Recovery of Zn^{2+}, Fe^{2+} and Mn^{2+} from Some Selected Edible Vegetables and Pumpkin using Modified Maize Cobs

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Abstract

This study reports on the pre-concentration of some essential trace elements from vegetables using modified maize cobs by sorption. This was enabled by some functional groups anchored within the chemical structure of the material. Modification was achieved by treating the dry powdered material with thionylchloride ($SOCl_2$) which was dispersed in dimethylformaldehyde (DMF) then reacting with ethylenediamine air drying the resultant for 24 hours. The presence of the anchored group was confirmed by FT-IR and it was used for Batch sorption experiments. The effect of pH, concentration, and dosage on the adsorption of zinc, iron and manganese ion by the parent and modified materials were carried out. Using the optimal parameters, the modified material was used for the pre-concentration of the trace metal ions from solutions of some selected vegetables samples. Pre-concentration of nutrients from fermented samples showed significantly high levels than non-fermented samples. This new method of pre-concentrating metal ions shows promising results and can improve the nutrition value in the preparation of dietary supplements. The method is effective and is of low cost.

Keywords: Pre-concentration; Supplements; Modification; Food stuffs.

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1. Introduction

Essential elements in food stuff are in trace levels and masked by matrices and therefore not easily available for the body uptake. This is because such elements could be held significantly in compound matrix and thus insoluble thus making the supply is of essential element from large quantities of food eaten insufficient [1]. This implies that for them to be of benefit to the body, the matrices holding the elements have to be eliminated. Traditionally, essential but trace elements were obtained by fermentation of starch material to make beverages such as gruel [2]. This simple procedure is aimed at improving accessibility of the nutrients from food materials and their bioavailability [2].

Conventionally, The main techniques used for pre-concentration of trace elements in aqueous media include membrane filtration, co-precipitation, ion exchange, flotation, solvent extraction and electrochemistry depositions [3–5]. The solid phase extraction (SPE) has become the most common technique in trace analysis, mainly because it does not involve the use of hazardous solvents [4]. In SPE an analyte present in aqueous solution is attached to the available sites of the adjacent solid phase [6]. It offers a range of advantages which include: flexibility in selection of solid phase, low costs due to less reagent consumption, lack of emulsion, high pre-concentration factor, sensitivity, use of non-toxic solvents, fast, simple its easy of automatization [4,7,8]. This paper reports on a simple technique applied for the pre-concentration of zinc, iron and manganese at trace levels from food samples to solve the problem of malnutrition and dietary quality.

The technique is a preconcentration tool to enhance nutrition value of the diet. It was achieved by the use of ethylenediamine functionalized powdered maize cobs as a solid phase material. The sorbent material was applied for pre-concentration of iron, manganese, zinc and iodine from solutions of the food material lost.

As a good food safety practice, fresh vegetables from the farm are washed with water just before cooking to remove soils and any other contaminant material before cutting. Then they are cut and washed again with clean water. The resulting water turns green due to leaching of highly soluble compounds such as chlorophyll, metallic micro nutrients and some poly phenols from the leaves. Foods such as fruits and tuber food products are washed and peeled before consumption. The resulting discarded material has its share of nutrients. In that process, some highly valuable and labile nutrients are lost. This is because the washing water is usually discarded. This study explored the possibility of recovering the lost nutrients from the washing process by running that water through the column packed with the prepared modified maize cob material for sorption of dissolved nutrients. The study also explored the avenues of recovering essential minerals from discarded pumpkin material. This was done using the freshly discarded pumpkin pealing seeds and kernels. As the nutritionally valuable and labile compounds within the foods are attracted to the surface of the adsorbent material which latter can be recovered by eluting with vinegar. The study also investigated the amount of nutrients extracted from the food items (vegetables and pumpkin) when they were fermented to compare their respective levels with their fresh forms. This was done when those food items were separately fermented; the resulting solution decanted and then run through column for sorption to extract the dissolved and valuable mineral nutrients. This was intended to recover most of the nutrients from the food materials. The attached metals were also recovered by eluting with vinegar. Using the modified material, all the nutrients from food

materials in the washing and fermentation process were recovered using modified maize cobs material and were available for human consumption in a labile form thus increase the nutritional value of the various foods which could have been otherwise lost.

2. Materials and Methods

The agricultural by products (maize cobs) meant for adsorbent were selected from different farms, packed in sealed polythene bags and transported to the laboratory. The samples were dried, pulverized and activated at 80 °C. The modification process involved weighing a sample (10.0 g each step) which was previously activated at 80 0C for 13 hours. The sample was then placed in a three necked flask containing 250 mL of dimethylformaldehyde (DMF). The mixture was heated to 80 0C then 35.0 mL of thionylchloride (SOCl2) was added dropwise while stirring using magnetic stirrer. The temperature of the mixture was maintained at 80 0C for 3 hours. The mixture was allowed to cool before washing with 25.0 mL of 2.0 M ammonium hydroxide four times until a neutral pH value was attained. Filtration of the mixture was done using glass sintered crucible No. 2 at room temperature[9]. The residue was dried at 80 0C for 12 hours. The resulting sample (12.0 g) was refluxed in 30.0 mL of ethylene-1, 2-diamine while stirring for 4 hours. On filtration the solid was dried at room temperature for 24 hours and kept under are tight plastic bags for use in adsorption and pre-concentration experiments. FT-IR spectroscopy was performed using a Perkin Elmer 100 on the ATR mode.

All green vegetables and pumpkins were sourced from a Nakumatt super market outlet at Ruaraka in Nairobi. They were transported to the labs and stored in a cold facility. The fresh vegetables were washed with water and left to dry. The resulting washing water was collected in 500 ml polythene bottles for column the extraction of valuable leached minerals. A sample (25.0 g) of the clean air dried fresh green vegetables and then placed in a food blender containing 200.0 mL of distilled water. The material was minced for 10 minutes to obtain a fine homogeneous mixture. All the contents of the blender ware filtered into a 250.0 mL Erlenmeyer flask. Each of the filtrates then diluted to one litre. The resulting mixture was divided into two. One portion was used for the fermentation process and the other portion was filtered and the resulting solution was run through the sorption column for the sorption process. To the fermented portion the resulting solution was decanted after four days, filtered and the filtrate ran through the sorption column. A similar process was performed on the pumpkin product. The attached nutrients were stripped with a solution of vinegar[10]. A similar process was carried out done using the freshly discarded pumpkin pealing seeds and kernels, with (25.0 g) of each material. The adsorbed metal ions were striped using dilute acetic acid. The extraction of metal ions from selected vegetable leaves was also done by weighing 10.0 g of fresh vegetables into a food blender. About 60 mL of 2 % acetic acid was added into the blender and run for 10 minutes. The mixture was then filtered into a 100.0 mL Erlenmeyer flask. The volume of the filtrate was adjusted to the mark using a 100.0 mL volumetric flask and the volume. This resulting solution was used in adsorption experiments. A 0.1 mg/L standard solutions of Zn^{2+}, Fe^{2+}, Mn^{2+} and Mn^{5+}were prepared by serial dilution of 1000 mg/L standard solution of each element and adjusting the pH to the optimum value. A 50 mL of vegetable extract was placed in a 100.0 mL beaker and a 50.0 mL of 0.1 mg/L standard solutions of Zn2+, Fe2+ and Mn2 standards were individually spiked into each of the samples. The spiked sample was loaded in the solid phased extraction (SPE) column. The 100 mL of solutions containing the metal ions were run through the column separately at a flow rate of 2.0 mL/min.

Adsorbed analytes were stripped with 50.0 mL of 1 mol/L acetic acid. The eluate was then analyzed for zinc, iron and manganese.

3. Results and Discussion

The modified (synthesized adsorbent) product formed were dark grey in colour. They were FT-IR characterized and then applied for the removal and pre-concentration process. The spectra of the UMC and MMC sorbents were as presented in Figure 1 and Figure 2.
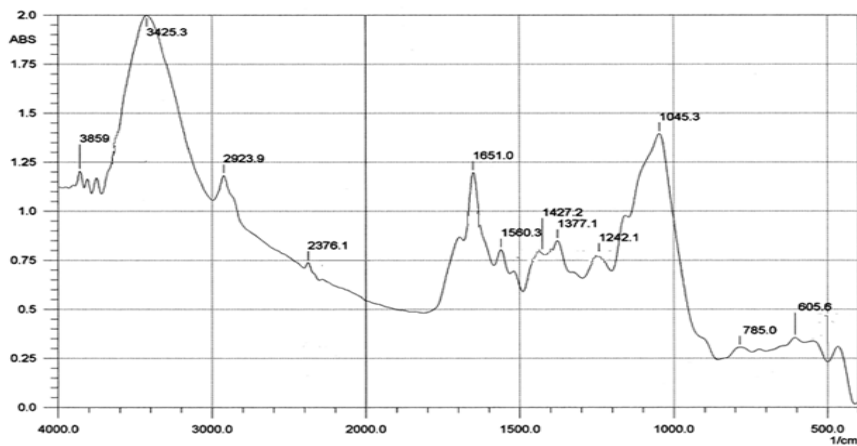

Figure 1: FT-IR spectrum of unmodified maize cobs

The absorption peak at 3425.3 cm-1 can be assigned O-H stretching with H-bonded or NH stretching [11], [12]. The band at 2923.9 cm-1 was assigned to C-H stretching due to sp3 hybridization [13].
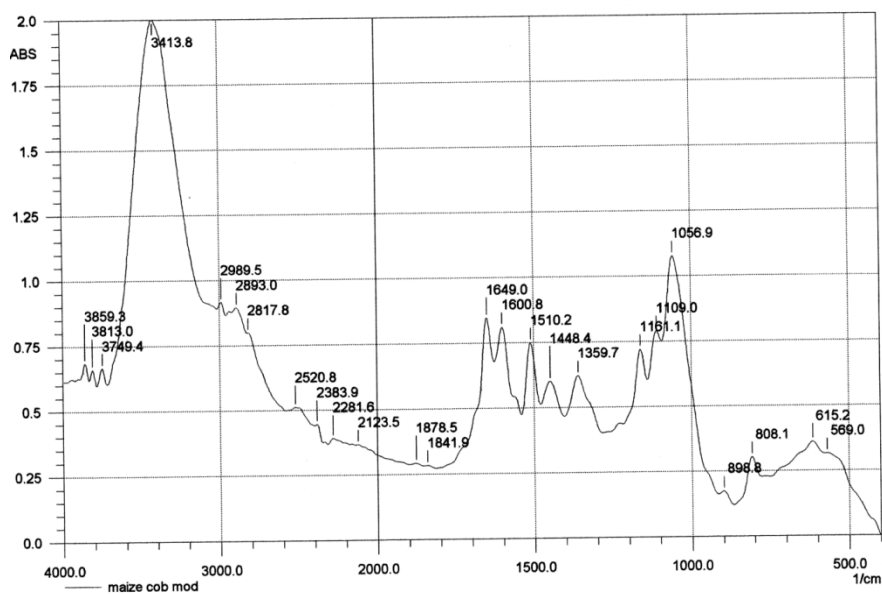

Figure 2: FT-IR spectrum of modified maize cobs

The band at 3413.8 cm-1 is sharp and of high intensity. This may be attributed by the modification process [11],

[12]. The peak at 2893 cm-1 was assigned to C-H stretching due to sp3 hybridization after shifting due to the presence of the large ethylenediamine group [13]. The characteristic bands located between 1510.3 and 1649.0 cm-1 could be as a result of an amide group within the structure [14]. The broad band at 1056.9 cm-1 in the modified was a shift from 1045.3 cm-1 and was assigned C-O-C stretching which is characteristic of cellulose structure [15]. The band at 1161.1 cm-1 in the modified material is characteristics of the C-NH group [16]. The peaks at 1649 and 1600 cm-1 are typical of N-H stretching of NH2 or NH [17,18]. The weak peak at 1427.2 cm-1 may be due to C-H. Modification shifted the band from 2923.9 to lower frequency of 2893 cm-1. This confirms that the ethylenediamine group was chemically anchored within the structure of the maize cobs material. Sorption process is pH dependant since the charge on the sorbent and the sorbate are both affected by the hydrogen ion concentration in the dispersing media [19]. The influence of pH in this study was monitored with the pH ranges of 3.0 - 6.9 for zinc, 2.0 - 6.0 for iron and 3.0 - 7.0 for manganese. Constant ionic concentration of 40.0 mg L-1 was used with adsorbent dose of 1.2 g L-1 for zinc and 1.0 g L-1 for Iron and Manganese respectively with contact time of 30 minutes. Figure 3 (A, B and C) shows the effects of pH on sorption of zinc, iron and manganese on unmodified and modified materials.
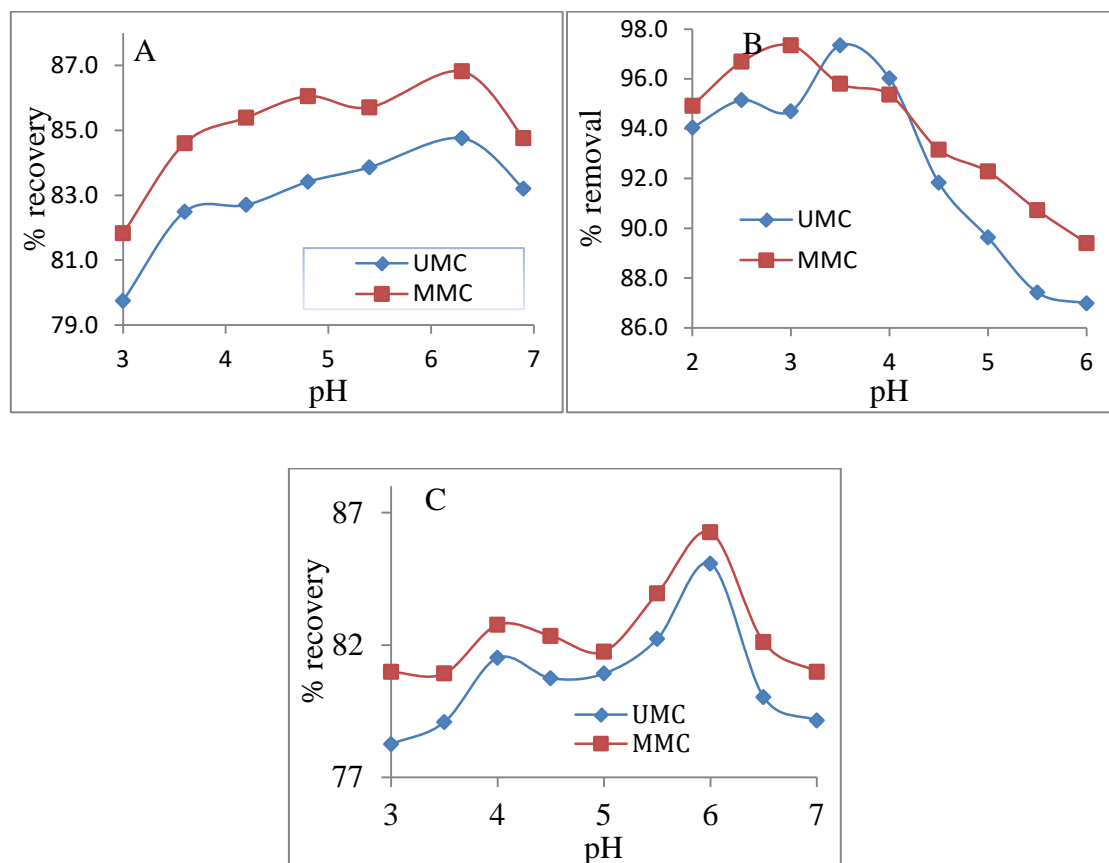

Figure 3: Effect of pH value on the sorption of (A) Zinc, (B) Iron and (C) Manganese

As illustrated in Figure 3A the optimum sorption of Zn^{2+} was attained at pH 6.3 for both UMC and MMC bio sorbents. A maximum of 86% of the metal ions are removed at pH 6.3 with the percentage removal being lower before and after this value. The adsorption then gradually decreases up to pH 7.0. These results agrees well with the literature values which indicates that the maximum sorption of zinc ions lies in the pH value range of 5.0 to

7.0 [20,21]. At pH values of 5.0 to 7.0, the divalent ionic form of the metal ion is predominant with smaller amounts available in form of $ZnOH^+$ at pH> 6.0. Sorption process is therefore favoured because of the negatively charged surface. At low pH values, H+ and Zn2+ ion compete for adsorption sites. There is a high concentration of H+ ions at low pH leading to low sorption of Zn^{2+}. At higher pH value, this effect is limited by the hydroxyl ions however, metal ions are precipitated in the form of $Zn(OH)_2$ [22]. Figure 3B shows the metal adsorbed by maize materials was at maximum (about 97.4 %) removal of Fe^{2+} at pH 4. At pH < 4, a low percent removal noted. This could be attributed to the point of zero charges for maize cobs which lie at around pH 3.0. Below that point of zero charge, the hydroxonium ions, H3O+compete with the Fe^{2+} cations, hence decrease in the percentage removal. Above that pH, the adsorbent surface is negatively charged, enhancing attraction of the metal cations [23,24].

In Figure 3C, the adsorption maxima for manganese ions were pH 4.0 and pH 6.0. This observation agrees well with the nature of manganese that has oxidation states of +2 and +5. There was a low sorption rate at lower pH as a result of the highly positive charge density at the surface of the adsorbent. This behaviour contributes to electrostatic repulsion of the metal ion leading to a lower rate of adsorption [25]. Electrostatic repulsions decrease as pH increases as a result of the reduction of positive charge density on the sorption sites of adsorbent. Therefore the rate of adsorption increases. However, the high pH values decreases the ionization state of the functional groups and solubility of metals[26,27]. In Figures 3 A, B and C, at low pH values, the adsorbate removal is low due to the competition between the H+ and Mn+ and a higher adsorption when the pH of the media is made moderately basic when the functional groups responsible for metal attachment are not protonated enhancing metal sorbent stability with little or no precipitation [28,29]. The effect of initial Zn^{2+}, Fe^{2+}, Mn^{2+} and Mn^{5+} concentration on its removal was carried out at their respective optimal pH values at a concentration from 10.0 to 200.0 mg L-1.

The results show that, with increased initial Zn^{2+} ions concentration (10.0 to 250.0 mg L-1), the percentage removal decreased for MMC and UMC decreased from 99.0 % to 55.8 % and 88.7 % to 61.8 % respectively at equilibrium. The amount of Zn^{2+} attached increased as the initial zinc ions concentrations increases. The average sorption capacities increased from 3.55 to 55.24 mg g-1 for UMC and from 3.96 to 60.98 mg g-1 for MMC for tests performed having different adsorbent doses. This was due to the effective pores diffusivity which increases with increasing initial metal ions concentration[30,31]. There is a greater diving force resulting in a more efficient utilization of the absorptive capacities[2,32].

Figure 4 B shows a reduced removal as the concentration of the dissolved ions increases. The metal ion uptake were found to be 89.2 %, 81.6 %, 50.2 %, 40.9 %, 31.4 % and 24.9 % for initial metal concentrations of 10, 50, 100, 150, 200 and 200 mg/L, respectively for MMC and 86.7 %, 78.2 %, 48.3 %, 39.4 %, 29.2 % and 22.9 % for initial metal concentrations of 10, 50, 100, 150, 200 and 200 mg/L, respectively for UMC as a result of saturation of the active sites of the adsorbent [33].
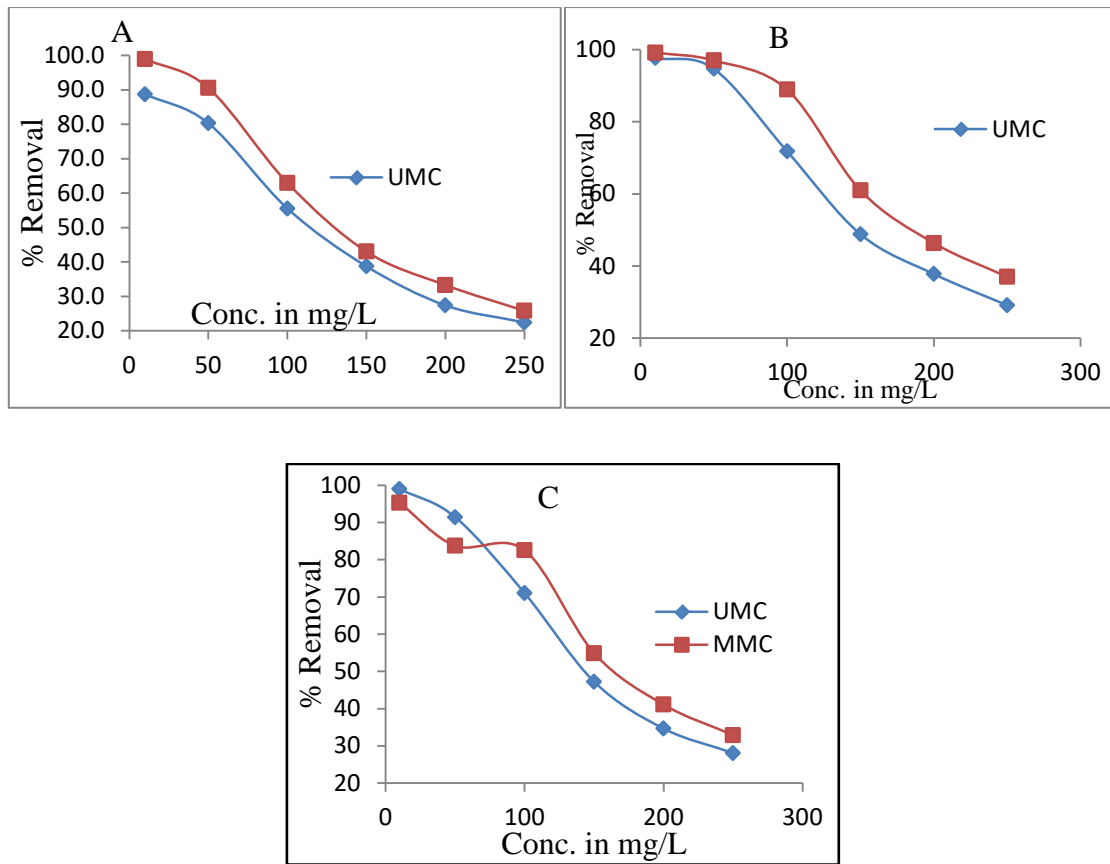
Figure 4: The effect of the initial concentration of ions on the sorption of (A) Zinc, (B) Iron and (C) Manganese.

In batch sorption processes, the removal of ions in solution can be related to the initial metal ions concentration (figure 8). Experiments were carried out at pH 6, adsorbent of 0.03 g 100 ml-1 for 120 minutes. It is evident that the percent removal decreased as the initial concentration of metal ions in solution increases. This can be attributed to the limited number of available active sites [34]. Despite the fact that percentage removal of metal ion reduces the equilibrium sorption capacity of the adsorbent, it increases with increasing metal ions concentration (4.7 to 95.12 mg/g for MMC). The initial analyte concentration provides an essential driving force in overcoming resistance between the sorbate and adsorbent A higher initial concentration of metal ion increases the sorption capacity [35].

Time is an important parameter regarding sorbent/adsorbent interaction. Sorption of zinc increases with time as shown in Figure 5A. However, above 90 minutes, there was no further increase in adsorption. The best sorption rate found at 60 minutes may be a result of the availability of a high number of vacant sites. With the increase in time, an equilibrium is established lowering the sorption process due to the unavailability of vacant sites [35].

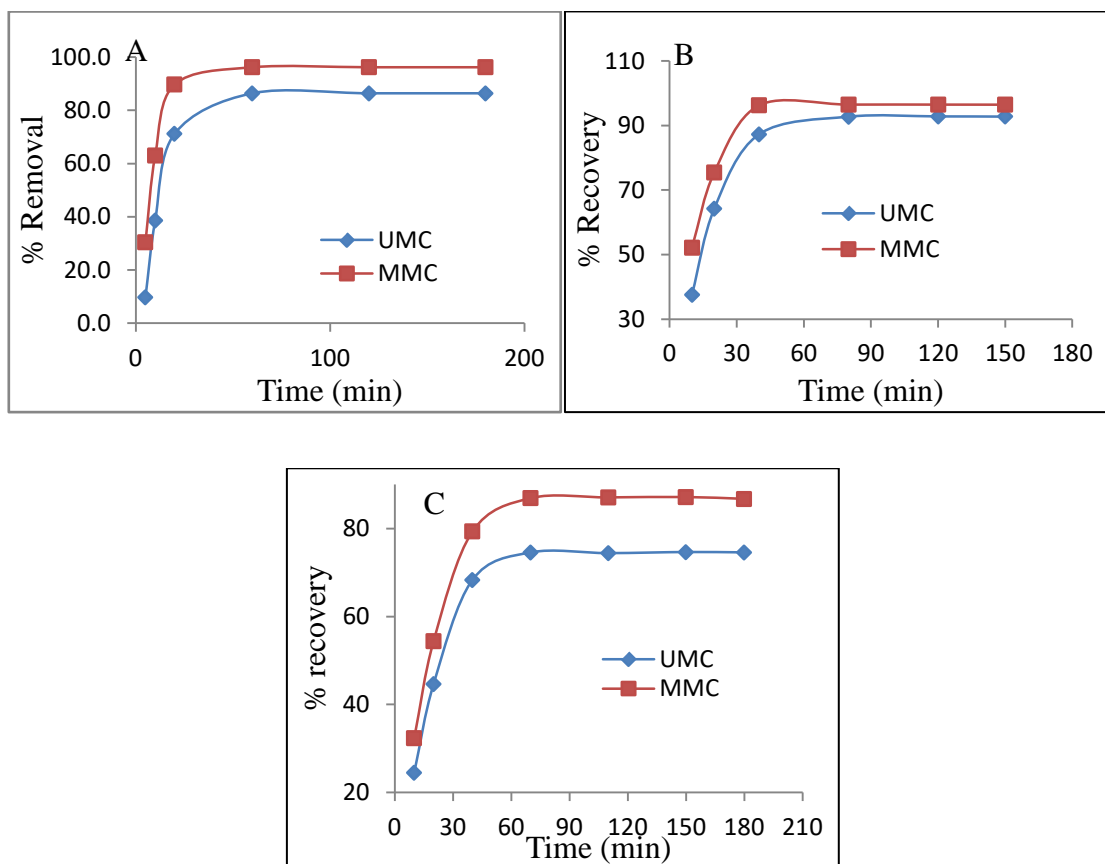Figures 5 (A, B and C) shows the effect of contact time on sorption onto UMC and MMC respectively.

Figure 5: The effect of contact time on the sorption of (A) Zinc, (B) Iron and (C) Manganese

Time as a parameter in the removal of Fe^{2+} was investigated with the initial concentrations of Fe^{2+} of 40 mg/L, 0.3 g L-1 of UMC and MMC. The results are presented in Figure 5. The equilibrium adsorption of iron onto UMC and MMC was completed within 90 minutes. The time required for the metal ions to reach the equilibrium was relatively short which demonstrates an economical viability for practical applications.

The equilibration time for maximum uptake of manganese by UMC and MMC were investigated as time for agitation ranging from 30 min to 180 min. The initial concentration was fixed at 40.0 mg L-1, bio sorbent concentration of 0.3 g L-1 and time being 120 min. The profile at different time intervals as presented in figure 5C show that the adsorption of manganese increased from time 30 to 90 minutes (from 33 % to 87.2 % for MMC and from 24.7 % to 74.7 % for UMC) and then plateaus. There was a high rate of manganese binding at the initial stages then decreases gradually. Thus 90 minutes was enough to remove almost all manganese ions by the bio material. The percentage removal of metal ions is higher at the initial stages due to high rate of collision and large number of available vacant active sites [23].

The effect dosage on zinc sorption was investigated by varying the masses of MMC and MMC from 0.01 g to 0.10 g in 50.0 mL of 40.0 mgL-1 solution at pH 6.3 for zinc ions, pH 4.0 for iron ions and pH 6.0 for manganese ions. The results for the effect of dosage on the sorption of zinc, iron and manganese ions are presented in
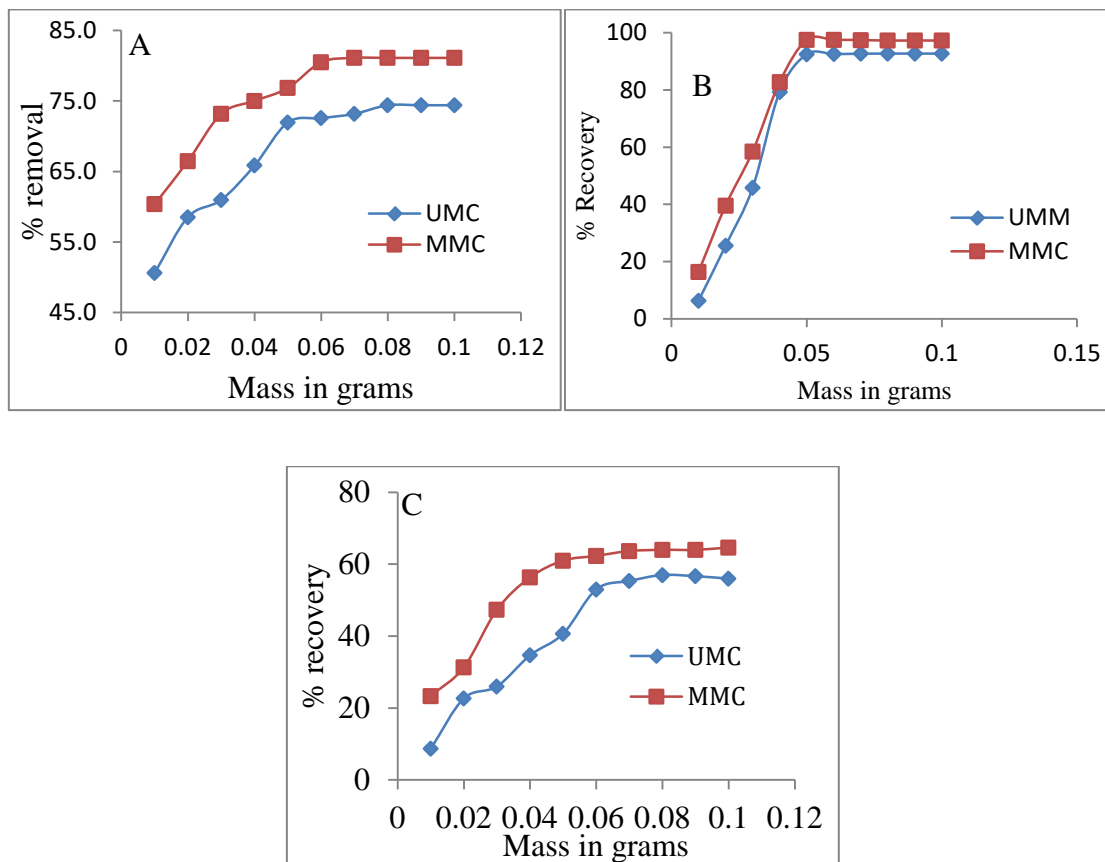
figures 6(A, B and C) respectively.

Figure 6: The effect amount of sorbent on the adsorption of (A) Zinc, (B) Iron and (C) Manganese

Figures 6 (A, B and B) shows an increase in percentage metal removal even after an increase of the dosage from 0.01 g to 0.06 g. A maximum removal of 80.5 % and 72.0 % for zinc, 77.9 % and 65.7 % for iron, and 63.0 % and 56.0 % for manganese respectively for modified and unmodified adsorbent with dosage of 1.2 g L-1 for zinc, 0.8 g L-1 for iron and 1.2 g L-1 for manganese (figure 12,13 and 14). This can be attributed to an increased binding sites available for sorption [36,37]. An increase in the amount of adsorbent after this stage, made no significant difference in the percentage removal of metal ions from the aqueous solution. The adsorbent recorded a maximum sorption capacity of 101.22 and 120.73 mg/g for Zn, 48.5 and 79.13 mg/g for Fe and 18.0 and 44 mg/g for Mn for UMC and MMC respectively. These results shows diminishing adsorption capacity as the sorbent dosages increases [38]. Similar behaviour was reported by [39–41] on the effect of sorbent dose on sorption of manganese ion on raw and oxalic acid modified maize husk. This can be explained by considering the number of binding sites available for metal ion sorption. At a dosage of 1.2 gL-1, an equilibrium between the metal ions in the adsorbent surface was attained [42,43]. At high sorbent dosage, agglomeration of particles occurs causing a more reduction in inter-particle distance. As a result of overcapacity of adsorbent particle occurs at a dose of 1.3 g/l leading to the reduction of sorption capacity. Particles agglomerate at high sorbent dosage resulting in reduced inter-particle distance, contributing to repulsive effects and obstructing binding sites from metals [44].

It was found that modified bio-material removed nearly 100% of metal ions from the solutions implying that those essential metal cations present in aqueous solution can attach to it surface. The sorption capacities of the materials were done using a fixed bed Perspex glass column of 30 cm long with 2.5 cm internal diameter. They were packed at a bed height of 5.0 cm, 10.0 cm and 15.0 cm by allowing the adsorbate solution to flow continuously. The material had a particles size range of 0.400 mm to 0.600 mm and a sample solution, 100.0 mL of the food extracts was loaded into the column to flow by gravity. The adsorbed metal ions were stripped using 2% acetic acid then analysed for using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Figures 7 (A, B and C) shows the effect of pH on the removal zinc in aqueous solutions treated in four different ways;

Distilled water extracted and not preconcentrated (WENP). Distilled water extracted and preconcentrated (WEP). Distilled water extracted, fermented and Preconcentrated (WEFP). 2% acetic acid extracted and preconcentrated (2% AAE)
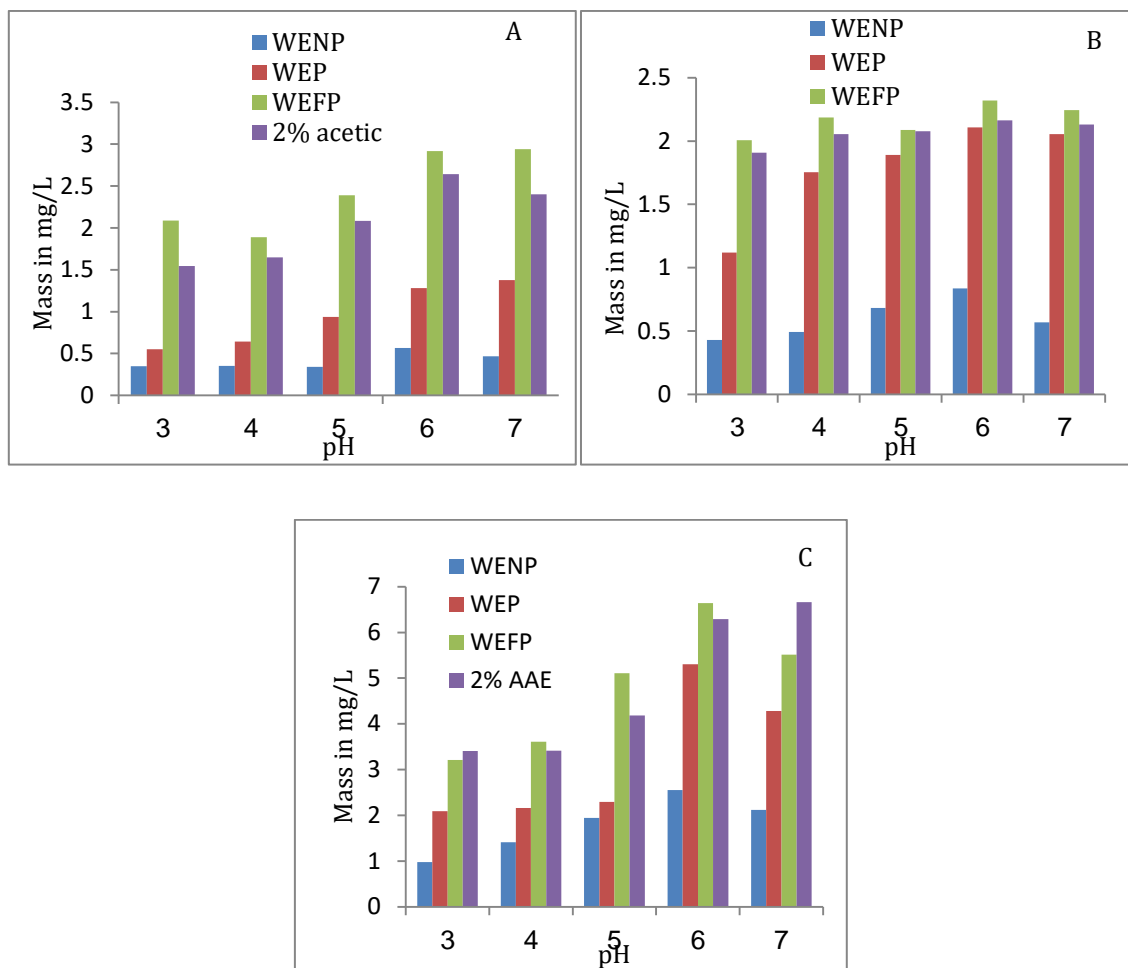

Figure 1: Mass of zinc obtained from aqueous solutions of spinach (A), black nightshade (B) and pumpkin flesh (C) using modified maize cobs adsorbent form solutions extracted as WENP, WEP, WEFP and 2 % AAE while varying pH from 3.0 to 7.0.

The highest amount of zinc was obtained between pH 6.0 and 7.0 with the lowest being around pH 3.0. The

amount obtained was in the range 0.98 to 3.45 mg/L, 1.41 to 3.61 mg/L, 1.95 to 5.12 mg/L, 2.55 to 6.64 mg/L and 2,12 to 6.66 mg/L at pH 3.0, 4.0, 5.0, 6.0 and 7.0 respectively. The method of extraction also has significant effect on the amount of zinc obtained. Vegetable extracts which were left to ferment prior to extraction shows significantly high levels of zinc than those not fermented.

Figures 8 (A, B and C) shows the effect of pH on removal of zinc in aqueous solutions of WEN, WEP, WEFP and 2 % AAE.
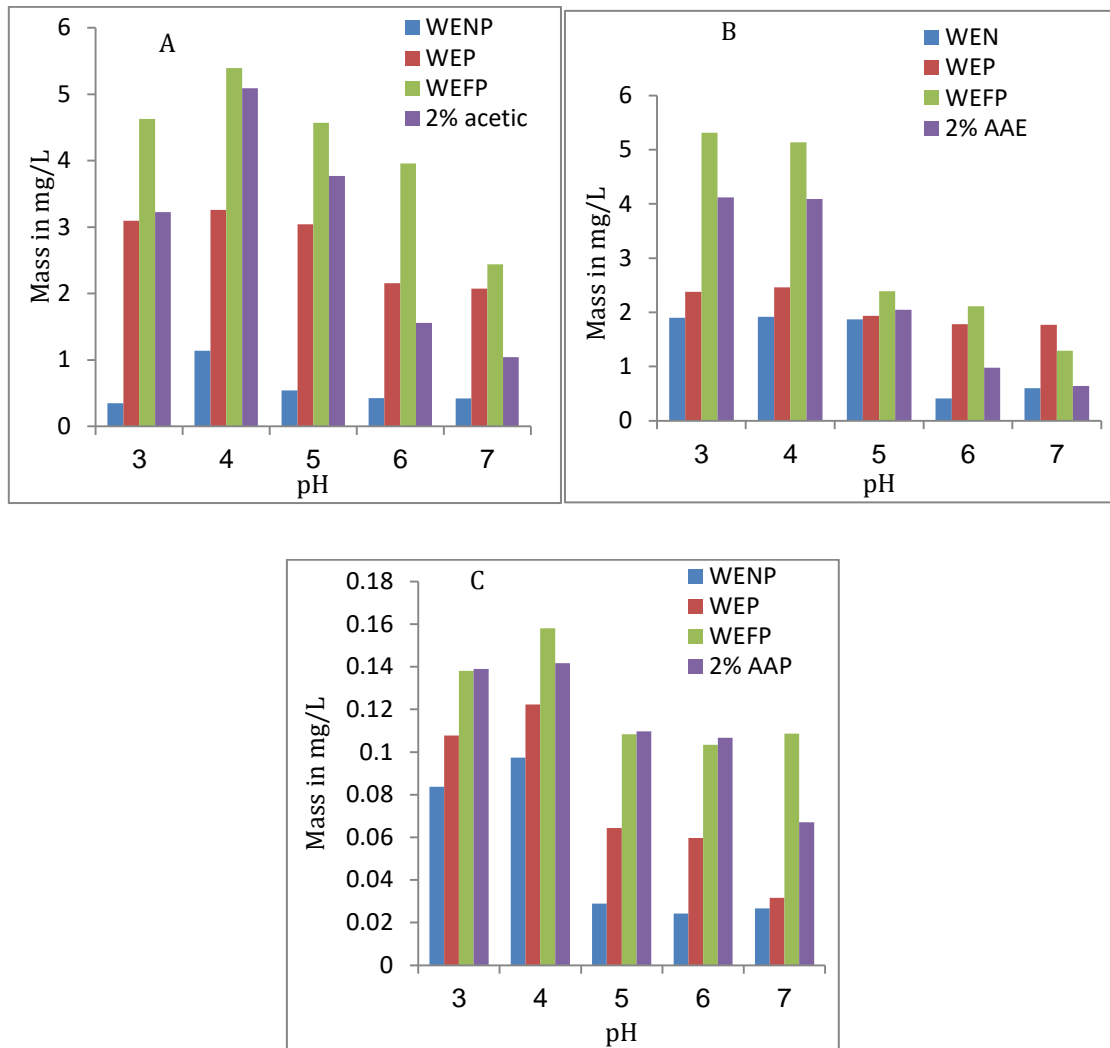

Figure 8: Mass of iron obtained from aqueous solutions of spinach (A), black nightshade (B) and pumpkin flesh (C) using modified maize cobs adsorbent form solutions extracted as WENP, WEP, WEFP and 2 % AAE while varying pH from 3.0 to 7.0.

The result shows that optimum removal of iron took place between pH 3.0 and pH 5.0. Figure 8 A shows the highest amount of iron of 5.39 mg/L was obtained in WEFP at pH 4.0 with the lowest being 0.34 mg/L while using WENP at pH 3.0. Preconcentration was shown to significantly increase the amount of iron in solution. The 2 % AAE method is also a good method of extracting metal ions into solution.

Figures 9 (A, B and C) shows the effect of pH on removal of zinc in aqueous solutions of WEN, WEP, WEFP and 2 % AAE.
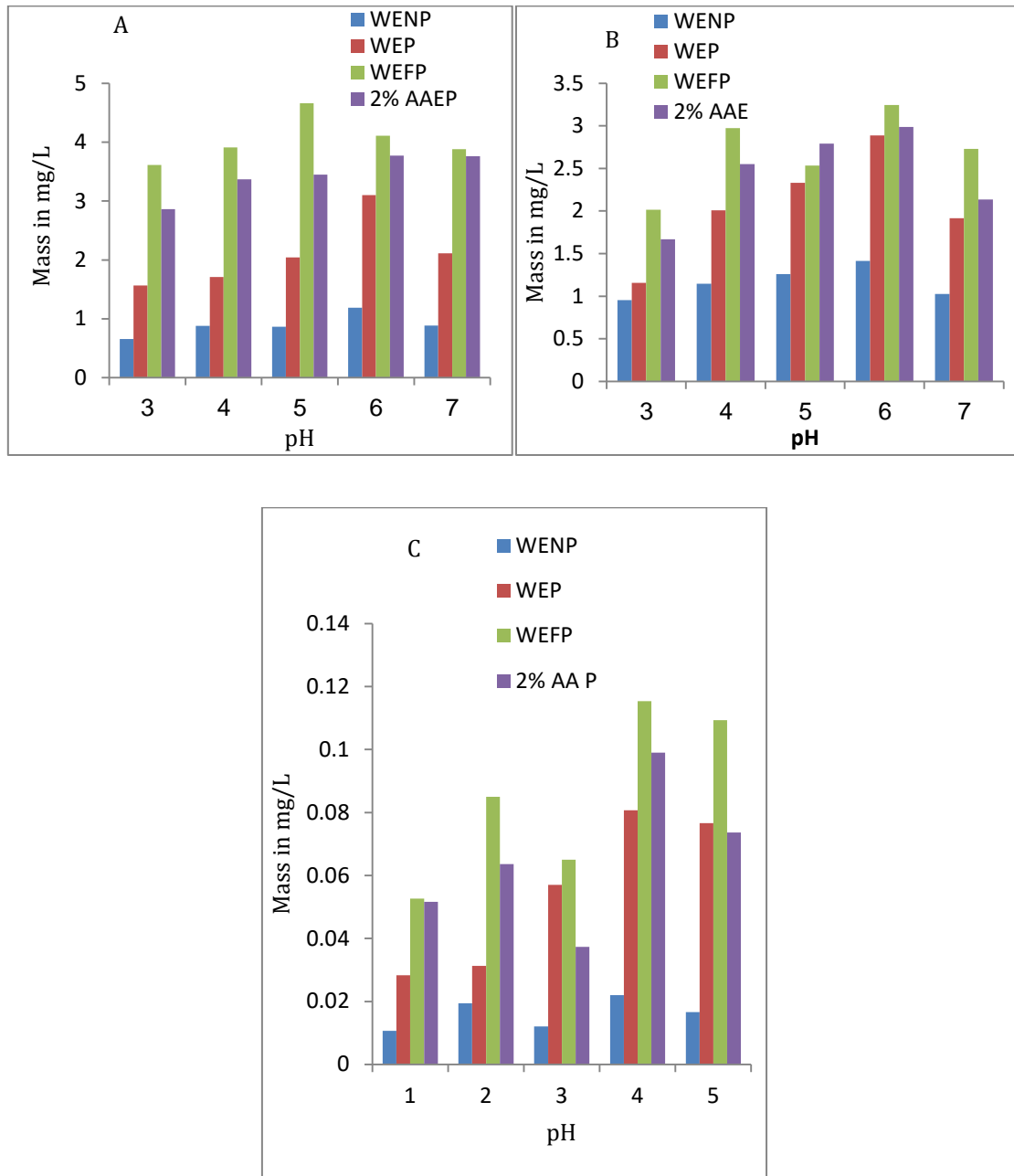

Figure 9: Mass of manganese obtained from aqueous solutions of spinach (A), black nightshade (B) and pumpkin flesh (C) using modified maize cobs adsorbent form solutions extracted as WENP, WEP, WEFP and 2 % AAE while varying pH from 3.0 to 7.0.

The results in figure 9 shows that preconcentrated samples spinach was high in manganese (highest at 4.66 mg/l) compared to those found in preconcentrated samples of pumpkin flesh (highest at 0.12 mg/L). In spinach extract, WEFP samples had higher concentration of manganese than WENP samples. Similar results were obtained in black nightshade and pumpkin flesh. This indicates that fermentation increases the levels of ions in solution. The acid extracted and preconcentrated samples had the second highest values to those of WEFP. The water extracted samples which was left to ferment gave better results than the acid extracted samples than acid extracted and fresh water extracted having the least amounts. It was established that fermentation enhances the extraction and release of metal ions into the solution. Fermentation makes the metal ions labile and available.

4. Conclusions

The study successfully modified an excellent sorbent material for pre-concentration of essential nutrients from aqueous media. It was characterized and confirmed by FTIR that the functional groups capable for adsorption were chemically anchored within the structure of the modified maize cobs. The material was the applied for sorption experiments where optimal parameters were established. The percentage removal of Zinc, Iron and Manganese ions using the unmodified maize adsorbent were 73%, 75% and 64% respectively while the modified maize material adsorbent gave 80% for Zinc and iron, and 72% for manganese in that order. Modified maize adsorbent gave significantly higher values than those of unmodified maize material adsorbent. Using 30.0 grams of black nightshade leaves and modified maize materials as adsorbent, 2.16 mg of Zinc, 3.25 mg of iron and 2.70 mg of iron were obtained. Weighing 30 g of spinach leaves and using in the pre-concentration experiment, zinc, iron and manganese 0.48 mg, 0.12 mg and 0.09 mg were obtained. Preconcentration of essential nutrients using modified maize materials as an adsorbent and aqueous solution of pumpkin, 4.8 mg of Zinc, 0.12 mg of iron and 0.8 mg of manganese were obtained. Sorption kinetics confirmed that sorption was sorbent could remove up to 95% of the nutrients in less than 15 min. Essential elements were successfully pre-concentrated in their fresh and fermented forms of aqueous solutions of black nightshade, spinach and pumpkin flesh. The extracts from the fermentation product gave higher levels of nutrients as compared to the fresh samples. Extracts from the washing water after cutting the vegetables also confirmed that some essential nutrients leached to the waste during the process. Results from this study show that there is a possibility of recovery of such micro nutrients and thus potential in the improvement of micro nutrients from locally available vegetables by pre-concentration and eventually extracting them with vinegar. Pre-concentration studies of some metal ions from selected foods shows promising results. It was established that modification of maize cobs yields low cost adsorbent that is good for adsorption of Zn^{2+}, Fe^{2+}, Mn^{2+} and Mn^{5+}. The material is therefore suitable for application at a point of use and will solve the problems associated with of malnutrition and improve the quality of life.

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