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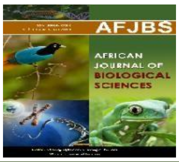

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Hydrochloric Acid Enhancing the eggshell flour water solubility by advanced characterization for Sustainable Resource Utilization

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ABSTRACT

This study investigates the solubility and metal content analysis of eggshell flour treated with various methods, revealing significant findings. The highest solubility, reaching an impressive 91%, was observed in the HCl-treated sample, indicating efficient calcium extraction. In contrast, the distilled water-ESP treatment exhibited the lowest solubility at 1.5%, emphasizing the treatment's impact on enhancing solubility. Additionally, turbidity analysis revealed that the HCl-ESP treatment displayed the lowest turbidity at 20.66 NTU, suggesting improved solubility due to increased porosity. Furthermore, ICP-MS metal analysis indicated minimal presence of heavy metals in the treated samples, affirming their safety for diverse applications. The combination of enhanced solubility and low metal content highlights the potential of treated eggshell flour for eco-friendly and sustainable utilization, underscoring the importance of optimized treatment processes in enhancing its quality and safety for various industrial and environmental applications.

Keywords: Eggshell flour, Acid, Solvent, Solubility, Turbidity, SEM, Porosity, Metals.

INTRODUCTION

In today's society, handling trash is an important concern. Fish, reptiles, and birds all make hard eggshells (Nath et al. 2021). Because eggs are used so extensively in the world, the food business produces a significant amount of wasted chicken eggshells. These abandoned eggshells pose a serious threat to the environment since they increase pollution levels and make trash management (Suryono et al. 2023). The environment and public health will be safeguarded by the quest for an effective method of appropriately disposing of agricultural waste. Recycling, reusing, and redirecting waste towards the production of items with additional value is necessary for sustainable development. Maintaining a zero-waste strategy while producing things with added value and protecting the environment is the goal (Mahani et al. 2021).

Eggshell calcium is a highly effective source of this mineral in the culinary arts. Because the eggshell powder has lower concentrations of vanadium, chromium, lead, aluminium, and cadmium than oyster shells or refined calcium carbonate, research has proven that it is safe to use as a natural supplement. Eggs from environment-friendly hens and eggs produced using organic methods have the lowest concentrations of dangerous heavy metals including cadmium and mercury (Schaafsma et al. 2000). Eggshells make up nearly eleven percent of the whole weight of an egg, and they are mostly made of calcium carbonate (94%), with smaller percentages of calcium phosphate (1%), organic matter (4%), and magnesium carbonate (1%). More and more of these highly mineralized structures are being used as waste material alternatives (Mijan et al. 2014). In addition to calcium, eggshells contain minimal quantities of iron, copper, boron, sulfur, zinc, silicon, and molybdenum. With a 90% absorbance percentage, calcium from eggshells is probably the best source of this mineral in nature (King'Ori 2011). Compared to oyster shells, the calcium carbonate from chicken eggshells is more soluble. Furthermore, its abundant mineral composition, including barium and strontium, makes it an excellent biomaterial for the production of nutritional supplements (Szeleszczuk et al. 2015).

It's possible that calcium lactate or citrate, which are soluble in water and found in milk, are more easily absorbed (Szeleszczuk et al. 2015). Studies focusing on in vitro calcium dissolution reveal that the carbonate of calcium generated from eggshells is easily soluble in gastric acid in contrast to other commercial calcium supplements. In an in vitro experiment, eggshell powder dissolved in 90 minutes at 37 °C by 75.0±4.5% in a 0.1 M hydrochloric acid solution with a pH of 1.00 (Bradauskiene et al. 2017).

Considering the sustainable use of eggshells and their inherent porous structure, there is limited information in the literature regarding the characterization of this biomaterial. Examining the different phases of eggshell formation using a scanning electron microscope yields valuable insights (Tsai et al. 2006). As an example of a porous biological substance, the eggshell is widely used. Because of the porosity present in each layer of this material, the transport of gases through the eggshell is better regulated. The impermeability of chicken eggshells has been examined using a variety of experimental methods, such as mercury intrusion porosimeter, scanning electron microscopy (SEM), and X-ray micro-computed tomography (Arzate-Vázquez et al. 2019). As stated by (Lin et al. 2021), eggshell powder has demonstrated potential as an effective adsorbent for eliminating toxic metals like arsenic, manganese, lead, copper, cadmium, chromium, and mercury from various environments. According to a study by (Abatan et al. 2020), eggshell flour is a useful adsorption for removing cadmium and hexavalent chromium ions from water-based solutions.

The study noted an enhancement in adsorption capacity with increasing initial concentration of adsorbate, pH levels, contact time, and dosage of the adsorbent. Moreover, powdered chicken eggshells, which may contain heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), and manganese (Mn), are a rich source of calcium and strontium supplementation. Higher initial adsorbate concentrations, higher pH values, longer contact times, and larger amounts of adsorption were all found to enhance the ability to adsorb. Furthermore, crushed chicken eggshells offer a significant source of calcium and strontium for supplementing; they may also contain trace levels of metals that are toxic as lead (Pb), cadmium (Cd), chromium (Cr), and manganese (Mn). But depending on where the eggshells came from, different dangerous metal concentrations exist. As an illustration, native chicken eggshells had the highest zinc concentration, quail eggshells had the highest iron content, and brown-colored eggshells had the largest amount of lead. A noteworthy finding was that all eggshells had amounts of chromium (Cr) and cadmium (Cd) below the detection limit, according to (Rokanuzzaman et al. 2022). The study also indicates that acid methods, such as the use of hydrochloric acid, can effectively disrupt disulfide bonds present in eggshell membrane proteins, leading to their solubilization (Han et al. 2023). Furthermore, the study elaborates on the process of preparing various solvents to produce eggshell flour, including a 4% HCl solution, aimed at extracting calcium from the shell while minimizing hazardous elements and organic substances. The end product, calcium chloride flour, has good solubility and a calcium chloride level of 87.38% (w/w). Consequently, it can be inferred that eggshell powder treated with HCl acid may contain metals, notably calcium, which can be extracted and rendered soluble for various applications (Rosnah et al. 2021).

Eggshells have the potential to be transformed into flour for consumption by employing a chemical extraction process. This method is recognized for enhancing the physical and sensory characteristics of eggshells while simultaneously diminishing harmful elements and eliminating organic compounds (Aminah and Meikawati 2016). Various chemical solutions, including CH_3COOH applied to shrimp waste during soaking and NaOH used with local gravy waste, prove to be reasonably efficient in enhancing the physical and sensory attributes of eggshell flour. The common mechanism among these solvents involves creating pores in the shell, facilitating better access for the solvent to reach its target and release the molecule bound to the mineral at an optimal rate (Yonata et al. 2017). In dielectric constant value influences the solvent's ability to bind the shell component chemical. A solvent becomes increasingly polar as its dielectric constant value increases. The degree to which a solvent is polar determines its capacity to pull specific materials and components out of the eggshell or dissolve them. Eggshell flour properties, both physical and organoleptic, are influenced by the kind of solvent used and the kind of chicken eggshell. When domestic chicken eggshells are removed using a CH_3COOH solution, the best shell flour is produced (Purnamasari et al. 2013). When compared to eggshell powder obtained by 2N acetic acid (CH_3COOH), the properties of chicken eggshell flour prepared using 4% hydrochloric acid (HCl) were superior. Eggshell powder processed using four percent hydrochloric acid produced higher quantities of calcium, calcium carbonate, phosphorus, ash, and overall output, but it also had lesser moisture content than eggshell powder taken in the amount of 2N acetic acid. Because it contains inert and non-hazardous chloride ions, hydrochloric acid is an aggressive acid that poses a smaller risk of handling threat when compared to other acids of comparable strength. In addition to producing hydrogen gas and metal chloride, concentrated hydrochloric acid disintegrates a wide variety of metals. Additionally, if a substance is hard to dissolve in water, it might make it more soluble (Rosnah et al. 2021).

This research aims to carry out extensive tests to investigate the effects of hydrochloric acid treatment on the turbidity and solubility of eggshell flour. Gravimetric analysis and turbidity measurements will be used to evaluate how well the treatment improves solubility and decreases cloudiness. Additionally, an investigation of metals utilizing techniques (ICP-MS analysis) has been conducted to ensure the security of the treated materials for a range of uses. In addition, SEM, FTIR, and EDX analyses will be carried out to get an additional understanding of the properties of the treated eggshell flour and the modifications resulting from the treatment procedure. The study intends to shed light on how eggshell flour is affected by hydrochloric acid treatment through rigorous testing and analysis, supporting the development of environmentally friendly resource utilization.

MATERIALS AND METHODS

The production process of eggshell flour

The eggshell trash was gathered from the Kalasalingam Academy of Research and Education in Srivilliputhur, Tamil Nadu, India. Recently acquired eggshell trash was washed with warm water and had its membrane manually peeled off (Brun et al. 2013). After being dried for two hours at 120 °C in an oven, the waste was pulverized, sieved into fine flour, and stored for later use enclosed in a tight enclosure (Dayanidhi et al. 2019).

Assessment of the solubility and turbidity of eggshell flour in solvents and acids

Using gravimetric analysis, the total suspended solids and total dissolved solids of eggshell flour were determined to assess the degree to which they dissolved (Kazi et al. 2009). Whatman no. 41 filter paper was covered with 0.2 g of eggshell flour of each solvent and acid, along with 15 ml of distilled water, solvents, and acids at room temperature (30° C) that were shaken for 24 hours at 90 rpm, vortexed for 5 minutes at 1600 rpm, and then poured drop by drop over the paper (Table 1). Continue doing this until the water starts to filter down. The filter paper was then dried in a desiccator for 15 minutes after being held in a hot air oven set at 120° C for 60 minutes. A digital weighing balance is used to record the final weight. (Aditya et al. 2020). The turbidity of the sample was estimated using a turbidity meter (Gaiani et al. 2009).

Calculation formula

$$\textbf{TDS mg/l} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Volume of sample}} \times 1000000$$

$$\textbf{TSS mg/l} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Volume of sample}} \times 1000000$$

Solubility % = Volume of taken sample – undissolved

$$= \frac{\text{Dissolved}}{\text{The volume of taken sample}} \times 100$$

Table 1 Composition of eggshell flour in solvents and acids

S. No	Sample	Particulars
1.	Distilled water+ ESP	10ml of distilled water + 0.2 g of ESP
2.	Acetone+ ESP	10ml of acetone+ 0.2 g of ESP
3.	Ethanol+ ESP	10ml of ethanol+ 0.2 g of ESP
4.	H_2SO_4+ ESP	10ml of H_2SO_4 + 0.2 g of ESP
5.	HCl+ ESP	10ml of HCL + 0.2 g of ESP

Microwave digestion

The sample, precisely weighing about 0.5g ± 0.1g of homogenized material, was carefully transferred into a microwave digestion vessel. To this, 5mL of concentrated supra undiluted nitric acid to produce a solution was incorporated along with 2 ml of hydrogen peroxide. It's noteworthy that both the sample and acid were placed in polymeric microwave containers known for their chemical inertness. In the microwave digestion system, the vessel was securely sealed and subjected to heating. Over 40 minutes, the microwave power was gradually increased up to 400 W to facilitate the digestion process of the samples. Once the desired temperature was attained, the vessels were allowed to cool thoroughly. Following cooling, the vessels were opened within a fume hood, and the lid and walls of the digestion vessel were rinsed with Milli-Q water to ensure complete transfer of the digested material. Subsequently, after air conditioning, the ensuing mixtures were adjusted to a final volume of 50 ml using Milli-Q water.

To further refine the samples, filtration was carried out using filter paper, by the methodology described by (Kumaravel et al. 2014: Moor et al. 2001). This exacting filtration process ensured the removal of any remaining particulate matter, yielding clear and analytically reliable solutions for subsequent analysis.

Analysis of metals

Calcium and magnesium were analyzed by (ICPMS) instrument (Chilek et al. 2018). Utilizing high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS), the concentration of each element was determined. Following the treatment of the eggshell flour with an HCl solution, the levels of toxic metals were identified.

The findings showed that there was very little harmful metal presence in the sample, with quantities of the metals below the quantitation limit. This determination was executed utilizing the IPL.CH.INS.STP.05 method, which employs an inductively coupled plasma mass spectrometry approach, as detailed by (Liu et al. 2017). The conclusion drawn from the study is that the HCl treatment of the eggshell flour resulted in the dissolution of heavy metals, which were not present at high levels in the sample. This outcome suggests that the treated eggshell flour could be considered eco-friendly due to the reduced levels of heavy metals after the eggshell flour treated with HCL.

RESULTS AND DISCUSSION

Estimation of Solubility

Table 2 Solubility of eggshell flour in solvents and acids

S. No	Sample	TSS (mg/0.2g/10ml)	TDS (mg/0.2g/10ml)	Solubility (%)
1.	Distilled water+ ESP	0.197	0.003	1.5
2.	Acetone+ ESP	0.167	0.033	16.5
3.	Ethanol+ ESP	0.163	0.037	18.5
4.	H_2SO_4+ ESP	0.169	0.031	15.5
5.	HCl+ ESP	0.018	0.182	91

Eggshell flour treatment in concentrated acid and solvents to find out the calcium solubilization enhancement from calcium carbonate molecular through breakdown through estimation of TSS and TDS. Higher TDS value recorder such as 0.182 (mg/l) in the treatment of HCL+ESP with 91% solubility while distilled water lower dissolved solid obtained 0.018 (mg/l) and lower 1.1% solubility. Based on the TDS value more solubility was obtained in the HCL+ESP treated sample followed by Ethanol+ESP 0.037 (mg/l) and Acetone+ESP 0.033 (mg/l), Following closely behind were the Ethanol-ESP and Acetone+ESP treatments with solubility percentages of 18.5% and 16.5% respectively. (Table 2) These findings are succinctly summarized.

Similarly, the eggshell calcium chloride, obtained from a 4% (w/v) HCl solution, demonstrated significant solubility, evident from its impressive yield of 87.38% (w/w). This remarkable solubility highlights the successful extraction of a substantial quantity of calcium chloride from the eggshells during the process, as emphasized (Garnjanagoonchorn and Changpuak 2007). $CaCO_3$ extractable amount of 98.4% was obtained from HCl-treated eggshell flour (Gongruttananun 2011).

Turbidity analysis

Table 3 Turbidity of eggshell flour in solvents and acids

S. No	Sample	Turbidity (NTU) Mean value
1.	Distilled water + ESP	420^{c}
2.	Acetone + ESP	220.33^{b}
3.	Ethanol + ESP	800.0^{e}
4.	H_2SO_4 + ESP	618.13^{d}
5.	HCl + ESP	20.66^{a}

The results detailed in (Table 3) of the study showed significant differences in turbidity values among the different acid and solvent-treated eggshell flour treatments. Specifically, ethanol-treated flour resulted in the highest turbidity at 800.0 NTU. In comparison, lower turbidity levels were observed in the HCL+ESP treated sample at 20.66 NTU, followed by acetone+ESP at (220.33 NTU), and Distilled water + ESP at (420 NTU). Based on the turbidity observed, there are fewer solids due to the lower turbidity and higher TDS in eggshell flour treated with HCL. The HCl treatment resulted in the lowest turbidity percentage but exhibited enhanced solubility due to the increased porosity of the eggshell flour. This implies that despite having lower turbidity, the HCl-treated eggshell flour showed significantly higher solubility compared to other treatments.

Investigating the turbidity of eggshells in HCl acids entails examining how hydrochloric acid affects the transparency of solutions containing eggshell particles. Studies suggest that HCl can dissolve raw eggshells, forming nano-calcium oxide, and getting clear transparency (Habte et al. 2019). The results of the process showed that 47.14% of TDS and 97.17% of turbidity were removed when eggshells were used as a bio coagulant. These results suggest that using eggshells as a biocoagulant can effectively reduce total dissolved solids (TDS) and turbidity in water purification (Rifqyawarman et al. 2024).

Screening of calcium and magnesium in raw eggshell flour and ESP/HCL

Table 4 Screening of calcium and magnesium in raw eggshell flour and eggshell extraction by HCL-treated sample

S. No	Parameters	Before HCL treated (g/100g)	After HCl treated (g/100g)
1.	Calcium	0.32	1.72
2.	Magnesium	0.12	0.16

The comparison between raw eggshell flour with treated HCL+ESP in (Table 4) indicates had a higher calcium content of 1.72g/100g, while raw eggshell flour had a lower calcium content of 0.32g/100g. HCL-ESP had a higher magnesium content of 0.16 mg/kg, while raw eggshell flour exhibited a lower magnesium content of 0.12 mg/kg (Table 4). This indicates a significant difference in calcium and magnesium between raw eggshell flour and HCl acid (W/V) treated flour demonstrating a much higher calcium concentration.

The chemical composition of eggshells was 36.4% calcium and 0.398% magnesium (Walton et al. 1973). Hydrochloric acid (HCl) was used in the investigation to extract calcium chloride from powdered eggshells. Eggshell powder and acid solution were diluted 1:15 (w/v) in a 4% (w/v) HCl solution for this extraction process. Eggshell calcium chloride was extracted with a high yield of 87.38% (w/w) reported (Garnjanagoonchorn and Changpuak 2007). According to Schaafsma et al. (2000), eggshell powder had a higher calcium level (66711.05±111.1 mg/100g) and a decent magnesium concentration (11.50±0.36 mg/100g). It was estimated that 580.61±0.66 mg of calcium per 100 grams of flour were present. We contrasted our results with the findings of a study (Hussein et al. 2013) that found that wheat flour contained 23 mg of calcium per 100 grams. The calcium content of the muffins was shown to be significantly influenced by the amount of eggshell powder used; T2% eggshell powder had the highest level of calcium at 3846.30±0.85 mg/100g, while T0 control had the lowest level at 631.31±0.60 mg/100g. Additionally, brownie items made with hen eggshells can contain extra calcium. The estimated magnesium content per 100g of flour was 5.51±0.37 mg. The expected magnesium content increased with the amount of eggshell used in the muffins; the maximum level was found in T2% eggshell powder (6.11±0.38 mg/100g), while the lowest amount was found in T0 control (3.81±0.38 mg/100g) (Afzal et al. 2020) conducted a study that revealed that fortified shell powder had the highest magnesium concentration in whole-based bread at all three levels. As a substitute and financially feasible supply of calcium and other vital micronutrients for human consumption, outcomes point to eggshell flour being used (Islam et al. 2019).

Screening of metals in eggshell flour and ESP/HCL

Table 5 Screening of metals in eggshell flour and eggshell extraction by HCL-treated sample

S. No	Parameters	Eggshell flour (mg/kg)	Eggshell extraction by HCL treated (mg/kg)
1.	Aluminium (Al)	86.47	51.4
2.	Barium (Ba)	3.89	3.84
3.	Beryllium (Be)	0.923	4.99
4.	Selenium (Se)	0.05	0.21
5.	Vanadium (V)	0.06	0.09
6.	Strontium (St)	118.25	73.26
7.	Tinas (Sn)	33.22	267.98

(Table 5) shows that in the analysis of raw eggshell flour, several elements exhibit notable concentrations. Strontium (St) stands out with a significant value of 118.25 mg/kg, while selenium has a much lower concentration of 0.05 mg/kg, and aluminum is present at 86.47 mg/kg. The range of values found in eggshell flour varies from 0.05 mg/kg to higher concentrations. However, the dynamics change notably when the eggshell is extracted using HCl. Tin (Sn) peaks at 267.98 mg/kg, vanadium shows the lowest value at 0.08 mg/kg, and the average values include 73.26 mg/kg of strontium and 51.4 mg/kg of aluminum. The extraction by HCl treatment of eggshell flour reveals a range of values from 0.21 mg/kg to 267.98 mg/kg.

According to (Shukla et al. 2023), using eggshell powder as a bio-implant necessitates understanding its densification behaviour. While eggshells primarily consist of calcium carbonate (CaCO3), they also contain strontium in the range of 320–411 ppm.

Analysis of micronutrients in eggshell flour and ESP/HCL

Table 6 Analysis of micronutrients in eggshell flour and eggshell extraction by HCL-treated sample

S. No	Parameters	Eggshell flour (mg/kg)	Eggshell extraction by HCL treated (mg/kg)
1.	Copper (Cu)	0.38	1.28
2.	Iron (Fe)	29.19	43.37
3.	Manganese (Mn)	1.92	3.26
4.	Molybdenum (Mo)	BLQ (0.05)	0.07
5.	Nickel (Ni)	0.55	1.08
6.	Zinc (Zn)	0.76	7.20

*-The BLQ is denoted as below the limit of quantification.

Upon analysis of the micronutrient content of eggshell flour and its extraction by HCL-treated samples, different concentrations of copper, iron, manganese, molybdenum, nickel, and zinc were found. In comparison to other nutrients, the eggshell flour had a greater micronutrient component of 29.19 mg/kg of iron and a lesser amount of 0.38 mg/kg of copper (1.92 mg/kg of manganese and 0.76 mg/kg of zinc, respectively). The result falls between 0.05 and 29.19 mg/kg. Conversely, the samples extracted using HCL treatment exhibited elevated iron levels of 43.37 mg/kg. The lowest value of molybdenum was recorded at 0.07 mg/kg. The average values of zinc, manganese, and copper, in that order, were 7.20 mg/kg, 7.20 mg/kg, and 1.08 mg/kg, respectively, following the lead of iron. Between 0.07 mg/kg and 43.37 mg/kg is the range of values. These results imply that the HCL treatment procedure may improve the micronutrients' solubility and availability in eggshells, especially those of iron, manganese, molybdenum, and zinc. To validate the bioavailability and possible health advantages of certain micronutrients in eggshell products, more research is necessary (Table 6).

According to (Hassan 2015), the values of eggshell powder (ESP) for Fe, Zn, Cu, and Mn were 13.06, 145.1, 4.1, and 149.9 mg/100g, consequently. The study highlighted that Brazilian eggs are substantial sources of Selenium, Molybdenum, Zinc, and Iron, emphasizing their nutritional significance according to (De Freitas et al. 2013).

Screening of metals below the limit of quantification in eggshell flour and ESP/HCL

Table 7 Screening of metals in eggshell flour and eggshell extraction by HCL-treated sample

S. No	Parameters	Eggshell flour (mg/kg)	Eggshell extraction by HCL treated (mg/kg)
1.	Antimony (Sb)	BLQ (0.05)	BLQ (0.05)
2.	Beryllium (Be)	BLQ (0.05)	BLQ (0.05)
3.	Cobalt (Co)	BLQ (0.05)	BLQ (0.05)
4.	Silver (Ag)	BLQ (0.05)	BLQ (0.05)

*-The BLQ is denoted as below the limit of quantification.

(Table 7) shows that Molybdenum (Mo) in eggshells treated with HCl reached its highest percentage at 0.07, while the lowest value in raw eggshell flour was 0.05 (BLQ) below the level of quantification. This was followed by Sb, Be, Co, and Ag.

The comparison between conventional and home-produced eggs revealed significant differences in the major elements studied. These variations are likely due to differences in production systems, such as feed composition and environmental conditions. The levels of Cobalt, Copper, Manganese, and Selenium in the eggs were found to align closely with global standards. However, discrepancies were noted, including lower levels of Lead and Cadmium (De Freitas et al. 2013). This study demonstrated how well eggshell flour works as a long-term, reasonably priced adsorption to remove metal ions from a range of wastewater sources (Özcan et al. 2018).

Screening of heavy metals below the limit of quantification in eggshell flour and ESP/HCL

Table 8 Screening of heavy metals in eggshell flour and eggshell extraction by HCL-treated sample

S. No	Parameters	Eggshell flour (mg/kg)	Eggshell extraction by HCL treated (mg/kg)
1.	Cadmium (Cd)	BLQ (0.05)	BLQ (0.05)
2.	Chromium (Cr)	BLQ (0.05)	BLQ (0.05)
3.	Lead (Pb)	BLQ (0.05)	BLQ (0.05)
4	Mercury (Hg)	BLQ (0.05)	BLQ (0.05)

*-The BLQ is denoted as below the limit of quantification.

(Table 8) demonstrates that heavy metals such as cadmium, chromium, lead, and mercury are also below quantifiable levels in both samples of raw eggshell flour and HCL+ESP. It has been confirmed that there are no toxic metals present, and it is also environmentally friendly.

Based on the provided sources, the heavy metal concentration in the samples falls within the Provisional Tolerable Daily Intake (PTDI) and the United States Environmental Protection Agency (USEPA) limits. This indicates that all egg samples studied were considered safe, taking into account the average egg consumption in the country. However, the study suggests that if the average egg consumption increases, there could be a potential risk of higher lead (Pb) consumption through egg intake, as highlighted by (Rokanuzzaman et al. 2022). Various toxic heavy metals such as chromium (Cr), lead (Pb), and arsenic (As) contents remained below the detection level in ESP samples (Islam et al. 2019). (Özcan et al. 2018) suggest that ESP is a cost-effective, high-capacity, and abundant source for removing Cd+2.

Scanning Electron Microscope (SEM) analysis

The SEM analysis at 500x magnification revealed distinct morphological disparities between undissolved and dissolved eggshell flour samples, as depicted in (Figure 1). Sample A, representing undissolved eggshell flour in distilled water, displayed an irregular morphology with non-uniform sizes, indicating insolubility. Notably, porosity was absent across all four samples, including the control, solvent, and acid-treated samples where the eggshell remained intact without dissolution. In contrast, the dissolved sample treated with HCL exhibited a markedly different morphology. It showcased a regular shape with uniform size, indicative of solubility achieved through the dissolution of the eggshell. Importantly, porosity was evident in sample E (HCL+ESP), illustrating the penetration of the acid through pores in the eggshell structure. This observation underscores the significance of the porosity process in enhancing the solubility of eggshell flour in HCL, suggesting a potential avenue for optimizing its dissolution.

An eggshell and orange waste biosorbent film enriched with banana starch was created, and its surface was assessed using field emission scanning electron microscopy (FESEM). The film's surface has a rough, porous structure without cracks, according to the

FESEM analysis, which can improve interactions with target analytes. According to (Vonnie et al. 2023), this suggests that the eggshell and orange waste-based film had an appropriate surface shape for successful interactions with chemicals. The investigation of the facilities of calcium enrichment of bread using eggshell powder can be used to deduce the microscopic observation of the porosity and solubility of the powder. This study examined the solubility of the eggshell powder by combining varying amounts with Lactobacilli-fermented rye sourdough for 12 hours. It was observed that the eggshell powder was well soluble in the fermented leaven samples. Additionally, the study assessed how eggshell powder affected the porosity, moisture content, acidity, true acidity, and bread's specific volume (Bradauskiene et al. 2017).

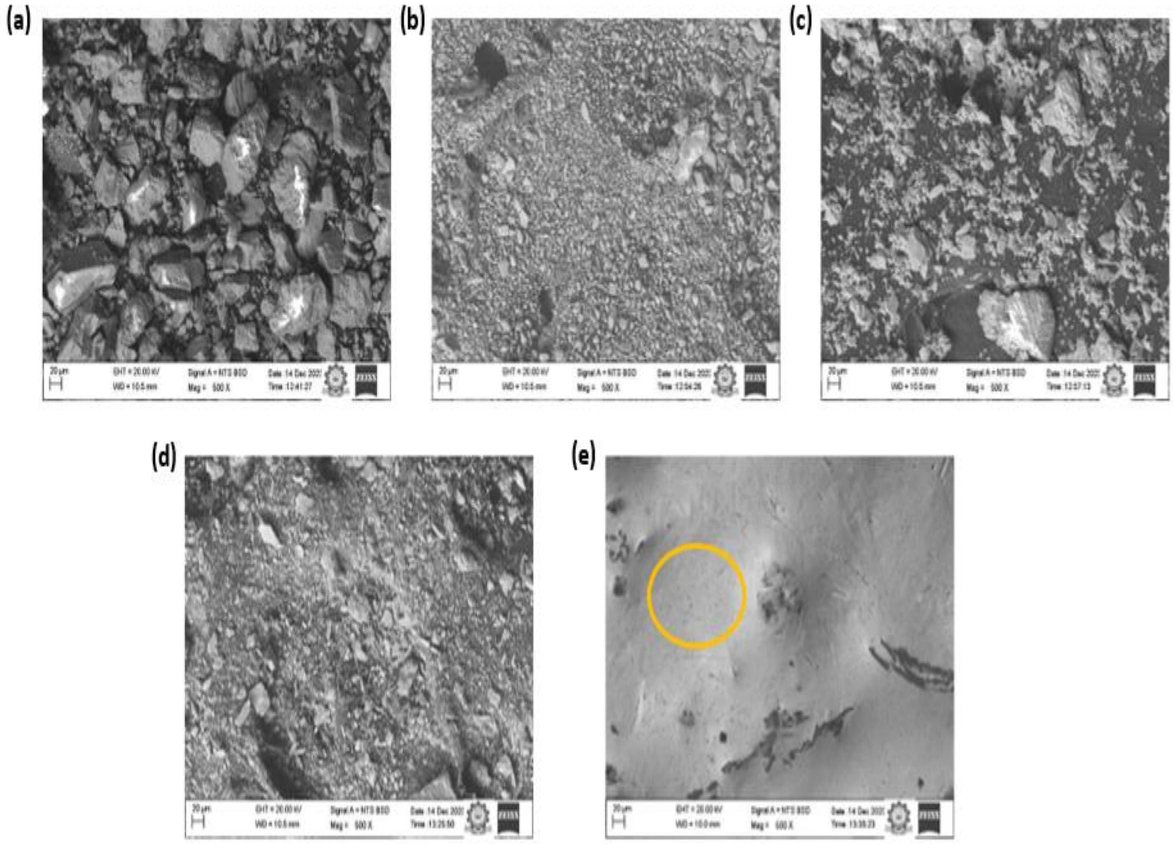

Figure 1 Characterization of scanning electron microscopy of eggshell flour in undissolved TSS sample (A) Distilled water (B) Acetone (C) Ethanol (D) H_2SO_4 and dissolved TDS sample (E) HCL

Energy Dispersive X-ray (EDAX) analysis

The energy-dispersive X-ray (EDAX) analysis of the eggshell flour samples revealed varying elemental compositions (Figure 2). Sample E (HCl+ESP) showed an increase in calcium (Ca) by 28.8%, a decrease in carbon (C) by 4.9%, and a decrease in oxygen (O) by 13.3%. On the other hand, sample D (H_2SO_4+ESP) exhibited an increase in carbon by 18.0% and oxygen by 56.3%, while calcium decreased by 15.5%. This indicates that eggshell flour treated with

HCl, a soluble acid, had a higher calcium content and lower levels of C and O. In contrast, treatment with H_2SO_4+ESP, an insoluble acid, resulted in higher values of C and O and a lower level of Ca.

The fundamental signatures of the substances that are found on the surface can be detected by the EDAX range (Hu et al. 2004). By employing grinding with balls and melting, the synthesis process was able to successfully convert eggshell flours from a micro-scale to a nano-scale. The basic composition of the three elements calcium (Ca), carbon (C), and oxygen (O) varied with the length of time the ball mill was run. Significantly, compared to the sample that underwent sintering and one hour of ball grinding, the combination of sintering and more than five hours of ball milling produced increases in Ca of 9.85% and decreases in C and O of 2.25% and 7.8%. On the other hand, because of oxidation during the sintering process, the non-sintered, 5-hour ball-milled eggshell flour showed the highest amounts of C and O coupled with the lowest Ca level (Puspitasari et al. 2019).

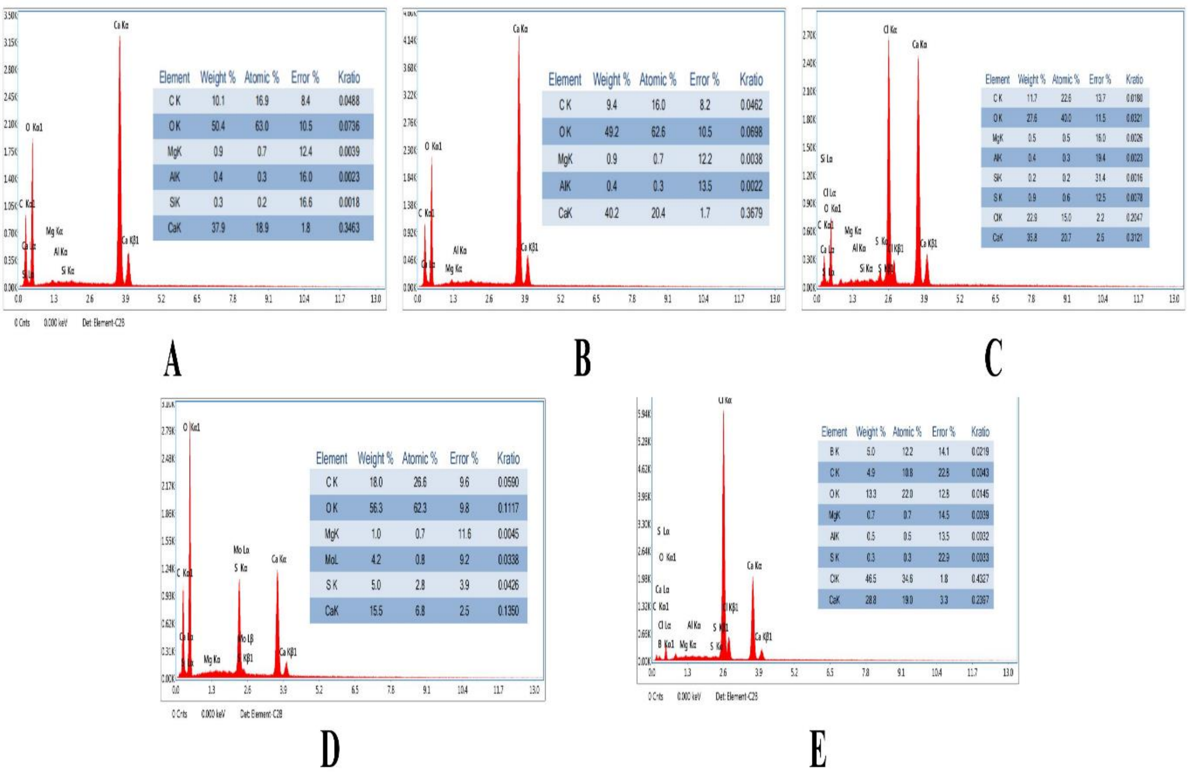

Figure 2 Characterization of EDAX of eggshell flour in undissolved TSS sample (A) Distilled water (B) Acetone (C) Ethanol (D) H_2SO_4 and dissolved TDS sample (E) HCL

Fourier Transform Infrared analysis

The Fourier transform infrared (FTIR) test is pivotal in identifying the functional groups within a compound. This analysis was conducted across wavelengths ranging from 4000 to 500 cm-1. The results obtained from the FTIR tests on various samples, including undissolved TSS samples in eggshell flour (labeled as A) immersed in distilled water (labeled as B), acetone (labeled as C), ethanol (labeled as D), and H_2SO_4, as well as dissolved TDS samples (labeled as E) with HCL in eggshell flour, are depicted in (Figure 3).

(Figure 3) presents the spectral peaks observed in samples A through E, with corresponding wavenumbers: 3415.93 cm^{-1} for A, 2873.94 cm^{-1} for B, 2872.01 cm^{-1} for C, 3550.95 cm^{-1} for D, and 1631.78 cm^{-1} for E. The intensity values of the peaks follow a trend: 40.57 cm^{-1} for A, 93.22 cm^{-1} for B, 63.79 cm^{-1} for C, 15.92 cm^{-1} for D, and 10.00 cm^{-1} for E. This data suggests a notable decrease in both peak intensity and wavenumber in sample E immersed in HCL, indicating a reduction in particle size. This decrease is particularly evident in the intensity values, demonstrating a trend towards lower values as the particle size diminishes. Furthermore, sample E, identified as eggshell flour immersed in HCL, exhibits higher solubility compared to the other samples, indicating a higher degree of porosity. The FT-IR analysis of eggshell flour treated with HCl showed characteristic peaks at 1420, 875, and 712 cm-1, which are indicative of being of calcium carbonate within the calcite formation. This suggests that the calcite in the eggshell flour did not undergo structural changes after treatment with HCl. Additionally, the FT-IR spectra of the treated and untreated eggshells were found to be identical, further confirming the composition of the eggshells as mainly calcium carbonate in the form of calcite. Therefore, based on the FT-IR results, it can be inferred that the solubility of eggshell flour with HCl did not significantly alter the chemical composition or structure of the eggshells Based on morphological findings, it was discovered that the tiny holes generated in the eggshell mechanism are responsible for the increase in the area of the surface (Kiryakova and Kolchakova 2023).

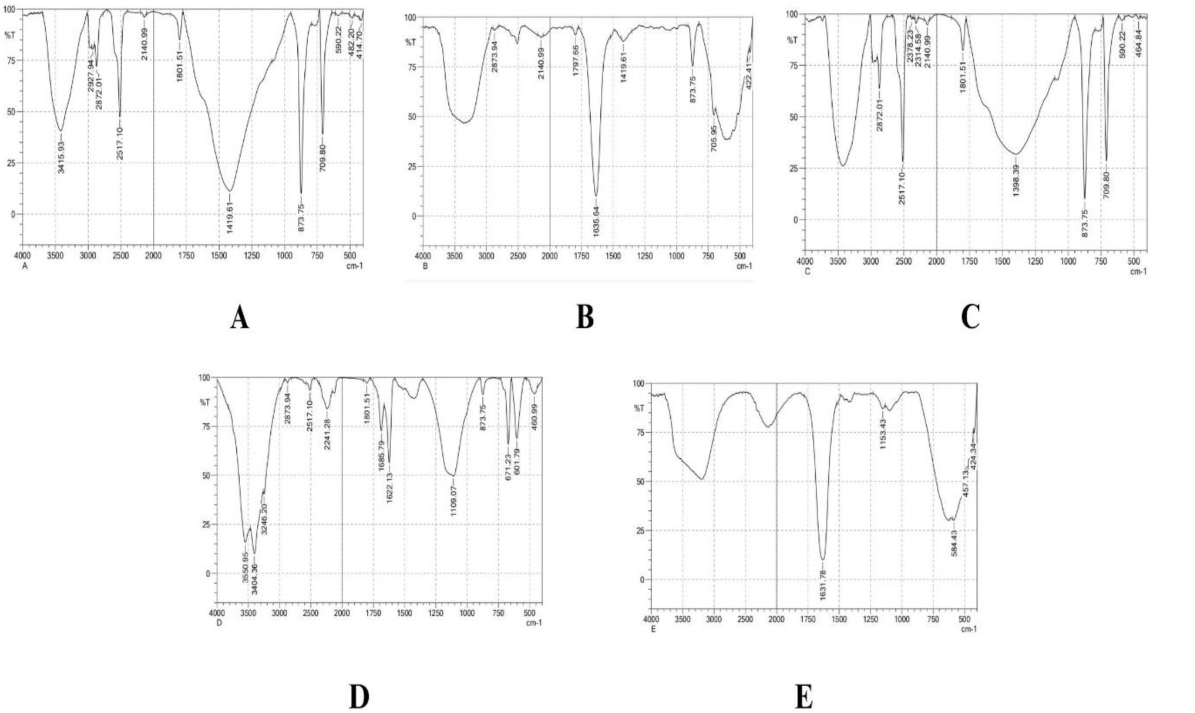

Figure 3 Characterization of FTIR of eggshell flour in undissolved TSS sample (A) Distilled water (B) Acetone (C) Ethanol (D) H_2SO_4 and dissolved TDS sample (E) HCL

CONCLUSION

The solubility percentages in various solvents and acids showed a notable elevation in the physical appearance and chemical qualities of eggshell flour. To conclude, the hydrochloric acid treatment of eggshell flour is highly effective in enhancing the solubility of macro and micronutrients. Through detailed assessments with technologies which are (ICP-MS) and microwave digestion, it was found that this treatment successfully dissolved calcium carbonate and reduced heavy metal content to eco-friendly levels. By converting agricultural waste into a soluble and safe product, this study contributes to eco-friendly and resource-efficient solutions across industries. Overall, the comprehensive study on optimizing the solubility and quality of eggshell flour through hydrochloric acid treatment highlights the potential for innovative approaches to waste management and resource utilization, emphasizing the importance of sustainable practices in modern scientific research and applications. The soluble forms of calcium (Ca) and magnesium (Mg), along with the most cost-effective components, are enhancing elements that could potentially replace the consumption of chemical elements by humans.

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