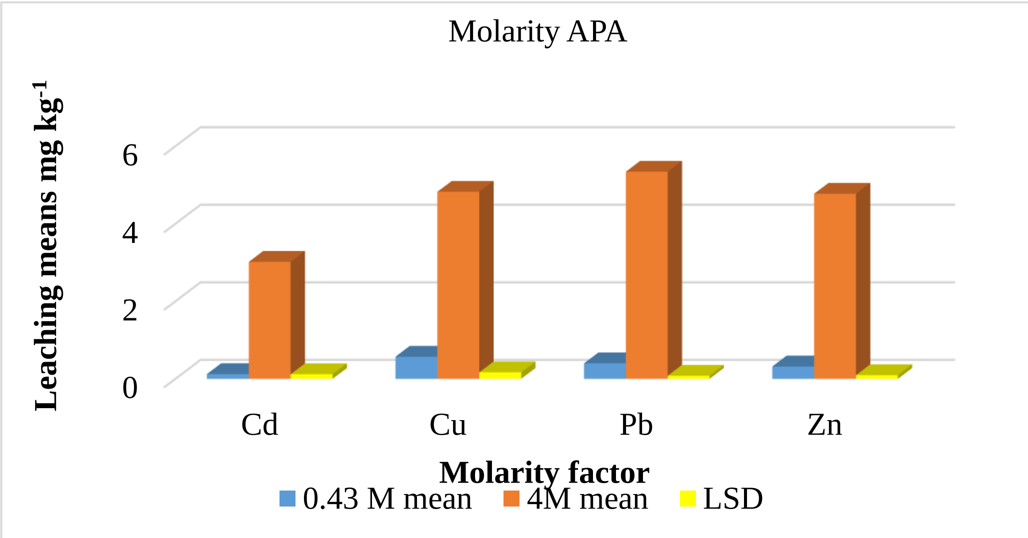


Figure18. APA molarity factor statistical analysis

3.9.2. Percentage % factor

This study examines the impact of varying ash percentages (1% and 3%) on the mean leaching concentrations of four potentially toxic elements: Cu, Cd, Pb, and Zn. Statistical analysis is performed to assess whether statistically significant differences between the two ash percentage levels exist. As presented in Figure 19 for AMA samples, the results consistently reveal that the absolute differences in leaching concentrations at these two ash percentage levels significantly surpass the corresponding Least Significant Difference (LSD) values. This unambiguously affirms the substantial role of ash percentage in shaping the leaching concentrations of these Potentially Toxic Elements.

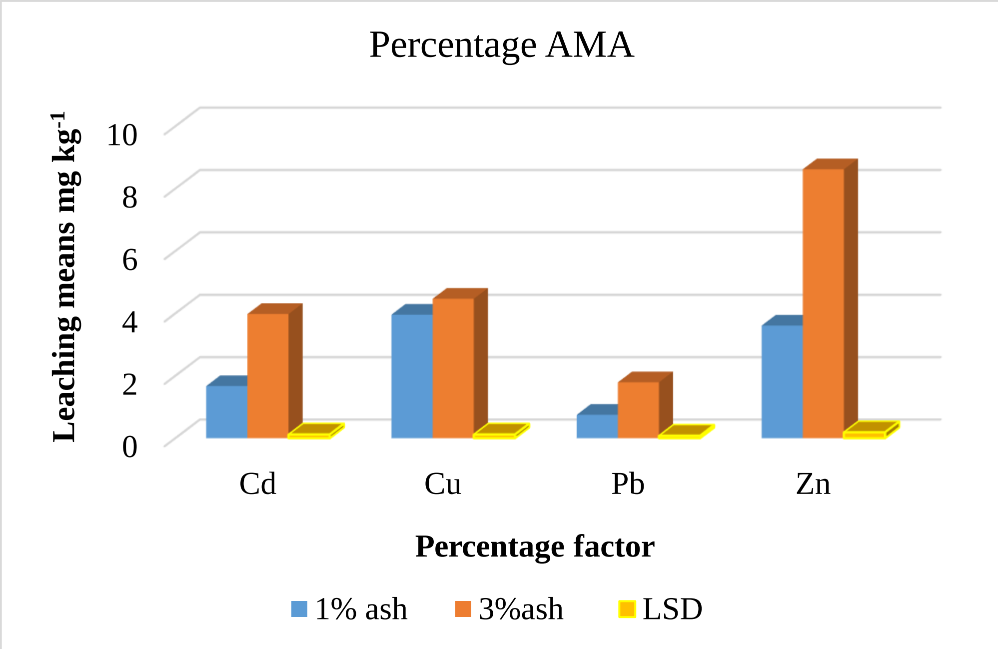


Figure19. AMA ash percentage factor statistical analysis

The statistical data for APA samples is illustrated in Figure 20. The p-values for all four elements (Cd, Cu, Pb, Zn) are less than 0.05. This means there is strong evidence to reject the null hypothesis (H0) for each element. The LSD values for each element represent the smallest difference between means that is statistically significant. The LSD values are smaller than the differences between the means for each element at the two percentage levels (1% and 3%). Therefore, we can conclude that the percentage has a significant factorial effect on the leaching concentrations of Cd, Cu, Pb, and Zn. The alternative hypothesis (Ha) is supported.

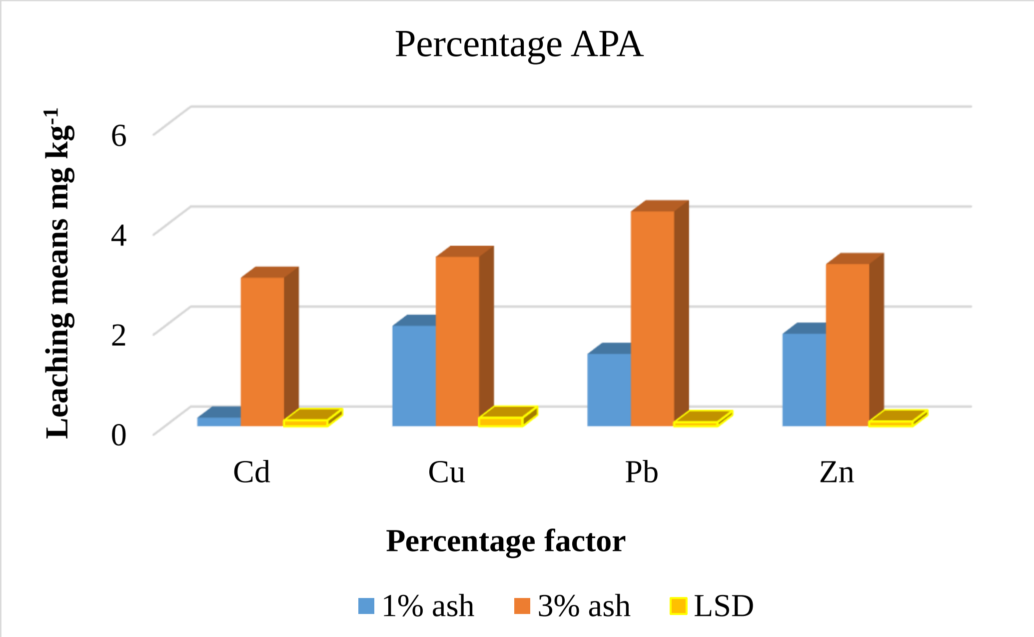


Figure20. APA ash percentage factor statistical analysis

3.9.3. Initial concentration factor

The initial concentration of Potentially Toxic Elements plays a pivotal role in leaching. As depicted in Figure 21, the AMA dataset offers a comprehensive view of the average leaching concentrations of Cadmium, Copper, Lead, and Zinc across a range of initial concentrations (0.5, 1, 5, 10, and 50) mg L^{-1}. The statistical analysis confirms that for most elements (Copper, Lead, and Zinc), there are statistically significant differences in leaching concentrations across the various initial concentrations, as indicated by p-values less than 0.001. However, it is noteworthy that the concentrations of Cadmium and Lead deviate from this trend. The calculations reveal that significant differences in Cadmium and Lead concentrations only became evident at the 5 mg L^{-1} initial concentration, as the absolute differences surpassed the respective LSD values. This suggests that, unlike the other elements, Cadmium and Lead required a higher initial concentration (5 mg L^{-1}) to exhibit statistically significant differences in leaching behavior.

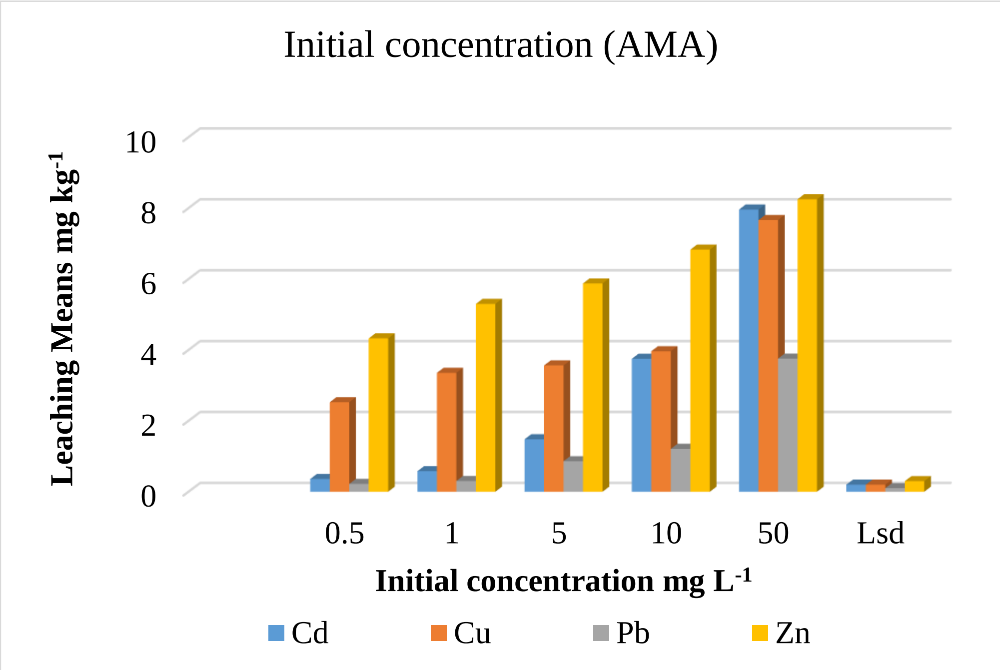


Figure 21. AMA initial concentration factor statistical analysis

The initial concentration statistical data for APA samples is illustrated in Figure 22. The p-values for all four elements (Cd, Cu, Pb, Zn) are less than 0.05. This suggests strong evidence to reject each element's null hypothesis (H0). The LSD values for each element represent the smallest difference between means that is statistically significant. The LSD values are smaller than the differences between the means for each element at the various initial concentrations. Consequently, we can conclude that the initial concentrations of Potentially Toxic Elements have a statistically significant impact on Cd, Cu, Pb, and Zn leaching concentrations.

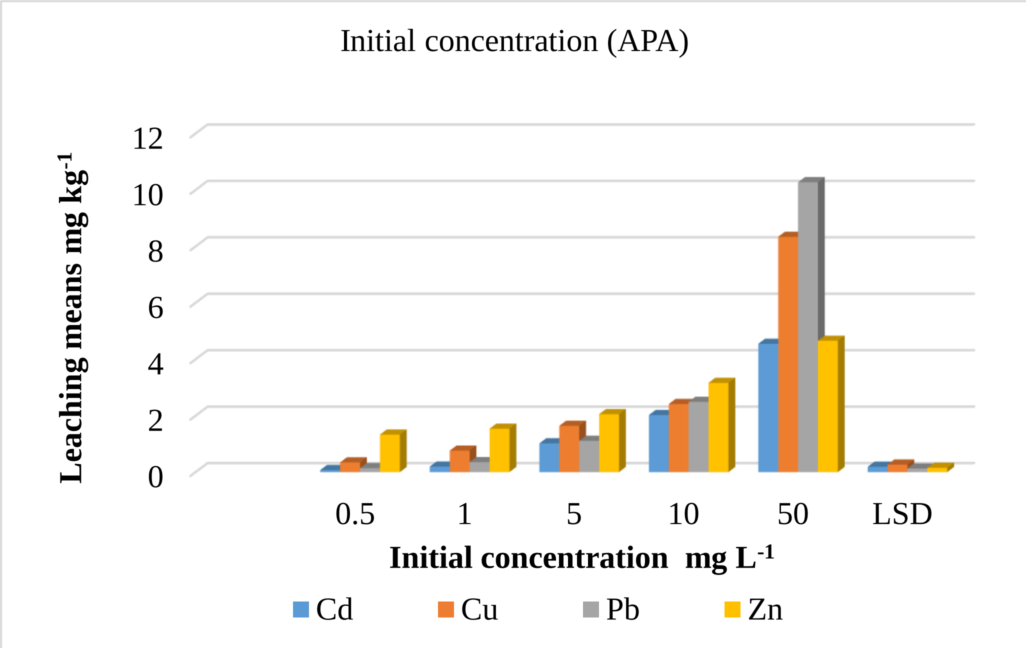


Figure22. APA initial concentration factor statistical analysis

4. CONCLUSION AND RECOMMENDATIONS

This research addresses the utilization of cellulose-based adsorbent ashes, specifically adsorbed paper ash (APA) and mulch ash (AMA), in mortar composites. The study investigates their affinity for potentially toxic elements (PTEs), their immobilization mechanisms, leaching behavior, and microstructure. This research contributes significantly to the development of sustainable construction materials by demonstrating the effectiveness of cellulose-based adsorbent ashes in mortar composites. By reducing waste and environmental impact while enhancing material performance, these findings align with the principles of waste-to-energy and the circular economy, offering a promising avenue for eco-friendly construction practices. Further research in these areas will lead to more widespread adoption and greater environmental benefits. In conclusion, this study highlights the potential of incorporating waste adsorbents into mortar mixes as a promising solution for addressing the environmental challenges associated with the adsorption of potentially toxic elements (PTEs). Our findings demonstrate the following key points:

-Effective immobilization of PTEs: the inclusion of APA and AMA in mortar matrices successfully immobilizes PTEs (Pb, Cu, Zn, and Cd) in accordance with EU directives, effectively preventing their leaching into the environment.

-Environmental safety: leaching tests indicate that PTE concentrations leached from the tested crushed mortar samples, even in aggressive conditions (0.43 M HNO_3), fall within the inert waste category. Although APA mortar samples slightly exceed the inert waste limit for Pb, both APA and AMA composites remain well below hazardous waste limits, ensuring environmental safety.

-Variable leaching behaviors: our research highlights different leaching behaviors for PTEs. Cd and Zn exhibit higher leaching tendencies in AMA mortar samples, while Pb and Cu are more prone to leaching in APA mortar samples. Therefore, careful consideration of the specific PTEs of concern is essential when selecting the appropriate waste adsorbent.

-Optimal weight ratio: the optimum weight ratio for the addition of APA or AMA to mortar mixes is determined to be 3%. Exceeding this ratio could potentially lead to leaching that exceeds permissible limits, posing a threat to environmental safety.

-Elemental mapping and microstructure: According to Scanning Electron Microscopy (SEM) analysis, the AMA mortar has a denser microstructure than APA mortar and blank mortar, lending credence to the idea that the addition of AMA and APA improved the mortar's microstructure thanks to their micro-filling capabilities. Elemental mapping results show that adsorbed Cd, Zn, Cu, and Pb are distributed reasonably uniformly throughout the APA and AMA mortar matrices, with a greater intensity of dispersion than the blank mortar sample, indicating evidence of immobilization of the PTEs.

Based on these findings, we recommend the following for future research:

-Extensive Analysis: Future studies should conduct more comprehensive analyses to further explore the utilization of APA and AMA in construction materials, with a focus on their long-term performance and stability. To assess the effects of aging and prolonged exposure, research should include studies on non-crushed mortar samples over extended periods.

-Mechanical Strength and Durability: Investigate the impact of APA and AMA on the mechanical strength and durability of mortar composites to ensure that these waste materials do not compromise the properties of the mortar.

-Civil Engineering Applications: Explore the use of APA and AMA mortar composites in various civil engineering applications, assessing their suitability and performance in real-world construction scenarios.

In addition to the previously mentioned recommendations, a proposed new avenue for future research is the study of adsorbent incorporation into white cement composites. While our current research focuses on conventional mortar mixes, exploring the application of adsorbed paper ash (APA) and adsorbed mulch ash (AMA) in white cement composites presents a promising direction. Future studies should investigate the following aspects:

Adsorption Efficiency, Aesthetic Impact, Environmental Performance, and the compatibility of APA and AMA with white cement, examining their effects on the mechanical properties and long-term durability of the composites. Exploring the integration of waste adsorbents into white cement composites aligns with the broader objective of sustainable construction materials. This research will not only contribute to reducing waste and environmental impact but also offer architects and builders eco-friendly alternatives without compromising the visual appeal and performance of white cement-based architectural elements.

5. NEW SCIENTIFIC RESULTS

1. The findings of this study indicate different affinities and capacities of mulch and paper in adsorbing PTEs. Notably, the paper-based adsorbent exhibited a superior capacity for adsorbing the investigated PTEs. Additionally, the study revealed that Cadmium, with a critical permissible leaching limit of 5 mg kg^{-1}, demonstrated better immobilization within the APA mortar composite, despite the paper adsorbing twice the quantity of mulch.
2. In the investigation of leaching concentrations of PTEs, including Cadmium, Zinc, Copper, and Lead, within both AMA and APA mortar composites, it has been discerned that these concentrations fall below the permissible leaching limits as outlined by the EU directive 1999/31/EC for waste categories. Furthermore, the study has unveiled a crucial revelation: an optimal weight ratio has been determined for the inclusion of APA or AMA in the mortar mixture, and this ratio is found to be 3%. It is of paramount significance that this ratio is not exceeded, as exceeding this threshold significantly increases the risk of leaching surpassing permissible limits, consequently posing a substantial threat to environmental safety.
3. In this study, scanning electron microscopy (SEM) was employed to analyze the microstructures of APA, AMA, and the reference blank samples. The results reveal a significant distinction: the blank mortar displays a higher prevalence of microcracks, and porosity compared to the APA mortar, which exhibits fewer such features. Notably, the AMA mortar demonstrates the densest and most compact microstructure among the three specimens. The SEM analysis indicates that the incorporation of AMA and APA in the mortar enhances its microstructure, primarily due to their exceptional micro-filling properties.
4. The study utilized elemental maps to assess the surface area coverage percentage of adsorbed PTEs and other major elements in mortar composites. An intriguing inverse correlation was observed between the surface area coverage of adsorbed PTEs and the leaching behavior of mortar composites, shedding light on the mechanisms behind PTE immobilization. The observed lower immobilization of Zn was demonstrated due to its unique characteristics, solubility in highly alkaline environments, and limited adsorption onto Calcium-Silicate-Hydrate (C-S-H). In contrast, Pb and Cd precipitated as hydroxides, occupying the cement paste's pore structure These findings offer valuable insights into the sequence of PTE behavior and the crucial role played by immobilization mechanisms in determining leaching patterns in mortar composites.

6. PUBLICATIONS RELATED TO THE DISSERTATION

1. Publication (Journal Article: Q2 - IF = 2.7)
Heba Naser; Mark Horváth; Imre Czinkota. Incorporation of Adsorbent Ash with Potentially Toxic Elements into Mortar: A Sustainable Approach. JOURNAL OF HAZARDOUS, TOXIC, AND RADIOACTIVE WASTE, 27(1), 04022037. (2023). https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000734

2.Publication (Journal Review Article: Q4 - IF = 0.73)
Heba Naser,;Imre Czinkota; Andrea Dorkota; Márk Horváth. "A review of the advancements of potentially toxic element adsorption by various cellulose-based materials and the used adsorbents' fate." PROGRESS IN AGRICULTURAL ENGINEERING SCIENCES (2023).

3.Accepted Publication (Journal Article: Q3 - IF = 1.9)
Heba Naser,;Imre Czinkota; Andrea Dorkota; Ibrahim G Al -Labadi; Márk Horváth. Elemental and microstructural characterization of incorporated adsorbent ash with Potentially Toxic Elements in a mortar. ECOLOGICAL CHEMISTRY AND ENGINEERING SOCIETY

4.Teaching activities (Agrokemia KORTUN15N), (Plant Nutrition KORTUN152N MSc).