

Pre-concentration of I⁻ present in aqueous solutions of *Solanumnigrum*, *Amaranthaceae* and *Cucurbitacucurbitacea* using chemically modified millet tassels, beans husks and maize cobs

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Abstract: Iodine in *Solanumnigrum*, *Amaranthaceae* and *Cucurbitacucurbitacea* was pre-concentrated using new adsorbent of a powdered mixture of millet tassels (MT), maize cobs (MC) and beans husks (BH). Prior to its use, powdered MT, MC and BH were separately treated with thionylchloride (SOCl₂) in dimethylformaldehyde (DMF), filtered then dried. The resulting solid was refluxed in ethylenediamine for 4 hours. The surface characteristics of the adsorbents were determined using fourier transform infrared. Batch sorption experiments were carried out to determine the optimum conditions of pH, concentration, dosage and time for the adsorption of iodine. Correlation coefficient obtains by modelling data to Langmuir and Freundlich isotherms were compared to determine the best model for adsorption. Sorption kinetics was studied using pseudo first order and pseudo second order.

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I. Introduction

Iodine is one of the most important trace essential elements in human nutrition. It plays an important role in proper functioning of thyroid gland. Its deficiency leads a common disorder of the thyroid gland a condition called goiter and hypothyroidism[1]. Insufficient or excessive exposure to iodine by pregnant mothers has been associated with congenital hypothyroidism, a condition which is manifested by severe mental dysfunction and a depressed intelligent quotient (IQ)[2]. In many developing countries, there is high prevalence of goiter and other iodine related disorders where there is poor fortification of table salts. Iodine supplementation is also necessary for vulnerable groups like pregnant women and young children. Excessive iodine intake can lead to autoimmune diseases of the thyroid gland, a condition in which the body starts to produce antibodies that destroy the thyroid gland, and hyperthyroidism. Breast milk is the only source of iodine for infants [3]. One unique characteristic of iodine is that it gets concentrated in the mammary glands. Iodine is naturally contained in milk powder, egg, fish, pig kidney and hay powder. However, poverty and poor nutrition may lead to low intake of foods rich in iodine by the mother. This can lead to iodine deficiency disorders (IDD). The IDD has been reported in all stages of humans as a characteristic of a variety of conditions. The world health organization (WHO) recommends a daily intake of 90 µg of iodine for children at the age of (0 to 59 months), 120 µg for the age range 6 to 12 years, between 150 µg and 200 µg for adolescents and adults and accepted maximum value is 500µg per day . A lot of work has been done on the fortification of iodine in table salts, however, no work has been reported on pre-concentration of iodine present in food stuffs as a solution to iodine deficiency. Determination of iodine value in different types of foods stuffs and biological matrices have been widely reported. Some of the techniques available for iodine analysis include; spectrophotometric[4], reversed-phase ion-pair liquid chromatography[5], ion-selective electrode and inductively coupled plasma mass spectrometry (ICP-MS) [6], [7]. The determination of the amount of iodine in pre-concentrated aqueous solutions of *Solanumnigrum*, *Amaranthaceae* and *Cucurbitacucurbitacea* was done using ICP-MS.

II. Material And Methods

a. Apparatus

An ICP optical emission spectrometer (spectro analytical instruments, Germany) mounded with axial plasma viewing was used. Wavelength corrections were performed manually at appropriate background positions for each analyte peak.

Table 1: IPC-OES operating Conditions

Generator	27.12 MHz
Power	1400W
Spray chamber	Double pass
Outer gas	15 L min ⁻¹
Intermediate gas	1.0 L min ⁻¹
Nebulizer gas	1.0 L min ⁻¹
Sample uptake rate	1.8 mL min ⁻¹
Analytical wavelength	183.04 nm

Digestion of the samples was done in a closed vessel in a microwave oven equipped with a rotor capable of holding ten samples at a go. The heating was programmed as indicated in table 2. A refluxing condenser mounted at the top of sample holder prevents the loss of volatile compounds.

Table 2: Microwave program for food extracts in a close vessel

Step	Power (W)	Time (min)
1	250	2
2	300	2
3	400	5
4	500	5
5	600	5

b. Reagents

All chemicals and reagents used were high grade analytical reagents and their respective solutions were made from double distilled water. Potassium iodide (99 %), silver nitrate, nitric acid (64.5 %), hydrogen peroxide (30 %) and ammonia (25 % m/m) were purchased from Kobian (K) limited which is subsidiary of Sigma Aldrich. All glass apparatus used were soaked in aqua regia reagent for 12 hour, cleaned using a detergent, rinsed thoroughly with distilled water. All stock solution were stored in a refrigerator and away from sunlight.

c. Sample preparation

Aliquots of 2.50 cm³ vegetable extract were weight into PTFE flasks of closed microwave digestion system. A known amount of I was added to the extract and reference materials which does not contain detectable levels of halide. A 1.0 cm³ of 1.0 M AgNO₃ solution was added to each aliquot, as well as to the blank sample. Before running the heating program, 4.0 cm³ of concentrated nitric acid and 5.0 cm³ of hydrogen peroxide were added systematically to each sample. A 15.0 cm³ of the mixture were transferred into polypropylene tubes then centrifuged 3500 rpm for 20 min. the resulting precipitate was washed with double distilled water to remove acid residue then dissolved by adding 2.0 cm³ of concentrated ammonia solution. The volume was adjusted to 10.0 cm³ in a volumetric flask with double distilled water. Similar procedure was used for the blank. The samples and blank was heated to 110 °C in a microwave. Atomic spectral line of 183.04 nm was chosen for the analysis of iodine.

d. Adsorption experiments

Adsorption experiments were carried out by weighing dried known masses of adsorbent (0.01 -0.07 g) into a known a KI concentration in a 100.0 mL screw cap bottles. Batch sorption experiments were carried out to optimise pH, contact time, concentration and adsorption dosage. The amount of iodine ions adsorbed were determine.

i. Optimization of pH

Studies of the effect of pH on adsorption of iodine was done by weighing 50.0 mg of bio sorbent onto 50.0 mL of 30.0 mgL⁻¹ test solution of range 2.0 to 9.0. The pH of solution was adjusted by buffering then solution before addition of 0.1 M HNO₃ or 0.1 M NaOH dropwise. The mixture was equilibrated for 180 min, filtered, its volume made 100.0 mL and iodine concentration determined using ICP-OES.

ii. Optimization of initial ion concentration

Solutions with 10.0 to 40.0 mgL⁻¹ iodine were prepared from 100.0 mgL⁻¹stock solution into 50.0 mL volumetric flask. The solution was buffered and pH adjusted to 5.0. A 50.0 mg of adsorbent was added to the 50.0 mL solutions of iodine in a plastic screw cap bottles (100.0 mL) and agitated for 120 min. The mixture was filtered and volume topped up to 100.0 mL before determination of iodine concentration.

iii. Optimization of contact time

The optimum contact time for iodine sorption was determined by weighing 50.0 mg of adsorbent into 50.0 mL of 30.0 mgL⁻¹ concentration of iodine solution at pH 5.0. Six test solutions were separately equilibrated for different periods of time in the range 30 min to 180 min, filtered and concentration of iodine in the filtrate established.

iv. Optimization of adsorption dose

Adsorbent masses in the range 10 mg to 100 mg was used in the investigation of the effect of dosage on sorption of iodine. For each experiment, 50.0 mL of iodine test solution having a concentration of 30.0 mgL⁻¹ and pH 5.0 was used. Mixtures were agitated for 180 min, filtered and volume adjusted to 100.0 mL before determination of concentration of iodine.

e. Calculation of amount adsorbed

The adsorbed amount of iodine ions onto the adsorbent was determined using Equation 1:

$$q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where q is the adsorbed amount to the surface of adsorbent, C₀ and C_e are the initial ion concentration and equilibrium ion concentration (mg L⁻¹) respectively. V is the volume of solution (in litres) and W is the mass (in grams) of adsorbent [8]

f. Preconcentration experiments

i. Preparation of aqueous solutions of vegetables

The *Solanumnigrum*, *Amaranthaceae* and *Cucurbitacucurbitacea* were collected from agricultural farms, transported to the laboratory. Sorting was done so that those food stuffs with very clean surfaces were used. A sample (40.0 g) of the clean air dried fresh green vegetables were hand divided into small pieces and put in a food blender containing 300.0 mL of distilled water. The blender was allowed to run for 10 minutes to obtain a fine homogeneous mixture. The contents of the blender were divided into three portions of equal volumes. To the first portion, filtration was done immediately, volume adjusted to 100.0 mL and iodine determined. Filtration was done to the second portion immediately, volume adjusted to 100.0 mL and preconcentration experiments done. The third portion was allowed to stand for 3 days before being filtering into a 250.0 mL Erlenmeyer flask. Using a 250.0 mL volumetric flask the volume of the filtrate was adjusted to the mark using distilled water. Vegetable extract were loaded into the column for extraction process to recovered nutrients.

ii. Preparation of the column and preconcentration

A small piece of cotton wool was place inside the bottom of a clean dry. A vertically clamped column was half filled with water at pH 5.0. About 10 g of powdered adsorbent was weighed into a beaker containing 20.0 mL of distilled water while stirring with a class rod. The free flowing slurry was carefully transferred to the column while allowing the liquid to drain at the outlet. More water was used until all the slurry was added and the solid appears inside the bottom of the column. The column was now ready for use. Before using the column, all the liquid was drain out, the tap closed out and 100.0 mL of aqueous food extracts (*Solanumnigrum*, *Amaranthaceae* and *Cucurbitacucurbitacea*) were separate introduced into the column slowly. The aqueous food stuffs were allowed to pass through the column at a flow rate of 5.0 mL/min with elute being discarded. The adsorbed nutrients on the adsorbent surface was stripped using vinegar and the nutrient (iodine) in it determined using ICP-OES.

III. Results and Discussion

a. Optimisation of parameters

The optimum condition for sorption of iodine ion onto adsorbent were determined and studied under the following sub-sections

i. Effects of pH on adsorption of iodine ion

The removal percentage of iodine varied from one adsorbent to another. Beans husks adsorbent recorded the highest percentage removal then maize cobs and millet tassels (Figure 1). There was a small variation in the percentage adsorbed at different pH values. The highest percentage removal was recorded between pH 4 and pH 6 while sorption was lower at pH <4 and pH >9. Beans husks adsorbent gave the highest percentage sorption of over 91 % at all the pH values studied (figure 1). Maize cobs adsorbent gave lower percentage removal than beans husks and millet tassels adsorbents.

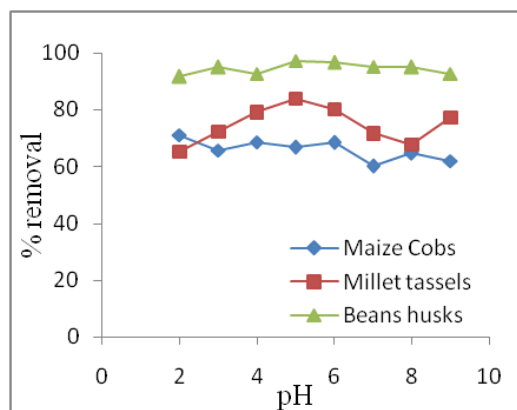


Figure 1: Effect of pH on sorption iodine onto maize cobs (60 min, 70 μg and 15 mg/L), beans husks (60 min, 15 mg/L and 40 μg) and millet tassels (60 min, 15 mg/L and 50 μg) adsorbents

ii. Effects of initial concentration

The variation of the initial concentration of iodine in solution at constant pH and mass was investigated. The results are presented in figure 2.

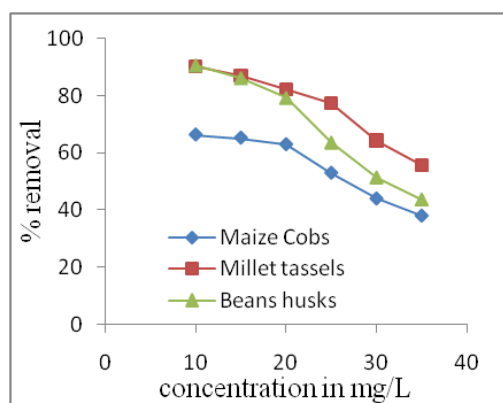


Figure 2: Effect of initial ion concentration on sorption I onto maize cobs (pH 6.0, 60 μg), millet tassels (pH 5.0, 50 μg) and beans husks (pH 5.0, 50 μg) adsorbents when all solutions are agitated for 120 min.

The result shows a steady decrease in percentage removal of iodine from aqueous solutions as the initial concentration of solution increases. A fixed mass of adsorbent has a fixed number of adsorption sites on its surface. At low concentration of iodine, the number of adsorption sites are more than adsorbate hence the high percentage removal. As the concentration increases, it will reach a saturation point where the number of adsorbate molecules in solution is more than the number of adsorption sites. This leads to a point where some adsorbate does not find sites to be adsorbed hence low percentage removal.

iii. Effects of contact time on adsorption of iodine ion

Sorption of iodine was investigated with a fixed mass of adsorbent, constant concentration and pH while varying the time of agitation. The results are presented in figure 3.

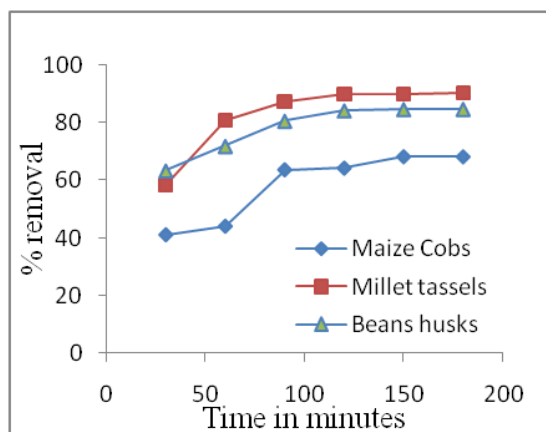


Figure 3: Effect of contact time on sorption of iodide onto maize cobs (60 μg , pH 4.0 and 20 mg/L), beans husks (40 μg , pH 5.0 and 20 mg/L) and millet tassels (50 μg , pH 5.0 and 25 mg/L) adsorbents. There was a steady and rapid increase in percentage removal with time. At time < 30 minutes, less than 80 % removal was achieved. Higher removal percentage was recorded up to around 90 minutes. The percentage removal becomes almost constant since maximum contact will have been attained for possible sorption.

iv. Effects of adsorbent dose adsorption of iodine

Effect of adsorbent dose on the adsorption of iodine was investigated by varying the amount of adsorbent used with constant pH, contact time and concentration. The results are presented in figure 4.

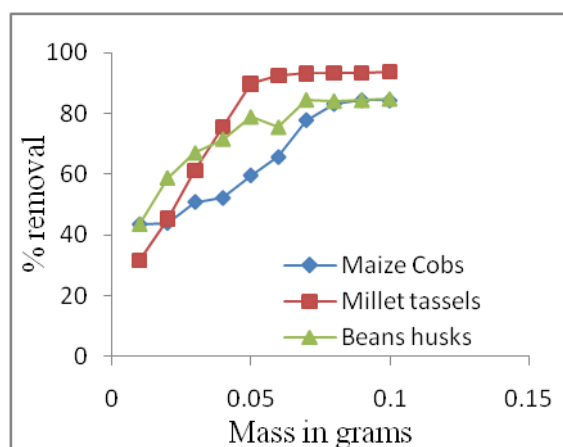


Figure 4: Effect of dosage on sorption of iodide onto maize cobs (90 min, pH 4.0 and 20 mg/L), beans husks (70 min, pH 5 and 20 mg/L) and millet tassels (90 min, pH 5.0 and 20 mg/L) adsorbents

b. Adsorption isotherms of iodine

The equilibrium relationship between adsorbent and adsorbed iodine can best be studied using Langmuir and Freundlich isotherms. Langmuir model is based assumption of an ideal homogeneous surface layer. Langmuir isotherm can be expressed by equation 2:

$$q_e = Q_{max} \frac{K_L C_e}{1 + K_L C_e} \tag{2}$$

Making $\frac{C_e}{q_e}$ the subject, the linear form is expressed in equation 3:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} K_L} + \frac{C_e}{Q_{max}} \tag{3}$$

C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the maximum monolayer adsorption capacity (mg/g), K_L is the Langmuir constant related to the affinity of the binding sites and energy of adsorption (L/mg). Calculated values of R_L gives the separation factor or equilibrium parameter. In fitting the data to Langmuir linearized equation, a plot of $\frac{C_e}{q_e}$ against C_e gives a straight line with $\frac{1}{Q_{max}}$ the gradient and $\frac{1}{Q_{max} K_L}$ is the intercept.

Freundlich model is expressed by equation 4 as:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{4}$$

Where q_e is the adsorption density (mg of iodine ion adsorbed per g adsorbent), C_e is the concentration of iodine ion in solution at equilibrium (mg/L), $K_f \text{ mg/g(L/mg)}^{1/n}$ and n are the Freundlich constants which determines the intercept and slope of the isotherm[9]. The affinity of the adsorbate towards the biomass is indicated by n . The linear form of equation 4 is expressed as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

A plot of $\log q_e$ against $\log C_e$ gives a straight line. The Langmuir and Freundlich constants Q_{max} , K_L , K_f and $1/n$ for the adsorption of iodine were calculated and presented in table 3.

Table 3: Fitted parameters of Langmuir and Freundlich isotherms of iodine adsorption

Adsorbent	Langmuir isotherm model				Freundlich isotherm model		
	Q_{max} (mg/g)	K_L (L/g)	R_L	R^2	$1/n$	K_f [mg/ g(L/mg) ^{1/n}]	R^2
Maize cobs	22.17	0.3314	0.7235	0.9794	0.3383	7.527	0.7508
Millet tassels	42.02	0.9754	0.6118	0.9973	0.2725	20.86	0.8510
Beans husks	31.54	3.3021	0.6343	0.9982	0.1545	21.45	0.6891

The highest values obtained for Q_{max} and K_f obtained were 42.02 mg/g and 21.45 mg/g(L/mg)^{1/n} respectively using millet tassel adsorbent. This indicates that millet tassel adsorbent exhibited higher adsorption capacities than maize cobs and beans husks. The calculated R_L values were all in the range $0 < R_L < 1$. Table 3 shows $1/n$ values were less than 1, indicating that the adsorbent/ adsorbate interphase was favourable[10]. As shown in table 3, maize cobs, millet tassel and beans husks adsorbents fitted with Langmuir model than Freundlich model indicating that the adsorption could best be described as chemisorption.

c. Adsorption kinetics of iodine

Adsorption kinetics of iodine were studied using pseudo first order and pseudo second order model in an effort to predicting the adsorption rate, the rate determining step and the mechanism of adsorption[11]. Experimental data was fitted to pseudo first order model (equation 6) and pseudo second order model (equation 7).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where q_t and q_e are adsorption capacity of adsorbent at time t and equilibrium adsorption capacity (mg/g) respectively, k_1 and k_2 are the pseudo first order and pseudo second order rate constants (min^{-1}) respectively while t is the adsorption time in minutes. A plot of t/q_t against t gives a straight line.

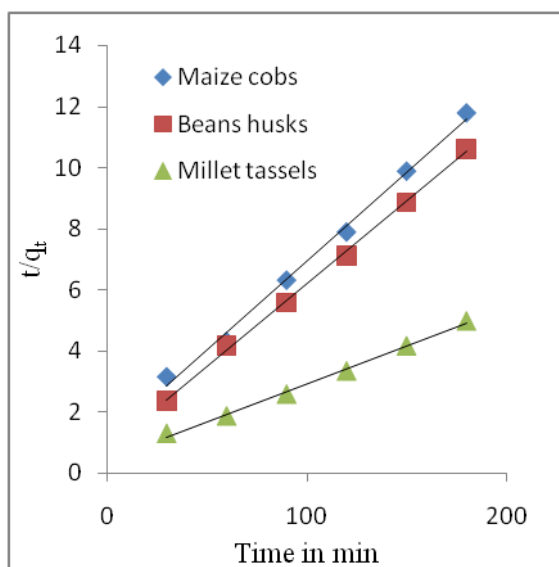


Figure 5: Pseudo second order kinetics model for iodine adsorption efficiencies by different adsorbent. The validity of the model was verified the fitness to a straight line which is indicated by R^2 values close to 1 and by comparing the closeness of the experimental values to the calculated values. The experiment demonstrated

significantly higher R^2 values of pseudo second order model than those of first order model (table 4). The $q_{e(cal)}$ were close to $q_{e(exp)}$ for maize cob and beans husk adsorbents.

Table 4: Pseudo-first order and pseudo second order kinetic model parameters of iodine

Adsorbent	$q_{e(exp)}$	Pseudo- first order			Pseudo second order		
		$q_{e(cal)}$	K_1 (min^{-1})	R^2	$q_{e(cal)}$	K_2 (g.mg.min)	R^2
Maize cobs	10.84	11.20	0.004	0.7102	17.10	0.003	0.9952
Millet tassels	35.51	187.4	0.001	0.8289	40.00	0.003	0.9987
Beans husks	31.28	23.73	0.062	0.8736	18.41	0.001	0.9964

A high rate value of pseudo second order model was $0.003\ min^{-1}$ obtain while using maize cobs and millet tassel. This is an indication that beans husks had the slowest rate.

d. Preconcentration

The results of the experiments described 2.6.1 and 2.6.2 are presented in figure 6.

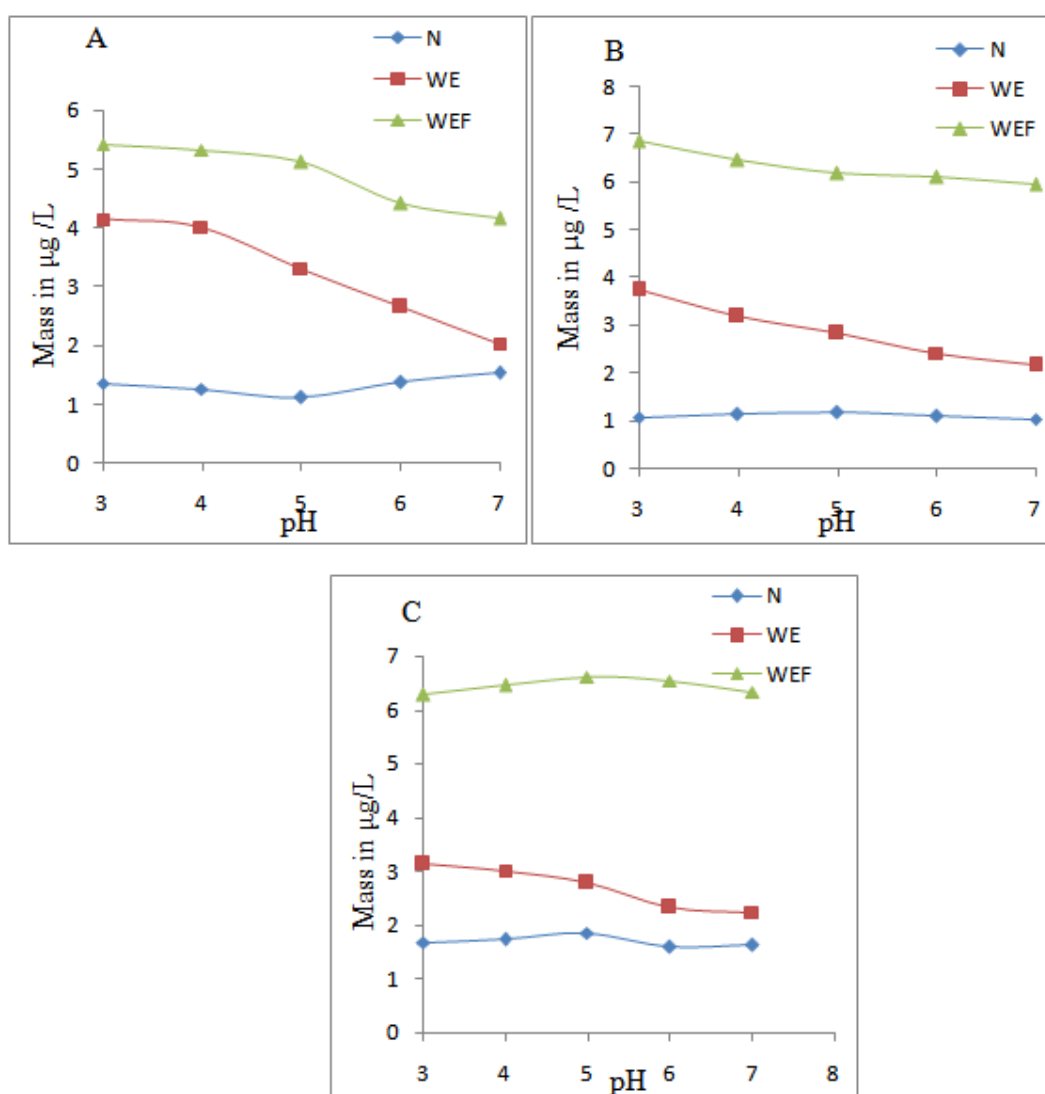


Figure 6: Effects of pH on adsorption of iodine on *Amaranthaceae* (A), *Cucurbitacurbitacea* (B) and *Solanumnigrum* (C) when a 1:1:1 mixture of maize cobs, millet tassels and beans husks are used.

The pH of the solution has a small effect on the adsorption of iodine to the adsorbent. It higher pH above 5, there is a general tendency of sorption of iodine to decrease. Fermentation and preconcentration of aqueous food extracts increases the amount of iodine present in solution. The fermented and preconcentrated solution (WEF) gave the highest mean values of iodine of $4.893 \pm 0.564\ \mu g/L$, $6.303 \pm 0.355\ \mu g/L$ and $6.446 \pm 0.139\ \mu g/L$ in, *Amaranthaceae*, *Cucurbitacurbitacea* and *Solanumnigrum* respectively (figure 6). The lowest

mean values of iodine obtained were $1.331 \pm 0.155 \mu\text{L}$, $1.103 \pm 0.056 \mu\text{g/L}$ and $1.701 \pm 0.104 \mu\text{g/L}$ in *Amaranthaceae*, *Cucurbitacucurbitacea* and *Solanumnigrum* respectively for the extract not pre-concentrated (N). The amount of iodine in extracts of *Amaranthaceae*, *Cucurbitacucurbitacea* and *Solanumnigrum* which were not fermented but were pre-concentrated (WE) were $3.234 \pm 0.900 \mu\text{g/L}$, $2.867 \pm 0.629 \mu\text{L}$ and $2.707 \pm 0.400 \mu\text{g/L}$ respectively (figure 6). From the results it can be seen that pre-concentration increases the food nutritional value. Fermentation makes the ions labile and free them from compound matrix which holds them.

IV. Conclusions

The study successfully used chemically modified maize cobs, millet tassels and beans husks in pre-concentration experiments. Batch sorption experiments were carried out to optimize parameters of pH, initial ion concentration, contact time and dosage used. The results indicate that maize cobs, millet tassels and beans husks adsorbents are good adsorbents for iodine as up to 97% removal was achieved. It was shown that all these parameters under study influence the amount of iodine adsorbed on the surfaces. Adsorption isotherms show that data fitted Langmuir isotherm model more than Freundlich. There were high correlation coefficients for isotherms and experimental data. The adsorption kinetics could best be explained by pseudo second order than pseudo first order. The bio sorbents (maize cobs, millet tassels and beans husks) successfully pre-concentrated iodine from aqueous solutions of food stuffs. This was best illustrated by comparing N, WE and WEF extracts of *Amaranthaceae*, *Cucurbitacucurbitacea* and *Solanumnigrum*. Fermentation was found to enhance the levels of iodine found in aqueous solutions of food stuffs. It was shown that it is possible to use chemically modified bio sorbents to increase the mineral value of foods and hence solve problems associated with malnutrition.

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