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Archives of Applied Science Research, 2014, 6 (6):61-66
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Determination of potassium ion concentration in red mangrove (*Rhizophora Mangle L*) bark aqueous extract (rmbae) in buffer 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 of buffer solutions (pH 1-7) and the aqueous extract from the bark subjected to titration against standard HCl and CH_3COOH 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 generally low levels of potassium ion concentration (14.820gm/dm^3 and14.333gm) in all the buffer solutions with both titrants (HCl and CH_3COOH). This result was in agreement with the results of AAS result (18,255.00 ppm). 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) in buffer media. One way analysis of variance revealed significant differences in the nature of acid as a function of the amount of potassium ion produced. The result also revealed that the mineral acid (HCl) gave better potassium ion concentration than the weak or organic acid (CH_3COOH)..

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

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INTRODUCTION

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. 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, researchers have found that aqueous extract from the bark of red mangrove plant has large quantities of tannins (as high as 20-75% dry weight) which prevent damage from herbivores [1] and [2]. Mangrove extracts have been used for diverse medicinal purposes and have a variety of anti-bacterial, anti-herpetic and anti-helminthic activities [3].

Again, the extracts of some mangrove species indicated significant anti-oxidant activity due to the presence of condensed tannin compounds in them [4]. They reported that condensed tannin extracts from mangrove species have very good DPPH radical scavenging activity and ferric reducing power, hence, a good antioxidant.

The pharmacological and toxicological evaluation of red mangrove, as a potential antiulcerogenic drug: Chemical compositions of active extract have been studied [3].It was established that this plant is good in human medicines for the treatment of gastro duodenal ulcers in mice, due to its gastro protective and anti-secreetory potentials without any toxicological effects. Similarly, red mangrove bark aqueous extract can be employed in the treatment of aphthos ulcers to reduce the time to repair mucosal tissue and especially mouth mucosa healing [5] and [6].

Apart from tannins, researchers have shown that the extract of red mangrove bark aqueous extract contained different elements in varying concentrations. Some of these elements included potassium, sodium, calcium, magnesium, phosphorous and nitrogen [7] and [8].The importance of these mineral nutrients to man, soil, plants and chemical industries, can not be overemphasized. Potassium is one of the body's most important mineral nutrients. Its deficiency, or hypokalemia, causes a variety of problems, such as fatigue, muscle and nerve 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, through water transport in the xylem, maintain high density cell turgor pressure which affects water tolerance, cell elongation for growth and most importantly regulates the opening and closing of the stomata which affects transpirational cooling and carbon dioxide up take for photosynthesis. Studies have shown that conditions that lower potassium levels in the blood such as severe prolonged diarrhea and vomiting, hormone problems, and diuretics can be treated with salts of potassium (KNO_3). Potassium nitrate has been reported as an effective active ingredient in treating dentinal hypersensitivity [9] and [10].

Potassium is also needed in our chemical industries in the combined form to produce fertilizers, salts etc. All these sources deplete the normal supply and demand for potassium, hence, the need to find a cheaper, saver and reproductive alternative to getting potassium.

Recently, potassium ion concentrations have been isolated and determined in plant tissues especially in mangroves species [11]. But enough studies on red mangrove bark is lacking in buffer media. Therefore, this study is to determine potassium ion concentration in red mangrove (*Rhizophora mangle L*) bark aqueous extract (RMBAE) in buffer media using HCl and CH_3COOH.

MATERIALS AND METHODS

2.1 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. The collected barks were extensively washed with de-ionized water and air-dried in sun (solar drying) for 120 hours to remove water content in the sample. The dried sample was then converted to finely granulated ash by burning. Seven sets of accurately weighed 100gm of the finely granulated burnt ash were dissolved differently in 500cm^3 of buffered solution (pH 1-7), 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 solution of HCl and CH_3COOH(0.5-2.0M),and potassium ion concentrations gotten by calculations. The acids used were of analytical grade.

2.2 Preparation of Buffer Solutions (pH 1-7).

KCl/HCl, $KHPO_4$/NaOH and KH_2PO_4 buffer solutions were prepared by mixing adjusters with a known volume of primary salt solution, and made up to 200ml with distilled water (Robin & Stokes, 1968).

pH1(134.0ml of 0.2M HCl was added to 50ml of 0.2M KCl and watered to 200ml).pH 2 (13.0ml of 0.2M HCl was added to 50ml of 0.2M KCl and watered to 200ml).pH 3 (44.0ml of 0.1M HCl was added to 100ml of 0.1M potassium hydrogen phthalate and watered to 200ml). pH4 (0.2ml of 0.1M HCl was added to 100ml of 0.1M of potassium hydrogen phthalate and watered to 200ml). pH 5 (45.2ml of 0.1M NaOH was added to 100ml of 0.1M potassium hydrogen phthalate and watered to 200ml). pH 6 (11.2ml of 0.1M NaOH was added to 100ml of 0.1M KH_2PO_4 and watered to 200ml). pH 7 (58.2ml of 0.1M NaOH was added to 100ml of 0.1M of KH_2PO_4 and watered to 200ml).

2.3 SPECTROPHOTOMETRIC METHOD (AAS).

In order to check for the presence of potassium ion content in the dry ash of red mangrove bark, 5.00gm of the dry ash was dissolved in 10 cm^3 of aqua reaga (mixture of HCl and HNO_3) 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.

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 moist red litmus paper	Turns moist red litmus paper to blue

Table2. AAS result of the measured potassium concentration in dry ash of red mangrove bark.

SAMPLE	POTASSIUM CONCENTRATION (PPM)
Dry ash of red mangrove bark 5g(DARMB)	18,255.00

Table 3: Results of potassium ion concentrations (g/dm^3) by titrating HCl with 100gm/500cm^3 of RMBAE at various pH

HCl Conc.(M)	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7
0.5	10.764	14.664	13.894	10.657	7.020	10.628	9.653
1.0	10.686	13.416	11.505	11.018	7.800	10.920	9.360
1.5	10.881	14.157	10.530	12.139	8.580	11.846	12.285
2.0	10.462	14.820	10.335	13.063	7.8	10.14	9.555

Table 4: Results of Potassium Ion Concentrations (g/dm^3) by titrating CH_3COOH With 100gm/500cm^3 of RMBAE at various pH

CH3COOH Conc.(M).	pH1	pH2	pH3	pH4	pH5	pH6	pH7
0.5	9.213	11.456	5.021	4.729	5.119	8.678	7.605
1.0	10.628	14.333	6.338	6.630	6.045	10.530	8.190
1.5	9.653	13.455	6.291	7.898	9.068	8.775	8.044
2.0	11.505	13.455	8.970	11.505	7.02	9.360	8.970

Table5. Percentage purity of potassium ion in HCl and CH_3COOH

ACID CONCENTRATION(M)	% PURITY IN HCl	% PURITY IN CH_3COOH
0.5	69.64	69.64
1.0	69.64	69.64
1.5	69.64	69.64
2.0	69.64	69.64

Table 6: Results of percentages of potassium ion concentrations in various pH titrated with HCl and CH_3COOH respectively

HCl Conc. (M)	% in pH 1	% in pH 2	% in pH 3	% in pH 4	% in pH 5	% in pH 6	% in pH 7
0.5	27.6	37.6	35.6	27.3	18.0	27.3	24.8
1.0	27.4	34.4	29.5	28.3	20.0	28.0	24.0
1.5	27.9	36.3	27.0	31.1	22.0	30.4	31.5
2.0	26.8	38.0	26.5	33.5	20.0	26.0	24.5
CH3COOH Conc.(M)	**% in pH 1**	**% in pH 2**	**% in pH 3**	**% in pH 4**	**% in pH 5**	**% in pH 6**	**% in pH 7**
0.5	23.6	29.4	12.8	12.1	13.1	22.3	19.5
1.0	27.3	36.8	16.3	17.0	15.5	27.0	21.0
1.5	24.8	34.5	16.1	20.3	23.3	22.5	20.0
2.0	29.5	34.5	23.0	29.5	18.0	24.0	23.0

Table 7: Results of titrimetric analysis of potassium ion concentration in RMBAE with Statistical Evaluation (n=28)

Acid	Mean ± SD	Coefficient of Variance	Standard Error
HCl	11.0272 ± 2.0230	0.1809	0.3836
CH_3COOH	8.9815 ± 2.5718	0.2846	0.4860

Table 8: Single factor analysis of variance for HCl titrant

ANOVA Table						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	89.84768571	6	14.9746143	14.6741951	1.5038E06	2.572711641
Within Groups	21.429925	21	1.02047262			
Total	111.2776107	27				

Table 9: Single factor analysis of variance for CH_3COOH titrant

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	126.6222429	6	21.1037071	8.51599784	9.1981E-05	2.572711641
Within Groups	52.040625	21	2.478125			
Total	178.6628679	27				

DISCUSSION

The results in table 1 were in agreement with the physical properties of a base, thus confirming that the aqueous extract from the bark of red mangrove is a base (KOH).

The AAS result confirmed the presence of potassium ion concentration in parts per million(ppm) in the red mangrove bark dry ash(RMBDA),which is in agreement with the works done previous scientist[7,8,11].

Furthermore, from tables 3 and 4 it was observed that the concentrations of potassium ion were higher in all the pH ranges studied except at pH5 (7.020-8.580g/dm^3).However, pH2 had the highest potassium ion concentration of 13.416-14.820g/dm^3 with the best concentration at 2M HCl (14.820g/dm^3). Similarly, same trend was observed in CH_3COOH. Potassium ion concentrations were higher in all the pH ranges studied except at pH3 (5.021-8.970g/dm^3). However, pH2 had the highest potassium ion concentration of 11.456-14.333g/dm^3, with the best at 1M CH_3COOH concentration (14.333g/dm^3). It can therefore be inferred that 2.0 M HCl and 1M CH_3COOH concentrations are the best concentrations for the determination of potassium ion from red mangrove bark aqueous extract in buffer media. The result also revealed that the mineral acid (HCl) gave the highest potassium ion concentration than the organic acid (CH_3COOH) in the concentration ranges studied.

The high amount of potassium ion in the mineral acid could be attributed to the ineffectiveness of the KCl/HCl buffer system to reduce the no of H^+ present in solution while increasing the no of K^+ and Cl^- spectator ions, thus exposing much of potassium ion in the uncombined form in solution. Again, the inability of K^+ as spectator ion to react with the buffer and other negative ions that might be present in solution could also be implicated unlike in the organic acid. The conjugate base CH_3COO^- has the ability to bind to K^+ in solution to form CH_3COOK, and thus reduced the total amount of K^+ exposed accounts for the observed result in CH_3COOH.

Furthermore, it could be attributed to the ability of the mineral acid to undergo complete ionization unlike the organic acid in solution and the molar concentration used.
Red mangrove bark aqueous extract contained large amount of tannins (hydrolysable, condensed and combined forms), which are polyphenols [12-14]. According to them, these numerous hydroxyl groups in the molecule of red mangrove bark aqueous extract represented main active sites for binding of ionic compounds. The observed result could be attributed to the ability of tannins (acidified hydroxyl phenols) to bond to other ions in solution in preference to potassium to the moiety, thus exposing more of K^+ in solution in the free state.

Tannins are easily protonated by acids during titration [12, 15-16]. This positively charged surface easily bond with anionic compounds like OH- present in solution but repels cations such as K^+, due to columbic forces of attraction. When this happens, more K^+ is exposed. The equation of the reaction is shown below:

At pH 2

$SUR - OH + H_3O^+ \rightarrow SUR - OH_2^+ + H_2O$ Equ (1)

Where SUR─ OH denotes the surface of the tannins. These protonated tannins that is positively charged, repels cat ions like K^+ due to columbic forces of attraction, thus exposing more of K^+ in solution as spectator ions. The equation of the repulsion is shown below:

$SUR - OH_2^+ + K^+ \rightarrow SUR - OH_2^+/K^+$ Equ (2).

Finally, the interference of other ions in solution with K^+ to masking it and hence reduce the amount that would have been exposed as spectator ions, is another major factor for the general low levels of potassium ion in the red mangrove bark aqueous extract as shown in their percentages values.

The result in table 5 showed that the percentage purities of potassium ion were constant (69.64) both in HCl and CH_3COOH using 100gm of dry ash of red mangrove bark. However, the constant value of percentage purity explained that percentage purity from red mangrove bark aqueous extract is not depend on acid concentration and type, but rather on the dry mass. Since the dry ash used was of equal weights, there will be no difference in percentage purity. The percentages of potassium ion obtained from red mangrove bark aqueous extract was generally low as shown in table 6.

To ascertain whether there is significant difference in the type or nature of acid used in the determination of potassium ion concentration in buffer media at various pH studied, statistical analysis of variance for single factor experiment, using F-distribution, was carried out on both acids as shown in tables 8 and 9 at 95% confidence level. From the anova table it can be seen that the sum of squares between for HCl is 89.8477, while the sum of square within is 21.4299. This gives us mean square value of 14.9746 and 1.0205, respectively. Similarly, the sum of squares between in CH_3COOH is 126.6224, while the sum of squares within is 2.4781. This gives us mean square values of 21.1037, and 2.4781 respectively.

The Mean Square Ratio (MSR) calculated for HCl is 14.6742, while the tabulated value is 2.5727. Similarly, at the same confidence level, the Mean Square Ratio for CH_3COOH is 8.5160 and the tabulated value remains as 2.5727. Since in the two cases, the calculated MSR is greater than the tabulated value, it implies that there is a significant difference ($p<0.05$) in the type of acid used. Hence, the mineral acid gave higher concentrations of potassium ion than the organic acid or weak acid (CH_3COOH) as was reported earlier.

CONCLUSION

The proposed methods were successfully employed to estimate the amount of potassium ion concentration in red mangrove bark aqueous extract in buffer media. The method was also simple, specific, reliable, environmentally friendly, and reproductive. Maximal potassium ion concentration was obtained at 2M HCl and 1M CH_3COOH concentrations, therefore, they are recommended as the best working concentrations for determination of potassium ion from red mangrove bark aqueous extract (RMBAE) in buffer media. However, the mineral acid (HCl) gave better potassium ion concentration than the weak or organic acid (CH_3COOH). Red mangrove bark apart from being a sink for heavy metals, are a major plant and natural source for scarce potassium ion. Finally, the purity level (69.64%) indicates that the obtained potassium ion 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 acid regulator for acidic stomach. Hence, the proposed methods could be employed for routine analysis of mineral composition in various plants, fruit extracts, vegetables etc.

Acknowledgment
We wish to express our profound gratitude to Linda Weje and Nnamoko Sunday for assisting in the collection of the red mangrove bark and processing.

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