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Determination of Potassium Ion Concentration in Red Mangrove (*Rhizophora Mangle L*) Barks Aqueous Extract (RMBAE) In Acid Media

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Abstract: *Studies were carried out on dry ash of red mangrove (Rhizophora mangle L) bark, an agricultural waste, to determine the potassium ion concentration in it, by titratory and spectrophotometric methods. 100gm of the dry ash were dissolved in 500cm*^{3} *distilled water and the aqueous extract from the bark subjected to titration against standard solutions of* CH_3COOH, *HCl and* H_2SO_4 *in the concentration ranges of 0.5-2.0M,while AAS was carried out using 5gm of the dry ash in GBC Avanta flame atomic absorption spectrophotometer version 2.02 . The results obtained from the titration reaction revealed that there were high levels of potassium ion concentration (19.50 to 31.91gm/dm*^{3} *and 21.52 to 37.0656gm/dm*^{3}*) in both HCl and* H_2SO_4 *solutions, but low in* CH_3COOH*(14.82 to 18.13 gm/dm*^{3}*).This result was in agreement with the results of AAS result (18.255ppm). The percentage purity calculated revealed that the potassium ion obtained from the red mangrove bark aqueous extract (RMBAE) had a purity of 69.94%,showing high purity of the potassium obtained by these methods. The proposed methods were successfully employed to determine potassium ion concentration in red mangrove bark aqueous extract (RMBAE). The methods were very simple, inexpensive, less time consuming. environmentally friendly and reliable.*

Keywords: *Potassium ion concentration, Red mangrove bark, Acid media and Titration*

I. Introduction

Mangroves are woody plants that grow in the inter-tidal areas between land and sea in the tropic and subtropical latitudes (Kathiresan and Bingham 2001). They have highly specialized features that made them adaptive to the coastal environment such as pnumatophores, prop roots and buttresses, salt-excreting leaves etc (Duke, 1992). Due to these unique adaptations, mangrove thrives well in the estuarine brackish water environment which is inhospitable to other plants.

Mangrove wetlands are a good nursery ground for a number of economically important aquatic organism (Raman et al., 2007). Besides, they play an important role in providing goods and services to humans which include aquaculture, forestry protection against shoreline erosion, firewood and building materials and other subsistence products like honey wax and essence (Hogarth,1999;Walter et al.,2008). It has also been implicated for phytoremediation of heavy metal pollution, one of the reasons why mangrove is regarded as a sink for heavy metals (Debargha et al., 2008).

The red mangrove (*Rhizophora mangle L*) is one of four mangrove species found in the mangrove ecological community. The other species within this community are White mangrove (*Languncularia racemosa*), Black mangrove (*Avicennia germinaas*), and Buttonwood (*Conocarpus erectus*). Mangrove community plays an important role in tropical and subtropical regions of the world. Different mangrove species protect and stabilizes low lying coastal lands and provide protection and food sources for estuarine and coastal fishing food chains.

Its wood is used for fuel, piling, crossties, and charcoal. The bark is seen as an agricultural waste in Nigeria with less attention given to its usefulness. Most recently, Mangrove extracts have been used for diverse medicinal purposes and have a variety of anti-bacterial, anti-herpetic and anti-Helminthic activities (Duke and Wain, 1981; Prabhakaran and Kavitha, 2012; Luz Maria et al., 2010).

Again, the efficiency of red mangrove bark aqueous extract in the treatment of aphthos ulcers have been reported to reduce the time to repair mucosal tissue and especially mouth mucosa healing (De Armas et al.,2005). This view was also corroborated by Berenquer et al., (2006).

Furthermore, in studying the elemental composition of red mangrove bark, it was considered that it contained different elements in varying concentrations (Debargha et al., 2008). Some of these elements included potassium, sodium, calcium, manganese, phosphorus and nitrogen (Marikandan et al., 2009; Mianpeurem et al., 2012). The importance of these mineral nutrients to man, soil, plant and chemical industries, can not be overemphasized. Potassium is needed by the body and its deficiency, or hypokalemia, causes a variety of problems, such as fatigue, muscle weakness and cramps, bloating, constipation and abdominal pain.

Medically, it is classified as an electrolyte, meaning it carries an electrical charge and helps to balance sodium levels in the body, by increasing the amount of sodium excreted in urine, thus reducing high levels in the body. Furthermore, it also plays a key role in Osmo-regulation process of water in plants, where it affects water transport in the xylem, maintain high density cell turgid pressure which affects water tolerance, cell elongation for growth and most importantly regulates the opening and closing of the stomata which affects transpiration cooling and carbon dioxide up take for photosynthesis.

Fertilizer and chemical industries also needs potassium and uses it in high quantities. All these sources deplete the normal supply and demand for potassium, hence, the need to find a cheaper, saver, reproductive and environmentally friendly alternative to getting potassium.

Recently, most plant sources have been explored to isolate and determine potassium ion especially in mangrove plants. But enough studies on the determination of potassium ion concentration in aqueous extract of red mangrove bark in acid media is lacking. Therefore, this study is to determine potassium ion concentration in red mangrove (*Rhizophora mangle L*) bark aqueous extract (RMBAE) in both organic acid (CH_3COOH), and mineral acids (HCl, and H_2SO_4) media.

II. Materials And Methods

2.1: Collection And Preparation Of Red Mangrove Bark Aqueous Extract (RMBAE)

The red mangrove (*Rhizophora mangle L*) bark was obtained commercially from Timber plank market, mile II Diobu, Port Harcourt, Rivers state, Nigeria during the dry season. The collected barks were extensively washed with de-ionized water and air-dried in sun (solar drying) for a few days to remove water content in the sample. The dried sample was then converted to finely granulated ash by burning. A set of accurately weighed 100gm of the finely granulated burnt ash were dissolved in 500cm^3 of de-ionized water, to bring the elements in the ash into solution, and the solution thoroughly stirred and allowed to homogenize for 48 hours. Afterwards, the solutions were filtered using a quantitative whatman filter paper number 41.The filtrates (red mangrove bark aqueous extract) were taken to determine potassium ion concentration by titrating with standard solutions of CH_3COOH ,HCl, and H_2SO_4 respectively with concentrations (0.5-2.0M),and potassium ion concentrations gotten by calculations. The acids used were of analytical grade.

2.2: Spectroscopic Method (AAS).

Procedure for Digestion:

In order to check for the presence of potassium ion content in the ash of red mangrove bark, 5g of the dry ash sample was weighed using an electronic weighing balance, and put into a beaker; 20ml of 1molar concentration of hydrochloric acid (HCl) was introduced into the beaker for the extraction of available minerals or metal. Thereafter, it was set on an electric heating mantle to heat to near dryness. The heated sample was allowed to cool; then it was filtered using a filter paper (Whiteman no 41), funnel and a calibrated measuring cylinder. Distilled water was added to make up to 50ml, after which the filtrate was transferred into a sample bottle. And was aspirated into the atomic absorption spectrophotometer using GBC avanta flame atomic absorption spectrophotometer version 2.02 and the result obtained is shown in table 2.

III. Results

Table 1: Physical parameters of the Red mangrove bark aqueous extract (RMBAE).

S/N	RMBAE	Observations
1	Color of solution	Umber
2	Touch of solution	Very slippery
3	Test with red litmus paper	Turns red litmus paper to blue

Table 2: AAS result of the measured potassium concentration in dry ash of red mangrove bark.

SAMPLE	POTASSIUM CONCENTRATION (PPM)
Dry ash of red mangrove bark(DARMB)	18,255.00

Table 3: Results of titration of CH_3COOH with 100g/500cm^3 RMBAE

Molarity of Acid (M)	Volume of Acid (Vcm^3)	Volume of RMBAE (Vcm^3)	Molarity of RMBAE (M)	Conc. RMBAE (g/dm^3)	Conc. K^+ (g/dm^3)	% purity both in 1000/500cm^3	% of k^+
0.5	19.00	25	0.3800	21.2800	14.8200	69.64	38.00

1.0	**10.375**	**25**	**0.4150**	**23.2400**	**16.1851**	**69.64**	**41.50**
1.5	**6.6667**	**25**	**0.4002**	**22.4112**	**15.6078**	**69.64**	**40.02**
2.0	**5.8125**	**25**	**0.4650**	**26.0400**	**18.1350**	**69.64**	**46.50**

Table 4: Results of titration of HCl with 100g/500cm^3 RMBAE

Molarity of Acid (M)	Volume of Acid (Vcm^3)	Volume of RMBAE (Vcm^3)	Molarity of RMBAE (M)	Conc. RMBAE (g/dm^3)	Conc. K^+ (g/dm^3)	% purity (%)	% of k^+
0.5	**25.00**	**25**	**0.500**	**28.0000**	**19.5000**	**69.64**	**50.00**
1.0	**15.33**	**25**	**0.6132**	**34.3392**	**23.8992**	**69.64**	**61.32**
1.5	**13.64**	**25**	**0.8182**	**45.8201**	**31.9100**	**69.64**	**81.82**
2.0	**7.26**	**25**	**0.5808**	**32.5248**	**22.6512**	**69.64**	**58.08**

Table 5: Results of titration of H_2SO_4 with 100g/500cm^3 RMBAE

Molarity of Acid (M)	Volume of Acid (Vcm^3)	Volume of RMBAE (Vcm^3)	Molarity of RMBAE (M)	Conc. RMBAE (g/dm^3)	Conc. K^+ (g/dm^3)	% purity (%)	% of k^+
0.5	**13.80**	**25**	**0.5520**	**30.9120**	**21.5280**	**69.64**	**55.20**
1.0	**7.25**	**25**	**0.5800**	**32.4800**	**22.6200**	**69.64**	**58.00**
1.5	**5.93**	**25**	**0.7122**	**39.8496**	**27.7524**	**69.64**	**71.22**
2.0	**5.94**	**25**	**0.9504**	**53.2224**	**37.0656**	**69.64**	**95.04**

Table 6: Summary of Potassium ion Concentration, Percentages and Percentage Purity in 100g/500cm^3 RMBAE

Molarity Of Acid (M)	CH_3COOH Conc.0f k^+ (g/dm^3)	HCl Conc.0f k^+ (g/dm^3)	H_2SO_4 Conc.0f k^+ (g/dm^3)	% purity In 500cm^3	CH_3COOH % of k^+ conc.(g/dm^3)	HCl % of k^+ conc. (g/dm^3)	H_2SO_4 % of k^+ conc. (g/dm^3)
0.5	**14.8200**	**19.5000**	**21.5280**	**69.64**	**38.00**	**50.00**	**55.20**
1.0	**16.1851**	**23.8992**	**22.6200**	**69.64**	**41.50**	**61.32**	**58.00**
1.5	**15.6078**	**31.9100**	**27.7524**	**69.64**	**40.02**	**81.82**	**71.22**
2.0	**18.1350**	**26.6512**	**37.0656**	**69.64**	**46.50**	**58.08**	**95.04**

Table 7: Results of Titrimetric Analysis of potassium ion Concentration in RMBAE with Statistical Evaluation (n = 4) in acid media (CH_3COOH, HCl and H_2SO_4)

Acids	Mean ± S.D	Coefficient of variance	Coefficient of standard error
CH3COOH	**16.1870 ± 1.4140**	**0.0757**	**0.7071**
HCl	**25.4901 ± 5.1954**	**0.1765**	**2.5977**
H_2SO_4	**27.2415 ± 7.0893**	**0.2254**	**3.5447**

IV. Discussion

The results in table 1 were in agreement with the known physical properties of a base, thus confirming that the aqueous extract from the red mangrove bark is a base (KOH). This also corroborated the previous work done by George et al.,(2014).

The AAS result further confirmed the presence of potassium ion in reasonably high quantities or concentrations in parts per million (PPM) in the red mangrove bark dry ash (DARMB),which is in agreement with other works done (Manikandan et al.,2009;George et al.,2014 and Mianpeuren et al.,2012). Furthermore, from tables 3 – 5, it was observed that the concentrations of potassium ion increased from 14.82g/dm^3 to 18.1350g/dm^3 in CH_3COOH, 19.50g/dm^3 to 31.91g/dm^3 in HCl and 21.528g/dm^3 to 37.0656g/dm^3 in H_2SO_4 respectively, as the acid concentration increased from 0.5 – 2M (CH_3COOH), 0.5 – 1.5M (HCl) and then reduced at 2M, but in H_2SO_4 increased from o.5 – 2M. The result also showed that 1.5M HCl, 2M (CH_3COOH and H_2SO_4) concentrations gave the highest amount of potassium ion concentrations in the acid range studied. The result also revealed that the organic acid (CH_3COOH) gave the lowest amount of potassium ion compared to the mineral acids (HCl and H_2SO_4) in the concentration range studied.

The low amount of potassium ion in CH_3COOH could be attributed to the partial or incomplete dissociation or ionization of CH_3COOH, to form CH_3COO^- and H^+. The CH_3COO^- spectator ion readily combines with potassium to form a water soluble complex of potassium acetate (CH_3COOK) which remained in solution. This complex formed reduces the total amount of K^+ available in the aqueous solution and exposes only a little fraction of the expected total available K^+ in solution, hence, the low concentrations obtained.

On the other hand, the high amount of potassium ion concentrations in the mineral acids could be attributed to the ability of the mineral acids to undergo complete ionization or dissociation in water to react with the KOH in RMBAE to produce KCl and K_2SO_4 salts and water only as neutralization products. The KCl and K_2SO_4 further dissociates in solution to form K^+/Cl^- and $2K^+/SO_4^{2-}$ spectator ions, thus exposing much of potassium ions in the uncombined form in solution.

Again, the inability of K^+ as spectator ion to be solvated by water and other negative ions present in solution had been implicated (George et al.,2014) .However,H_2SO_4 gave the best or highest potassium ions than HCl, this could be attributed to the stoichiometry and ionization steps of the acids. The basicity of the acid is another important reason for the observed results in the mineral acids. H_2SO_4 with a basicity of two gave the highest potassium ion concentration of 37.0656g/dm^3 (95%) compared to 31.91g/dm^3 (81.82%) 0f HCl with a basicity of one.

Furthermore, neutralization steps of the acids also played a major role. The polyprotic acid (H_2SO_4) has two neutralization steps while the monoprotic acid (HCl) has only one neutralization step. For H_2SO_4, the neutralization steps are shown below:

$H_2SO_4 + OH^- \rightarrow HSO_4^- + H_2O$ step (1).

$HSO_4^- + OH^- \rightarrow SO_4^{2-} + H_2O$ step (II).

From the above equations, it means that two moles of KOH would be required to completely neutralize one mole of H_2SO_4. Thus, for complete neutralization to take place, more moles of potassium ion will be exposed, hence, the observed result in H_2SO_4.

For HCl, the neutralization step is shown below:

$HCl + OH^- \rightarrow Cl^- + H_2O$ step (1).

Similarly, for complete neutralization to take place, equimolar amounts of HCl and KOH is required, hence, the observed results being lower than that of H_2SO4 that needed two moles of KOH.

The ability of acids to protonate tannin surfaces contained in red mangrove bark aqueous extract has been reported (Seey et al., 2012 and Karamac, 2009). These positively charged surfaces easily bond with anionic compounds like OH- present in solution but repel cations such as potassium, due to columbic forces of attraction, thus exposing more of potassium in the red mangrove bark aqueous extract. The equation of repulsion is shown below:

$SUR\text{-}OH + H_3O^+ \rightarrow SUR\text{-} OH_2^+ + H_2O$ equ (1)

Where SUR-OH denotes the surface of the tannins. These protonated tannins that are positively charged, bonds with anionic compounds like OH- present in solution, in this form:

$SUR\text{-}OH_2^+ + OH \rightarrow SUR\text{-}OH_2{+}OH^-$ equ(II).

But with cations, repulsion due to columbic forces of attraction occurs, thus exposing more potassium ion in solution as spectator ions. The equation of repulsion is shown below:

$SUR\text{-}OH_2^+ + K^+ \rightarrow SUR\ \text{–}OH_2^+/K^+$ equ(III).

Finally, the results in table 7 showed only small differences and low values of the co-efficient of variance and standard errors; Standard deviation about the mean was also very small. This is a confirmation that the method used was precise and accurate.

V. Conclusion

The proposed methods in acid media were successfully employed to estimate the amount of potassium ion concentration in red mangrove bark aqueous extract. The method was also new, simple, specific, cost effective, reliable, environmentally friendly, and reproductive. Maximal potassium ion concentration was obtained at 1.5M HCl, 2M (CH_3COOH and H_2SO4) concentrations, therefore, these acid concentrations are recommended as the best working concentrations in $100g/500cm^3$ RMBAE. However, H_2SO_4 is the best acid for best potassium ion amount determination from RMBAE. Finally, the purity level (69.64%) illustrated that the potassium ion concentration obtained from this plant is a good quality food additive with good nutritive and medicinal properties as a good salt (KCl) substitute for sodium chloride that causes high blood pressure. Similarly, CH_3COOK is also a good food additive, preservative and acidity regulator for acidic stomach, while K_2SO4 is used in fertilizer and chemical industries. This method could be employed for routine analysis of mineral composition in various plants, fruit extracts, vegetables etc.

References

[1]. Berenquer B, Sanchez L.M, Quile A, Lopez-Barrero M., de Haro, Galvez J.and Martin MJ. Protective and antioxidant effects of Rhizophora mangle L. agent NSAID-Induced gastric ulcers. J. Ethnophamacol 2006, 103(2):194-200

[2]. De Armas E,Sarracent Y,Marrero E,Femandez O,and Branford-White C. Efficacy of Rhizophora mangle aqueous bark extract (RMBAE) in the treatment of aphthous ulcers : a pilot study.Curr Med Res Opin.2005,21(11):1711-1715.

[3]. Duke NC (1992). Mangrove floristics and biogeography,in:Robertson AI,Alongi DM(eds).Tropical mangrove ecosystems, American geophysical union,Washington DC,pp 63-100.

[4]. Duke,JA and Wain,KK(1981). Medicinal plants of the world. Computer index with Editorales de la imprenta Nacional.Bogota

[5]. Debargha C., Subhajie B., Jayjit M., Santra S. (2008). Heavy metal pollution and phytoremediation potential of Avicennia officinalis L in the southern coast of the Hooghly estuarine systems. International journal of environmental science. 3(6): 2291-2303.

[6]. George DMC. Okpara K, Waribo HA.,(2014). Determination of potassium ion concentration in red mangrove (Rhizophora Mangle L) barks aqueous extract (RMBAE) in HCl. International journal of engineering and science research. 4(1):1-5.

[7]. Hogarth PJ (1999).The Biology of Mangroves. Oxford university press, New York.

[8]. Luz MSP,Arturo E,Caden S,Ma, AR and Betty M(2010). Pharmaceutical and toxicological evaluation of Rhizophora L., as a potential antiulcerogenic drug:chemical composition of active extract. Journal of pharmacy and phytotherapy, 2(4): 56-63

[9]. Kathiresan K., and Bingham BL.,(2001). Biology of mangroves and mangrove ecosystem; Advances in marine biology. 40:81-251.

[10]. Manikandan T, Neclakandan T. and Usha Rani G. Effects of salinity on the growth, photosynthesis and mineral constituents of the red mangrove Rhizophora Apiculata L seedlings.Recent Research in science and technology.2009,1(3): 134-141.

[11]. Magdalena Karamac.: Chelation of Cu(II), Zn(II), and Fe(II) by tannin constituents of selected edible nuts. Ini. J. Mol. Sci. 2009, 10: 5485-5497.

[12]. .Raman DJ., Jonathan MP., Srinivasalu S., Altrin JS.,Mohan ASP., and Mohan VR.,(2007). Trace metal enrichment in core sediments in muthupet mangrove.SE coast of India: Application of acid leachable technique, environmental pollution. 145:245-257.

[13]. Prabhakaran J and Karitha D.,(2012).Ethno medicinal importance of mangrove species of pitchavaram. International journal of research in pharmaceutical and biomedical sciences. 3(2):611-614.

[14]. Solomon Raja A.J.,Henry Jonathan K and Parnachandra Rao S. Traditional extraction of bark tannin from the mangrove tree,ceriops decandra(Griff.) Ding Hou and its uses in treating cotton fishing nets .Natural Product Radiance. 2008, 7(2): 173-175.

[15]. Tarkadjiel Mianpeuren, Mbaiguinam Mbailao, Ngaram Nambatingai, Mahmout Yaya and Allaramadji Ngarmadji.:Elemental compostion of vegetable salts from ash of four common plant species from Chad. International Journal of pharmacology. 2012, 8(6): 582-585

[16]. Seey, Tan Lean and Mohd Jain Noordin Mohd Kassim. Characterization of mangrove bark adsorbent and its application in the removal of textile dyes from aqueous solutions.Journal of applied phytotechnology in environmental sanitation. 2012, 1(3): 121-130.

[17]. Walter BB., Ronnback P., Kovacs JM Publiched date 03 May 2014., Crona B., Hussain SA., Badola R., Primavera JH., Barbier E and Dahdouh GF.,(2008). Ethno biology, socio-economic and management of mangrove forest: a review. Aquatic botany, 89:220-236.