



## Research article

# Biosorption of potassium ion using bean seeds and its energy saving application

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## ABSTRACT

Ca and Mg have been implicated in causing hardness in beans resulting in relatively long cooking time. This study used potassium to replace the cations and determined the adsorption of potassium solution to bean seeds. Then, plantain peel, a natural source of potassium, was used to cook beans and its impact on the cooking time of beans was investigated. The adsorption experiments were performed using batch technique, while metal compositions of the bean seeds and plantain peel were determined by spectroscopy. Optimum removal conditions of potassium ion biosorption using bean seeds were observed at pH 10.2, 2 g bean seed dosage, 180 min agitation time, with 75 ppm as initial metal concentration. The kinetic model correlate with pseudo-second order reaction and the Langmuir adsorption model best fitted the adsorption. After cooking the beans with plantain peel, the concentration of Mg reduced in the bean seeds by about 48%, while the concentration of Ca reduced by about 22%, but the concentration of K increased by over 200% in the cooked bean seeds. Beans treated with plantain peel cooked earlier than the control experiment. This may be affected by pH, adsorbent dosage, metal concentration and contact time.

## 1. Introduction

Beans are among the leguminous food crops which are cultivated and harvested solely for their seeds [1]. Studies reveal that it accounts for 50% of the grain legumes consumed worldwide [2]. Bean seeds (BS) are cheap dietary source of proteins, vitamins, minerals, fiber and carbohydrates [3,4]. Bean seeds exist in different colours, shapes and sizes. There are many types or varieties of common beans which include black-eyed pea, black beans, kidney beans, haricot and pinto. Structurally, a mature dry common bean seed comprises mainly of two parts: the embryo (cotyledons) and a seed coat. The cotyledons constitute 80–90%, while the seed coat is 8–20% of the total seed dry matter [5].

The cooking time of most beans varieties is relatively long, sometimes, more than 2 h, with negative economic and environmental effects. The prolonged cooking time has discouraging implications on its inclusion in the menu including (1) high energy consumption with high economic cost [6], (2) long exposure of people to poisonous chemicals from combustion of fuel which is deleterious to human health [7,8], (3) environmental degradation due to release of greenhouse gases from fuel combustion and (4) degradation and reduction of some important nutrients required in human nutrition [9]. Some factors that have been identified as influencing the hardening of beans resulting in its long cooking time include genetic factors [10], the colour of the seed coat, the extrinsic factors (storage and processing conditions) [11,12] and some chemical compounds that occur naturally in beans. These include dietary fibre,

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divalent cations, phytic acid, protein, starch and pectin molecules [13].

Calcium and magnesium are the most implicated cations in the hardening of pectin molecules which contribute to the long cooking time of beans [12,14,15]. Several methods including chelation, chemical precipitation, ion exchange and membrane separation are used to remove metals from various matrices [16]. Sorption has been considered one of the most promising techniques because it is efficient, economic, safe and of easy operation for the removal of these metals [17].

In the present study, potassium ions are applied to remove the metals that contribute to the hardening of bean seeds. The adsorption of the sorbate (potassium ion) to the biosorbent (bean seed) is investigated under different conditions.

This study is used to investigate the potential of saving energy by a treatment of bean seeds with plantain peel which is a natural source of potassium [18]. The study was carried out at the Biomass Laboratory of the National Centre for Energy Research and Development, University of Nigeria, Nsukka.

## 2. Materials and methods

### 2.1. Materials

The raw dry black-eyed pea (bean) seeds (*Vigna unguiculata* L) (BS) and a bunch of unripe plantain fruits were purchased from Oigie market in Nsukka, Enugu State, Nigeria. Analytical grade chemicals, including potassium standard solution 1000 mg/L (Scharlau Chemie SA), 0.1 M HCl (Sigma-Aldrich Laborchemikalien, Germany) and NaOH (BDH Laboratory, Poole, England) were without further purification. Deionised water was used throughout the experiments. A digital pH meter (pHep, Hanna Instruments) was used to monitor the pH values during adjustment with either the acidic or basic solution. Atomic absorption spectrophotometer (AAS) (Model AA-6800, Shimadzu Corporation, Japan) was for determining elemental compositions.

### 2.2. Sample preparation

Bean seeds were used as adsorbent (biosorbent) for this study. They were sun-dried, then oven dried at 105 °C for 2 h, before grinding with a mechanical grinder, and then screened with a 250-µm standard test sieve (Rupson Industries, New Delhi).

### 2.3. Preparation of metal (adsorbate) solutions

Analytical grade standard potassium solution of 1000 mg/L (stock solution) was used for this experiment. Working solutions were prepared from the stock solution by calculating the volume of stock solution required for dilution to the needed concentration, based on the formula:

$$C_1V_1 = C_2V_2$$

Where  $C_1$  and  $V_1$  are the concentration volume of the stock solution, while  $C_2$  and  $V_2$  are the desired concentration and volume of the dilute working solution.

The volume from the stock solution was transferred into a standard flask which was made up to the mark with deionised water.

### 2.4. Adsorption studies

The adsorption studies of the potassium ion by the bean seeds in batch mode were carried out at different pH levels, metal concentrations, biosorbent dosages and contact time.

#### 2.4.1. Effect of pH

Exactly 100 ml of 75 ppm potassium solution was added to 2 g of BS powder in different conical flasks. The pH of the solution in the flasks was adjusted with 0.1 M HCl and 0.1 M NaOH to obtain pH values of 3.9, 4.7, 6.5, 8.1 and 10.2 and measured with a pH meter. The solution in each flask was agitated with a magnetic stirrer for 180 min before filtering into a clean sample bottle. The filtrate was analysed for the concentration of potassium ion by atomic absorption spectrometry using AAS (Model AA-6800, Shimadzu Corporation, Japan). The optimum pH level, which is the pH that produced the highest adsorption, was noted [19].

#### 2.4.2. Effect of initial adsorbate concentration

Potassium solutions of different concentrations (25, 50, 75, and 150 ppm) were prepared as described in section 2.2. Respective 2.5, 5, 7.5 and 15 ml of the stock solution were transferred into 2 g of the powdered bean seeds in five separate 100 ml standard flasks. Each solution was adjusted to the optimum pH and agitated with a magnetic stirrer for 180 min before filtering into a clean sample bottle. The filtrate was analysed for the concentration of potassium ion adsorbed at different concentrations of potassium solutions by spectrometry using AAS (Model AA-6800, Shimadzu Corporation, Japan).

#### 2.4.3. Effect of biosorbent dosages

Varying dosages (0.5, 1.0, 1.5 and 2 g) of the powdered BS were weighed into standard flasks. Exactly 100 ml of 75 ppm potassium solution was added to each of the flasks. Each solution was adjusted to the optimum pH and the solution was agitated with a magnetic

stirrer for 180 min before filtering into a clean sample bottle. The filtrate was analysed for the concentration of potassium ion adsorbed at different dosages by spectrometry using AAS (Model AA-6800, Shimadzu Corporation, Japan) [19].

#### 2.4.4. Effect of contact time

Exactly 100 ml of 75 ppm potassium solution was added to 2 g of BS powder in different standard flasks. The pH of the solution in the flasks was adjusted with 0.1 M HCl and 0.1 M NaOH to the optimum pH and the solutions were agitated with a magnetic stirrer at different contact time intervals (30, 90, 120 and 180 min) before filtering into a clean sample bottle. The filtrates were analysed for the concentration of potassium adsorbed at different contact time by spectrometry using AAS (Model AA-6800, Shimadzu Corporation, Japan).

The adsorption behaviours of the adsorbent were studied from the percentage removal efficiency of potassium ion based on Equation (1):

$$\text{Removal efficiency} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

Where  $C_o$  is the initial concentration of potassium ion,  $C_e$  is the solution concentration after adsorption.

#### 2.5. Isotherm studies

Langmuir, Freundlich and Temkin isotherms were applied to explain the nature of adsorption of potassium ion to the bean seeds.

#### 2.6. Kinetic studies

In order to verify the kinetics of potassium adsorption to BS in the metal solution, curve fitting for pseudo first-order, second-order, intraparticle diffusion and Elovich plots were carried out.

### 3. Application of the study using plantain peel

This study was used to investigate the cooking time of beans on treatment with plantain peel, a natural source of potassium.

#### 3.1. Determination of metals' composition of the bean seed coat, bean seeds and plantain peels and bean seeds treated with plantain peels

The metal contents of the dry bean seed coat, bean seeds and the plantain peels were determined by wet digestion method as described by Ugwu & Ofomatah [20]. In the method, exactly 1 g each of seed coat, BS and plantain peel was digested using 30 ml *aqua regia* (3:1 HCl and HNO<sub>3</sub>). From each of the sample solutions, K, Na, Ca, Mg, Zn, Fe, Cu, Cr, Mn, Pb and Cd in the samples were determined with AAS (Model AA-6800, Shimadzu Corporation, Japan). Blank solutions, containing only solvents, were analysed. The concentration of each metal was obtained after subtraction from the concentration in the blank solution. Duplicate analysis was carried out as a quality control measure. Recovery experiments were done with a slight modification of the method in an earlier work [20].

#### 3.2. Determination of metals' composition of bean seeds treated with plantain peels

The bean seeds (3 g) were treated with plantain peel (1 g) in 120 ml of deionised water under heat (100–135 °C) of an electric stove until the texture of the bean seeds softened. After cooling, the BS was digested with *aqua regia* before analysis for the aforementioned metals as already described.

#### 3.3. Quality control on the metal analysis of bean seed coat, bean seeds and plantain peel

To ensure the integrity of the results from metal analysis, the quality control protocols outlined by Ugwu & Ofomatah [21] were followed. Some of the quality control protocols followed include: (1) Standard solutions of the metals being determined were used to obtain the calibration curves which were used to establish the Limit of detection (LOD) and the Limit of Quantitation (LOQ). (2) The instrumental analysis was carried out by a certified public analyst at the National Centre for Energy Research and Development, University of Nigeria, Nsukka.

#### 3.4. Evaluating the cooking time of dry beans (black-eyed pea variety) with and without plantain peel treatment

The black-eyed pea variety of bean seeds was sorted to remove dirt, stones, twigs, chaff, cracked and broken seeds. An experiment was set up that involved four beakers: A, B, C and D, in two groups (A, B and C, D). One group consisted of two beakers (A and B) in which each beaker contained 3 g of dry bean seeds, 1 g of unripe plantain peel and 60 ml of deionised water. Deionised water was used to avoid possible interference of ions in water. The second group of two beakers (C and D), each beaker contained 3 g of dry bean seeds and 60 ml of deionised water only. This second group served as Control. The four beakers with their contents were heated and a stop-clock was used to check the cooking time. Finger pressing (tactile method) was used to ascertain the texture of the bean seeds. The bean

seeds were considered well-cooked when the texture is soft and the seeds disintegrate on finger pressing. The time to get the soft texture was recorded. Finger pressing, which is a subjective method, is an accepted means for evaluating the cooking time of beans [22, 23].

### 3.5. Sensory characteristics of beans treated with plantain peel

The taste, odour and flavour of the cooked bean seeds treated with plantain peels were compared with cooked beans without treatment by a panel.

### 3.6. Statistical analysis

The data were statistically processed as the means were compared. The statistical evaluation of the data was performed using IBM SPSS 20.

## 4. Results and discussion

### 4.1. Effect of pH on the adsorption of potassium ion

Presented in Fig. 1 is the plot of pH values against removal Efficiency, which is the quantity of adsorbate removed in percent from a particular volume of adsorbate solution by the adsorbent. At pH 3.9, the removal efficiency was 95.36%, which reduced to 93.50% at pH 4.7. Afterwards, the removal efficiency increased with higher pH values. The highest adsorption occurred at pH 10.2 (optimum pH) with 98.56% of the initial metal concentration removed.

This is similar to the result on the attraction between MB dye and adsorbent surface in which the removal increased as the pH of the solution increased [24].

### 4.2. Effect of metal concentrations on the adsorption of potassium solution

Initial concentration of  $K^+$  was varied from 25 to 150 ppm and the quantity of adsorbent was kept constant at 2 g, and pH 10.2 maintained with contact time of 180 min. Fig. 2 is a plot of removal Efficiency against initial potassium ion concentration.  $K^+$  had maximum adsorption at 75 ppm with 98.04% corresponding to  $C_e$  of 1.4698 ppm adsorbed. The percentage potassium bound decreased from 94.74 to 92.73% as the concentration progressed from 25 to 50 ppm, before it increased as the  $K^+$  concentration increased. This is consistent with the reported works of some analysts [25,26].

The rapid increase in the rate of adsorption after 50 ppm may be attributed to the sufficient surface area to accommodate more metal available in the solution due to the effect of concentration gradient which is the main driving force for the adsorption process [27]. Removal efficiency stabilized with higher concentrations as there were low absorption sites.

### 4.3. Effect of different dosages of the adsorbent on the adsorption of potassium solution

The effects of variation in bean seed powder dosage on the amount of potassium solution adsorbed are shown in Fig. 3. The adsorption of potassium solution was studied at various adsorbent dosages of 0.5, 1.0, 1.5 and 2.0 g with each dissolved in 100 ml of 75 ppm potassium solution. Sorption increased significantly with increase in adsorbent dose until 1.0 g. This can be attributed to increased adsorbent surface area and availability of more adsorption sites [28]. Between 1.0 and 1.5 g, sorption slowed down but increased rapidly afterwards, until 2 g, when increase in dosage does not affect sorption significantly. Therefore, 2 g was the optimum dosage. This is in line with a report that after a particular dosage level, adsorption is not significant with increase in dosage and may even decrease [29].

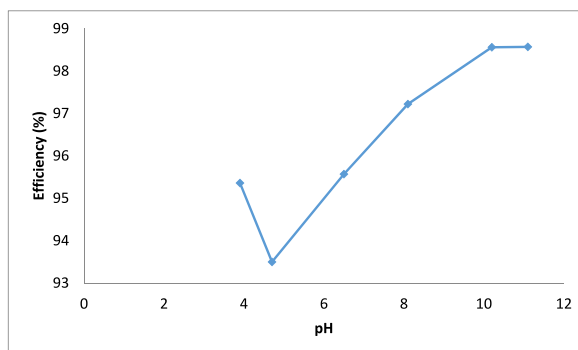


Fig. 1. Effect of pH on the percent adsorption of  $K^+$  (75 ppm, 2 g of bean seed and 100 ml potassium solution).

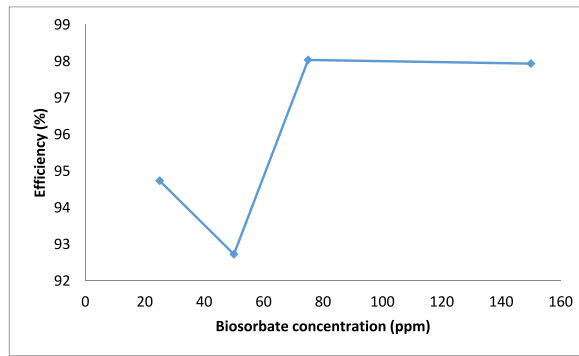


Fig. 2. Effect of biosorbate concentration (pH 10.2, 2 g of bean seed, 180 min and 100 ml potassium solution).

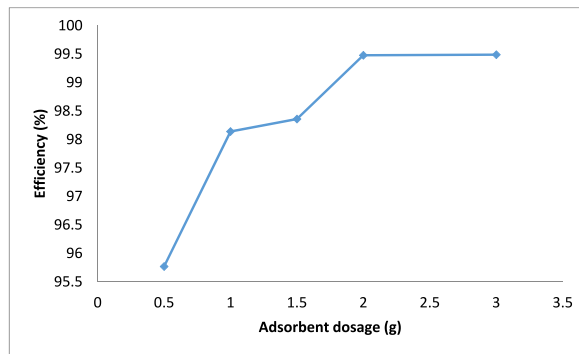


Fig. 3. Effect of adsorbent dosage on adsorption of  $K^+$  on to the adsorbent (pH 10.2, 75 ppm, 180 min and 100 ml potassium solution).

#### 4.4. Effect of variation of contact time on the adsorption of $K^+$ with the adsorbent

Effect of contact time on adsorption was studied and the results are shown in Fig. 4.

The amount of potassium solution adsorbed increased with contact time before equilibrium was reached. Other parameters: dose of adsorbent, concentration and pH of solution, were kept constant. The rapid initial uptake at 97.5% in the first hour could be attributable to the availability of a large number of adsorption sites [24]. After 180 min, there is no noticeable change in the amount of potassium solution adsorbed, hence the adsorbent reached equilibrium at 180 min.

#### 4.5. Adsorption isotherms

In the present investigation, the equilibrium data (Table 1) were analysed. Langmuir, Freundlich and Temkin isotherms were employed to investigate the adsorption behaviours.

$Q_e = \frac{C_0 - C_e}{M} V$ , where  $C_0$  = Initial concentration;  $C_e$  = Equilibrium concentration;  $V$  = Volume of test solution;  $M$  = Mass of

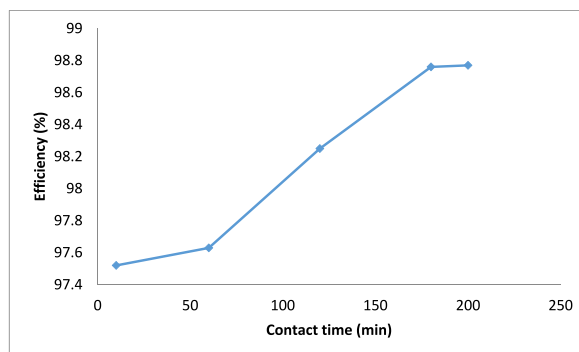


Fig. 4. Effect of contact time on  $K^+$  adsorption to the adsorbent ((pH 10.2, 75 ppm, 2 g and 100 ml potassium solution).

adsorbent

The adsorption data were fitted to the three commonly used adsorption isotherm equations: the Langmuir, the Freundlich and Temkin models.

The equilibrium adsorbed amount ( $Q_e$ ) was plotted against the equilibrium pollutant concentration ( $C_e$ ) in solution to generate the isotherms. Fig. 5 displays the isotherms for the adsorption of potassium ion onto the adsorbent. It can be seen that the adsorption of the potassium ion onto the adsorbents was large, as can be judged from the equilibrium adsorbed amounts ( $Q_e$  values).

Figs. 6–8 display the Langmuir, the Freundlich and Temkin plots, respectively for the adsorption of potassium ion onto the bean seed adsorbent.

The Freundlich plot for potassium ion sorption by the adsorbent is displayed in Fig. 7. In order to generate the Freundlich plot, Log  $Q_e$  was plotted against Log  $C_e$ .

Fig. 8 presents Temkin plot of  $Q_e$  against in  $C_e$ .

The correlation coefficients ( $R^2$ ) of the Langmuir, the Freundlich and Temkin plots are 0.620,  $-207$  and  $-0.42$  respectively. The Langmuir model has a greater correlation coefficient than the others, implying that the adsorption process best fits the Langmuir model. This model describes adsorption on homogeneous surfaces, that is, the surface of the adsorbent is uniform, with equivalent adsorption sites.

#### 4.6. Adsorption kinetics

The experimental adsorption data obtained from the effect of contact time were fitted to the three commonly used adsorption kinetic models: the pseudo first-order, second-order and intraparticle diffusion models. Figs. 9–12 display the pseudo first-order, second-order, intraparticle diffusion and Elovich plots respectively for the adsorption of potassium ion by the adsorbent.

From Fig. 9,  $R^2$  value is 0.8619. The plot did not correlate data as  $R^2$  value is and there is large disparity between theoretical  $q_e$  and experimental  $q_e$ .

From Fig. 10,  $R^2$  value is 0.9999. The data correlate with pseudo-second order because the  $R^2$  value is high (equivalent to 1), and the theoretical  $q_e$  is very close to the experimental  $q_e$ .

From Fig. 11,  $R^2$  value is 0.8997. Plot did not pass through the origin and so did not correlate the data.

From Fig. 12,  $R^2$  value is 0.7765. The plot did not correlate the data.

Therefore, the kinetic model correlates with pseudo-second order reaction.

#### 4.7. Metal compositions of the bean seed coat, bean seeds and the plantain peels

The results of quantitative analysis for some metals in bean seed coat, uncooked bean seeds, cooked bean seeds and uncooked plantain peels are presented on Table 1.

On Table 2, the concentrations of the selected metals in the bean seed coat are presented. It shows that the seed coat contains Ca as the principal component, followed by Mg, Na and then K. Moraghan & Grafton revealed that 84% of Ca and 18% of Mg in beans are in the seed coat [30]. It follows that the removal of beans seed coat will lead to loss of minerals and reduces the effect of Ca and Mg which increase hardening of beans. Table 2 also shows that the analysed uncooked dry bean seeds contain elements: K, Na, Ca, Mg and Fe as major elements. In decreasing order, the concentrations of the selected metals in the raw beans are  $Mg > Na > Ca > Fe > K > Mn$ , while in the beans cooked with plantain peel, the metal concentrations in descending order are  $Na > K > Ca > Mg > Fe/Cr > Cd > Zn > Mn$ . These minerals are essential for proper body functions. Mg is the principal metal component of the analysed metals in the sampled uncooked dry bean seeds, followed by Na and then Ca. After cooking the beans with plantain peel, the concentration of Mg reduced in the bean seeds by about 48%, while the concentration of Ca reduced by about 22%, but the concentration of K increased by over 200% in the cooked bean seeds. The concentration of K in the plantain peel increased after cooking with beans, while the concentrations of Na, Ca and Mg decreased.

The p-value for the mean of tested metals in untreated and treated beans is 0.834 ( $p > 0.05$ ), implying that there is no significant difference in the values.

It can be inferred from the results that reactions occurred between the various materials in the pot while cooking beans with plantain peel in deionised water. Displacement of ions takes place such that Mg and Ca ion concentrations decreased. The displacement of Ca and Mg weakens the cell wall and soften the texture of the beans which were hardened by the presence of these cations. The displacement reaction will invariably reduce cooking time of beans.

**Table 1**  
Isotherm data for adsorption of Potassium ion onto Bean seed adsorbent.

Ce (ppm)	Ce/ $Q_e$	Log Ce	Log $Q_e$	In Ce	$Q_e$ (mg/g)
10.2432	$6.44 \times 10^{-4}$	1.01	4.20	2.33	15902.72
1.2376 mg/L	$1.03 \times 10^{-4}$	0.09	3.99	0.21	9752.48
1.0829 mg/L	$1.66 \times 10^{-4}$	0.03	3.81	0.08	6522.28
1.5470 mg/L	$3.40 \times 10^{-4}$	0.19	3.66	0.44	4545.30

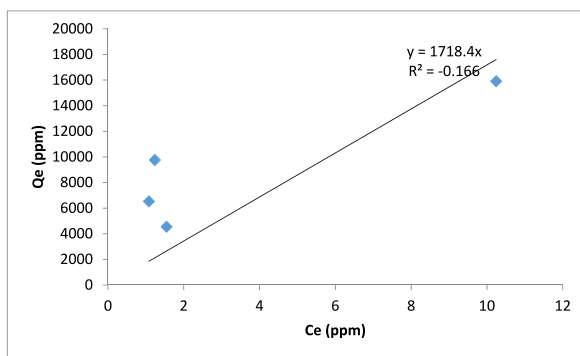


Fig. 5. Isotherm for the sorption of potassium ion by BS adsorbent.

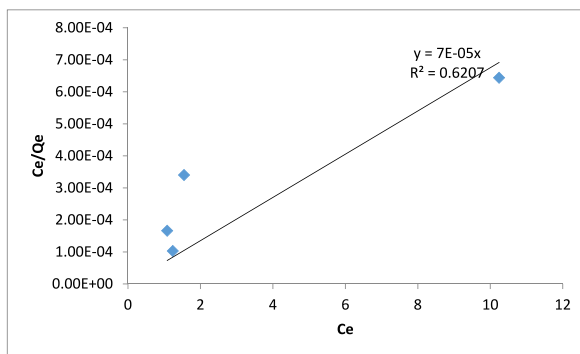


Fig. 6. Langmuir plot for the sorption of potassium ion by bean seed adsorbent.

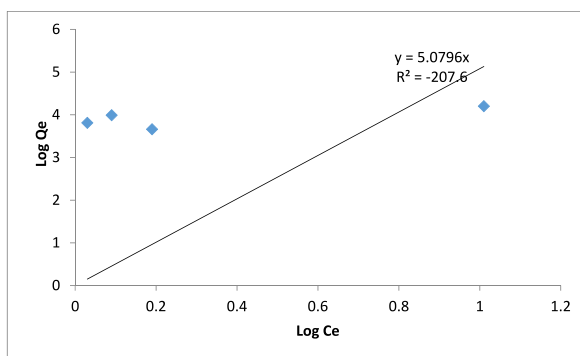


Fig. 7. Freundlich plot for the sorption of potassium ion by BS adsorbent.

#### 4.8. Cooking time of dry beans

Fig. 13 presents the cooking time for beans treated with plantain peel and for untreated beans (Control). The treatment with plantain peels showed that the cooking time reduced by 10 min compared with the untreated bean seeds under the same cooking conditions. There is no significance difference in the values 0.0578 ( $p > 0.05$ ).

#### 4.9. Sensory characteristics of cooked BS

The panel that evaluated some sensory characteristics of the cooked beans opines that the appearance and colour remained the same but the control has preferable taste and flavour compared to the treated beans.

The adsorption studies showed that pH,  $K^+$  concentration, adsorbent dosage and contact time influence the sorption of  $K^+$  by the bean seeds. It connotes that these parameters influence the mechanism of displacement reaction of Ca and Mg (in beans) cations by K ion (in plantain peel).

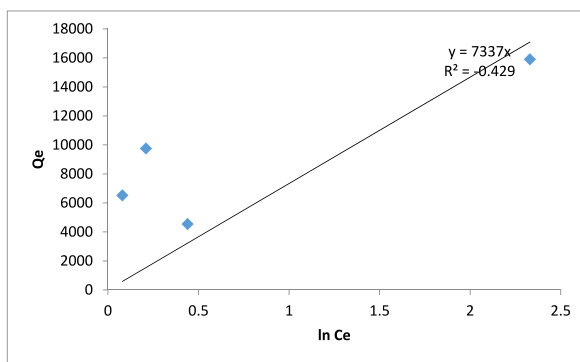


Fig. 8. Temkin plot for the sorption of potassium ion by BS adsorbent.

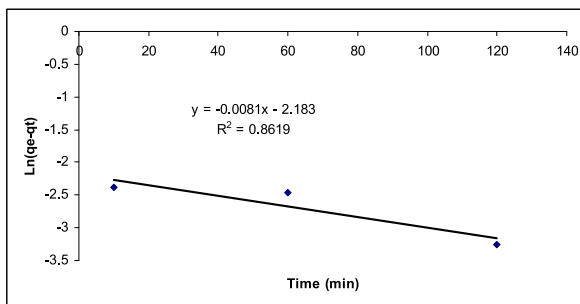


Fig. 9. Pseudo-first order kinetic plot for the adsorption of potassium ion by bean seed.

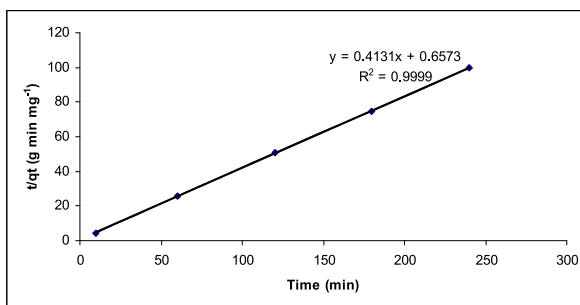


Fig. 10. Pseudo-second order kinetic plot for the adsorption of potassium ion on bean seed.

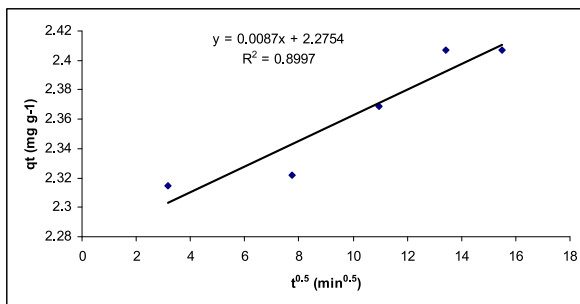


Fig. 11. Intraparticle diffusion model kinetic plot for the adsorption of potassium ion on bean seed.



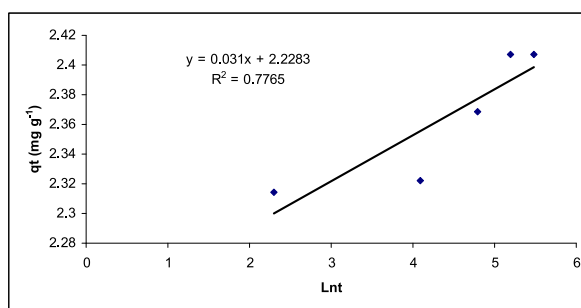


Fig. 12. Elovich model kinetic plot for the adsorption of potassium ion on bean seed.

Table 2

Mean metal concentrations (in ppm) bean seed coat, uncooked bean seeds, cooked bean seeds and uncooked plantain peels.

Matrix	Mean concentrations of metals											
K	Na	Ca	Mg	Zn	Fe	Cu	Cr	Mn	Pb	Cd		
A	4.56	6.34	13.33	7.54	0.02	2.20	0.00	0.00	0.03	0.60	0.11	
B	1.39	6.09		6.00	8.21	0.00	1.59	0.00	0.00	0.03	0.00	0.00
C	5.03	6.03		4.67	4.30	0.04	0.12	0.00	0.12	0.03	0.00	0.07
D	3.71	6.33	12.67	5.59	0.03	0.61	0.00	0.00	0.13	0.15	0.79	

A: Bean seed coat; B: Bean seeds (untreated); C: Bean seeds treated with plantain peel; D: Plantain peel (untreated).

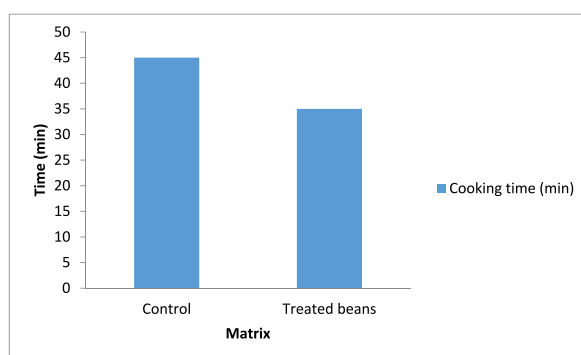


Fig. 13. Cooking time vs Beans.

This research is not exhaustive on the potential of using plantain peel to save energy as other compounds in beans such as starch and protein affect the cooking time of beans.

## 5. Conclusion

The adsorption of potassium solution by bean seeds as an adsorbent was determined. The experiment was performed using batch technique. Maximum optimum removal conditions for potassium ion was observed with 2 g adsorbent, at pH 10.2, 180 min agitation time, with 75 ppm as initial metal concentration that gave 98.04% adsorption of potassium ion. The kinetic model fitted well with pseudo-second order reaction and Langmuir adsorption model as it has highest  $R^2$  values. It was observed that cooking beans with plantain peel reduced the cooking time, due to sorption of potassium. This result shows that energy, time and cost could be saved in cooking beans.

## Author contribution statement

Kenekchukwu Ugwu: Conceived and designed the experiments; Performed the experiments; Analysed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Julius U. Ani: Analysed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Anthony C. Ofomatah: Performed the experiments; Contributed reagents, materials, analysis tools or data.

## Data availability statement

No data was used for the research described in the article.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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