Journal of Applied Chemistry

ENRICHED PUBLICATIONS

Journal of Applied Chemistry

Aims and Scope

Journal of Applied Chemistry is a peer-reviewed, journal that publishes original research articles as well as review articles related to all aspects of applied chemistry. These includes the fields of analytical, inorganic, organic, physical and applied chemistry area. Review articles discussing specific areas of chemistry of current chemical importance are also published.

The journal welcomes publications of high quality papers on theoretical developments and practical applications in applied chemistry. Original research papers, state-of-the-art reviews, and high quality technical notes are invited for publications.

Journal of Applied Chemistry

Managing Editor
Mr. Amit Prasad

Dr. Alok Maitani SBS PGI, Balawala, Dehradun alok_maithanii@rediffmail.com	Ian S. Haworth University of Southern California ihaworth@usc.edu
Dr. Aiman Ahmad Faculty of Engineering and Technology Aligarh Muslim University Aligarh-202002 aiman.ahmad1@gmail.com	Dr. Manjeet Singh Barwa Assistant Professor at Bhaskaracharya College of Applied Science, University of Delhi, Dwarka. manjeetbarwa@gmail.com

Dr. Deepak Gupta
Assistant Professor Bhaskaracharya College
of Applied Sciences, New Delhi, Dwarka
deepakg2003@gmail.com

Advisory Board Member

Pratik M Tailor
Maliba Pharmacy College,
Department of Quality Assurance, Surat
pratikmtailor@gmail.com

Journal of Applied Chemistry

(Volume No. 6,   Issue No. 2, May - August 2020)

Contents

Effect of Acid and Ionic Strength on the Kinetics of Electron Transfer Reaction of N-(2-Hydroxy-Ethyl) Ethylenediamine-n, N', N'-Triacetatocobaltate (ii) Complex with Hypochlorite Ion in Aqueous Acidic Medium

Y. Ahmed [1*], A. D. Onu [2], S. O. Idris [3], S. S. Iliyasu [3], Y. B. Abiti [3]

1 Department of Chemistry Kano University of Science and Technology, Wudil-Kano
2 Department of Chemistry Federal College of Education, Zaria
3 Department of Chemistry Ahmadu Bello University, Zaria
*Corresponding author E-mail: bnahmad20@yahoo.com

A B S T R A C T

The influence of acid and ionic strength on the rate of electron transfer reaction of N-(2-hydroxy-ethyl)ethylenediamine-N,N',N'- triacetatocobaltate(II)(hereafter,[Co(II)HEDTA(OH2)]−) complex with Hypochlorite ion in aqueous nitric acid medium have been stud- ied at I = 0.2 mol dm-3(NaNO3), [H+] = 1 × 10-2 mol dm-3, , T = 300 ± 1 K and λmax = 525 nm. Stoichiometric study showed 1:1 `mole ratio. The rate law derived from the kinetic study under pseudo first order condition is d [Co(III)HEDTA(OH2)] = k [Co₂(II)HEDTA−][ClO−].
$$\frac{}{dt}$$

The rate constant of reaction, k2 varies inversely with acid concentration, [H+]. The overall rate law is therefore represented as:

$\frac{d[Co(III)HEDTA(OH2)]}{dt} = 2.28 \times 10−4[H+]−1[Co₂(II)HEDTA(OH)−][ClO−].$ The reaction

displayed positive salt effect which suggests the activated complex was made up of similar charged species. The reaction was catalysed by addition of formate, HCOO- and potassium, K+ ions and the Michaelis-Menten's plot gave zero intercept indicating the absence of intermediate complex. A reaction mechanism via an outer-sphere pathway is proposed for this reaction.

Keywords: Aminocarboxylate; Electron Transfer Reaction; Hyphochlorite; Ionic Strength; Kinetics.

1. INTRODUCTION

Aminopolycarboxylic acids form strong complexes with metal ions when its acidic protons are lost (Anderegg et al., 2005). This property makes it useful complexone in a wide variety of chemical, environmental and medical applications (Michihiko and Sakayu, 1999; Vuckovic et. al., 2011 and Onu et al., 2009, 2011, and 2015). Metal amino carboxylate complexes are used to study phenomenon of the structure, stability, magnetic properties and non-covalent interactions, molecular recognition and regulation of biochemical processes (Vuckovic et. al., 2011). These properties play an important role in metalloenzyme catalyzed reactions. Typical example of the complex- es is N-(2-hydroxy-ethyl) ethylenediamine-N, N', N'-triacetatocobaltate (II) ion. Despite the applications of these important complexes, there is a paucity of information on the kinetics of electron transfer reaction of aminocarboxylatocobalt (II) with oxyanions such as hypo- chlorite ion, ClO- though, other researchers

(Onu et al., 2008, 2009, 2015 and 2016; Naik et al., 2007 and 2010 and Mansour, 2003) have carried out the study using different oxidants. Both inner-sphere and outer-sphere have been reported in these works. Moreover, ClO- ion is the strongest oxidizing agent of the chlorine oxyanions (Mohammed et al., 2010), thus its reaction with this complex will give us more insight on the mechanism of oxidation of the complex. The kinetic study of these complexes may be used as a model in understanding the mechanism of oxygen transport and metalloenzyme reactions in biological systems (Vuckovic et al., 2011). Also, the study will be used as simple models to understanding or to mimic the biochemical pathways of some metabolic processes which involve the use of co- enzymes.

The interest in this research is to study the influence of acid and ionic strength on the rate of electron transfer reaction of N-(2-hydroxy- ethyl) ethylenediamine-N, N',N'-triacetatocobaltate(II) complex with hypochlorite ion in aqueous nitric acid medium with hope the study will complement much needed kinetic information in the field and highlight more on the pathway of the reaction.

2. EXPERIMENTAL

All chemicals and reagents used were of analar grade and distilled water was used in preparing the solutions. While sodium nitrate was used to maintain and investigate the influence of ionic strength of the reaction medium, Nitric acid was used for the investigation of ef- fect of hydrogen ion on the reaction rate. N-(2-hydroxy-ethyl)ethylenediamine-N, N', N'-triacetatocobalt(II) complex (hereafter, $[Co(II)HEDTA(OH_2)]^-$) and sodium hypochlorite (NaClO-) were the reductant and oxidant respectively. The $[Co(II)HEDTA(OH_2)]^-$ was prepared according to the method adopted by Onu et al., (2015). This gave λ_{max} of 526 nm after characterization using Cary series 300 Uv-Vis spectrophotometre in the wavelength range of 400 – 800 nm. Stock solution of various reagents were prepared by dissolving accurately weighed amounts of each in a known volume of distilled water.

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method (Onu et al., 2009, 2010, and 2015). The concentration of $[Co(II)HEDTA(OH_2)]^-$ was kept constant at 5.0×10^{-3} mol dm^{-3} while that of ClO- was varied from 4 folds below and above. The reactions were allowed to go to completion at constant [H+] (HNO3 = 1.0×10^{-2} mol dm-3), ionic strength (NaNO3 = 0.1 mol dm^{-3}), λ_{max} = 525 nm T = 300 ± 1 K. The stoichiometry (indicated by the point of inflexion) of the reaction was de- termined from the plot of absorbance against mole ratio [ClO-]/ [Co(II)HEDTA(OH2)−]

The rate of the reaction was monitored by recording the change in absorbance at 525 nm on a Sherwood Colorimeter 254. The kinetic study was carried out under pseudo-first order conditions with the

concentration of [Co(II)HEDTA(OH$_2$)−] = 5.0 × 10^{-3} mol dm^{-3} and that of the oxidant, ClO- in at least 12-fold excess over the reductant at temperature of 300 ± 1 K, ionic strength of 0.5 mol dm^{-3} and [H+] = 1.0 × 10^{-2} mol dm^{-3}. Pseudo-first order rate constants (kobs) for the reactions were obtained from slope of the plots of log (A$_\infty$-A$_t$) versus time. Where A$_\infty$ is the absorbance at infinity and At is the absorbance at time t. The order with respect to the oxidant concentration ([ClO$^-$]) was determined from the slope of the plots of log kobs versus log [ClO$^-$]. The second order rate constants, k$_2$ were obtained from kobs as kobs/[ClO-] and the results are presented in Table 1.The effects of change in acid concentration, ionic strength on the reaction rate were studied under the reaction condition stated in Table 2 and 3 respectively. Effect of added ions is investigated and reported in Table 4 to help us assign the mechanistic pathway for the reaction. Likely presence of free radical species was tested by the addition of 5.0 cm^3 of acrylamide to a partially oxidized reaction mixture.

3. RESULT AND DISCUSSIONS

The result of spectrophotometric titration showed that one mole of the reductant was oxidised by one mole of the oxidant. This is in con- formity with stoichiometric equation presented in Equation 1:

$$[Co(II)HEDTA(OH_2)]− + ClO− 2H+ \rightarrow [Co(III)HEDTA(OH)_2] + 1 C_2l_2 + H O_2 \quad (1)$$

This stoichiometry (1:1) may be attributed to the fact that, one mole of electron was transferred in the reaction of complex to form Co (III) complex. Similar results have been reported in converting Mn(III) to Mn(V) during the Jacobsen epoxidation reaction and in the conversion of Ce^{3+} to Ce^{4+} (Perumareddi et al., 2003) which involved hypochlorite ion. The spectrum of the reaction product showed two maxima at 381 and 534 nm using Carey series 300 Uv-Vis spectrophotometre in the wavelength range of 400 – 800 nm. This is typical spectrum of Co (III) (Abdel-Khalek et al., 1993; Mansur, 2003; Perveen et al., 2013 and Onu et.al., 2009, 2015 and 2016).

The pseudo – first order plots was linear to more than 70% extent of the reaction which suggests a first order dependence of rate on[Co(II)HEDTA(OH$_2$)−]. The slope obtained from the logarithmic plot of kobs versus [ClO-] was 1.03 indicating first order dependence with respect to [ClO-].The reaction is second order overall at constant [H+] concentrations. Therefore the rate equation for the reaction is

$$\frac{d[Co(III)HEDTA(OH2)]}{dt} = k [C_2o(II)HEDTA(OH)−]_2[ClO−] \quad (2)$$

Where k$_2$ = (3.13 ± 0.09) × 10$_{-2}$dm$_3$ mol$_{-1}$ s$_{-1}$

Variation in hydrogen ion concentration showed that the reaction rate decreased with increase in [H$^+$] within the concentration range investigated. This inverse relationship implies that there is deprotonation

pre-equilibrium step and the rate determining step involves both the deprotonated and undeprotonated species (Wilkins, 2002 and Onu et al., 2009, 2015 and 2016).

Similar inverse dependence on the acid has been reported (Onu et al., 2009, 2015 and 2016) for reaction involving this complex with oxyanions. The slope obtained from the plot of log k_1 vs [H^+] was -0.70, indicating negative first order with respect to acid concentration. Also plot of k_2 vs [H^+] - was linear with zero intercept. The overall rate equation showing acid dependence effect is represented in Equa- tion 3:

$$\frac{d[Co(III)HEDTA]}{dt} = (a[H+]-1)[Co(II)HEDTA-][ClO-] \qquad (3)$$

Where $a = 2.280 \times 10^{-4} \, dm^3 \, mol^{-1} \, s^{-1}$

The observed first order dependence of the reaction rates on both [reductants] and [ClO-] is a common feature of hypochlorite ion reac- tions (Jiann-Kuo, 1987; Idris et al., 2015).
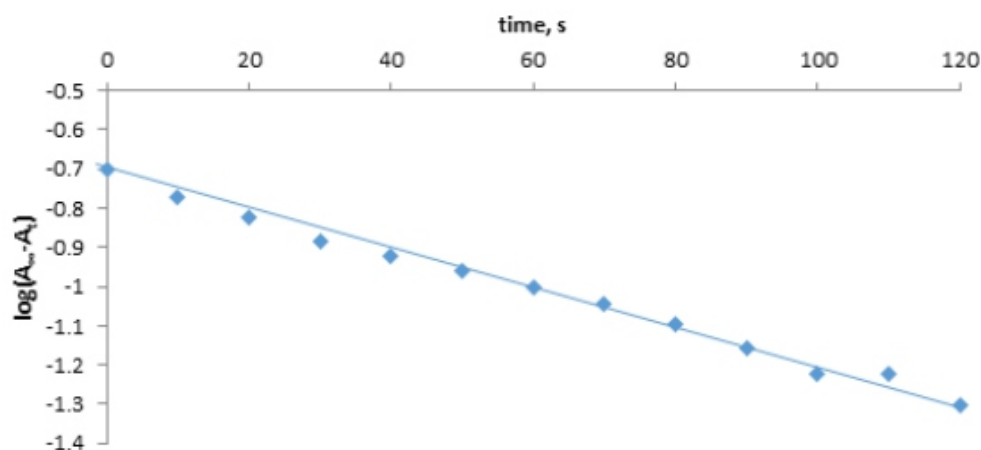
Fig. 1: Typical Pseudo-First Order Plot for the Reaction.

Table 1: The Pseudo-First Order And Reaction Rate Constants for the Reaction of [Coiihedta (OH$_2$)]⁻ and Clo⁻ at [Coiihedta (OH$_2$)⁻] = 5.0×10^{-3}mol Dm⁻³, T = 300 ± 1K and Λmax = 525 Nm

10^3 [ClO⁻], mol dm⁻³	10^3 [H^+] mol dm⁻³	10 I mol dm⁻³	10^3 kobs S-1	10^2 k2 dm³ mol⁻¹S⁻¹
50	10	2	1.6	3.2
60	10	2	1.8	3
70	10	2	2.1	3
80	10	2	2.5	3.2
90	10	2	2.8	3.1
100	10	2	3.2	3.2
110	10	2	3.5	3.2
120	10	2	3.7	3.1

Table 2: Effect of Acid on the Reaction Rate for the Reaction of [Coiihedta (OH$_2$)]$^-$ and Clo$^-$ at [Coiihedta (OH$_2$)$^-$] = 5.0 × 10^{-3}mol Dm^{-3}, T = 300 ± 1K and Λmax = 525 Nm

10^3[ClO$^-$], mol dm^{-3}	10^3[H$^+$] mol dm^{-3}	10 I mol dm^{-3}	10^{3}kobs S-1	10^{2}k2 dm^{3}mol^{-1}S^{-1}
90	6	2	4	4.4
90	8	2	3.4	3.8
90	10	2	2.7	3
90	12	2	2.4	2.6
90	14	2	2.1	2.4
90	16	2	1.8	2
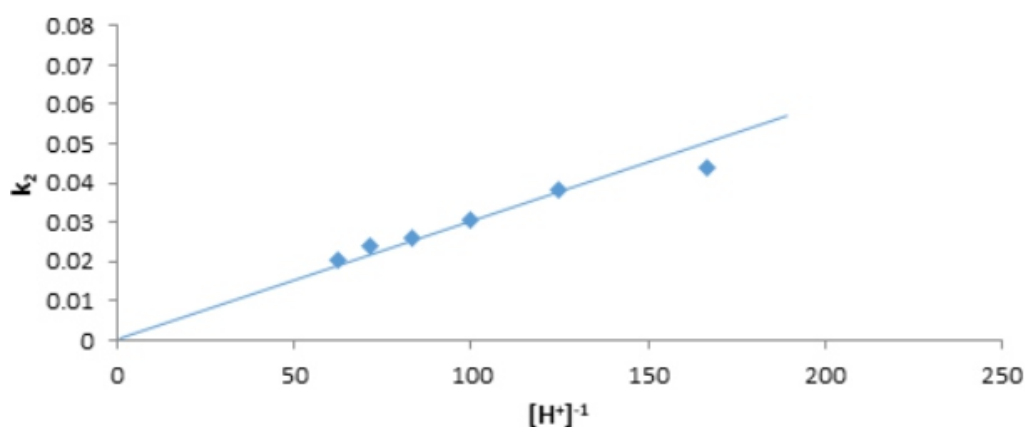
Fig. 2: Plot Of K$_2$ Versus [H$^+$]$^{-1}$ for the Reaction at [Coiihedta(OH$_2$)$^-$] = 5.0 ×10^{-3}mol Dm^{-3}, Clo$^-$ = 9.0 × 10^{-2}mol Dm^{-3}, I = 0.2 Mol.

Table 3: Effect of Ionic Strength of the Medium on the Reaction Rate for the Reaction of [Coiihedta(OH$_2$)]$^-$ and Clo$^-$ at [Coiihedta(OH$_2$)$^-$] = 5.0 × 10^{-3}mol Dm^{-3}, T = 300 ± 1K and Λmax = 525 Nm

10^3 [ClO$^-$], mol dm^{-3}	10^3 [H$^+$] mol dm^{-3}	10 I mol dm^{-3}	10^3 kobs S-1	10^2 k2 dm^{3}mol^{-1}S^{-1}
90	10	2	2.9	3.2
90	10	3	3.2	3.6
90	10	4	3.8	4.2
90	10	5	3.9	4.4
90	10	6	4	4.5
90	10	7	4.3	4.8
90	10	8	4.8	5.3
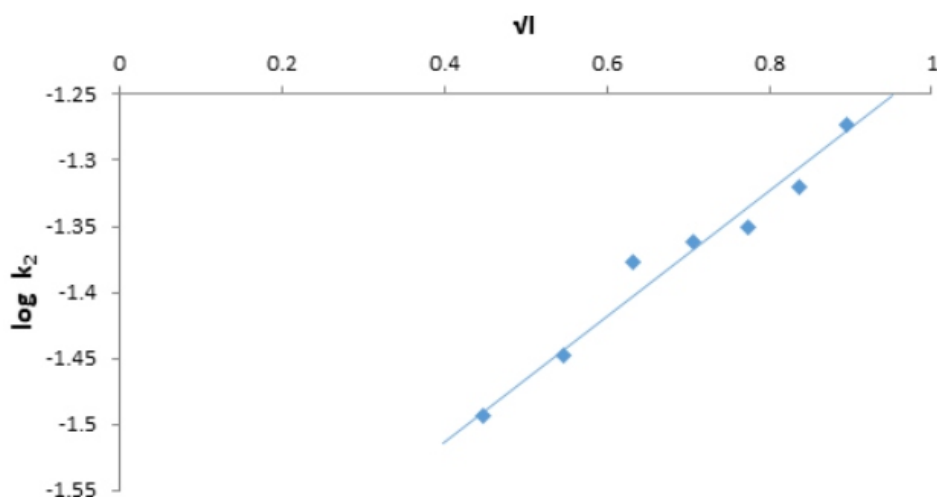
Fig. 3: Plot of Log K$_2$ versus √I for the Reaction.

Table 4: Effect of Added Anions on the Reaction Rate of [Co (II) HEDTA (OH$_2$)]$^-$ with Clo$^-$ at [Co (II) HEDTA (OH$_2$)$^-$] = 5.0 × 10^{-3} mol Dm^{-3}, [Clo$^-$] = 9.0 × 10^{-2} mol Dm^{-3}, I = 0.2 Mol Dm^{-3}, T = 299 ± 1K and Λmax = 525 Nm

X	10^2 [X], mol dm^3	103kobs, s-1	10^2k2, dm^3 mol^{-1} s^{-1}
HCOO$^-$	0	2.76	3.07
	1	2.7	3
	2	2.63	2.92
	3	3.02	3.36
	4	2.84	3.16
	5	2.58	2.87
K+	0	2.76	3.07
	1	2.78	3.09
	2	3.03	3.36
	3	2.46	2.74
	4	3.13	3.48
	5	3.22	3.58

Fig. 4: Michaelis-Menten Plot for the Reaction

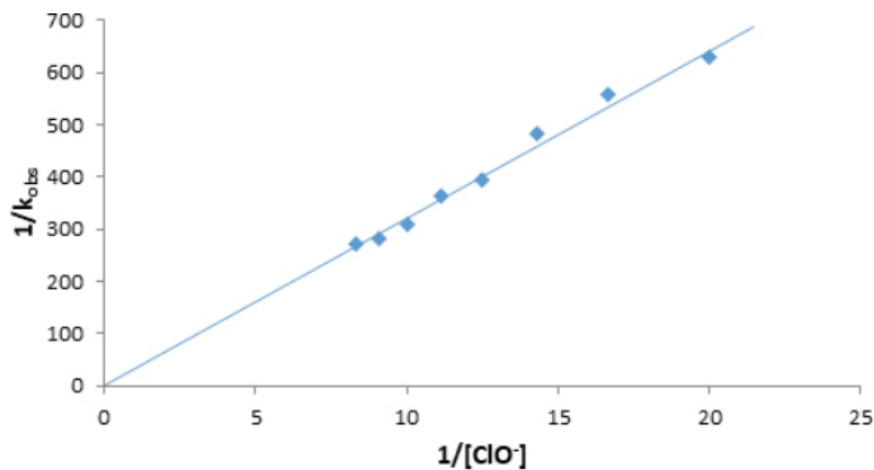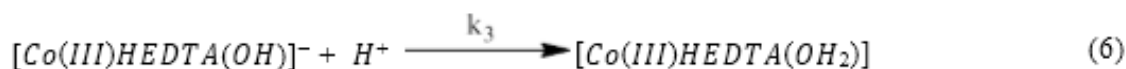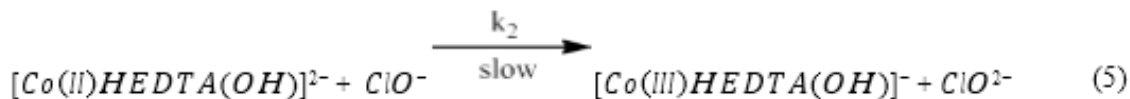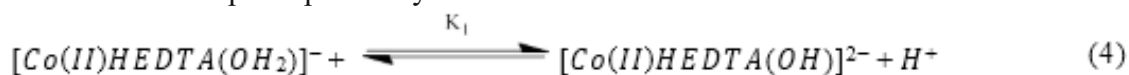The rate of the reaction increased with increase in ionic strength of the reaction medium in the concentration range investigated (Table 3) suggesting positive Bronsted-Debye salt effect (Benson, 1969). This shows that there may be the presence of similar charged species during the formation of activated complex (Atkins and de Paula, 2002) for the reaction. Positive value of the slop of plot of log k2 versus $\sqrt{}$ I (Figure 3.0) supported the presence of two similar charged species at the rate determining step.

The rate of reaction was found to decrease by the addition of formate ion and increase with addition K+ ion. The result is presented in Table 4. This showed that the reaction is catalysed by the presence of both added cation and anion which implies that an outer-sphere mechanism is likely to be in operation. This may be supported by the Michaelis - Menten plot of 1/kobs versus 1/ClO- which had zero intercept suggesting the absence of an intermediate in the rate determining step, thus, an outer-sphere mechanism is likely to be in opera- tion. The free radical species was not detected as the reaction progresses evidenced by absent of gel formation upon addition 5.0 cm3 of acrylamide.

In view of the above results obtained and discussions, the following reaction mechanism is hereby proposed via an outer-sphere path- ways:

$$[Co(II)HEDTA(OH_2)]^- + \xrightleftharpoons{K_1} [Co(II)HEDTA(OH)]^{2-} + H^+ \tag{4}$$

$$[Co(II)HEDTA(OH)]^{2-} + ClO^- \xrightarrow[slow]{k_2} [Co(III)HEDTA(OH)]^- + ClO^{2-} \tag{5}$$

$$[Co(III)HEDTA(OH)]^- + H^+ \xrightarrow{k_3} [Co(III)HEDTA(OH_2)] \tag{6}$$

$$ClO^{2-} + 2H^+ \xrightarrow{k_4} \frac{1}{2}Cl_2 + H_2O \tag{7}$$

$$\frac{d[Co(III)HEDTA(OH_2)]}{dt} = k_2[Co(II)HEDTA(OH)^{2-}][ClO^-] \tag{8}$$

$$\text{But } [Co(II)HEDTA(OH)^{2-}] = \frac{K_1[Co(II)HEDTA(OH_2)^-]}{[H^+]} \tag{9}$$

$$\text{Hence,} \frac{d[Co^{(III)}HEDTA(OH_2)]}{dt} = \frac{K_1k_2}{[H]^+}[Co(II)HEDTA(OH)^-][ClO^-] \tag{10}$$

This is analogues to Eq. 3, where a = K$_1$k$_2$

4. CONCLUSION

The influence of acid and ionic strength on the rate of electron transfer reaction of N-(2-hydroxy-ethyl)ethylenediamine-N, N',N'- triacetatocobaltate(II) complex with hypochlorite ion in aqueous nitric acid medium was carried out. While the rate of the reaction was found to increase with increase in ionic

strength of the reaction medium, the rate was inversely dependent on acid concentration, [H+]. The experimental data showed that, the electron transfer reaction proceeds through outer-sphere mechanism and a plausible mechanistic pathway which explained the data was proposed for the reaction.

ACKNOWLEDGEMENT

REFERENCES

[1] Anderegg, G.; Arnaud-Neu, F.; Delgado, R.; Felcman, J.; Popov, K. (2005). "Critical evaluation of stability constants of metal complexes of com- plexones for biomedical and environmental applications* (IUPAC Technical Report)". Pure Appl. Chem. 77 (8): 1445–1495. https://doi.org/10.1351/pac200577081445.

[2] Michihiko, K. and Sakayu, S. (1999). Cobalt proteins. European journal of Biochemistry. 261(1), 1- 9. https://doi.org/10.1046/j.1432- 1327.1999.00186.x.

[3] Vuckovic, G.; Antonijevic-Nikolic, M.; Tanaskovic, S.B.; and Zivkovic-Rodovanovic, V. (2011). New Cu (II) and Co (II) octaazamacrocyclic complexes with 2-amino-3-phenylpropanoic acid. J. serb. Hem Soc. 76(5), 719 – 731. https://doi.org/10.2298/JSC101201062V.

[4] Onu, A.D., Iyun, J.F. and Idris, S.O. (2009) The Kinetics of the Reduction of Tetraoxoiodate (VII) by n-(2-Hydroxyethyl) Ethylenediaminetri- acetatocobaltate(II) Ion in Aqueous Perchloric Acid. Transition Metal Chemistry, 34, 849-853. https://doi.org/10.1007/s11243-009-9273-1.

[5] Onu, A. D. (2010) Kinetics and mechanism of redox reactions of two aminocarboxylatocobaltate (II) compexes with oxy-anions and hydrogen per- oxide in aqueous acidic medium. PhD. Dessetation Ahmadu Bello University Zaria, Nigeria.

[6] Onu, A.D., Iyun, J.F. and Idris, O.S. (2015) Kinetics and Stoichiometry of the Reduction of HydrogenPeroxide by an Aminocarboxylactocobaltate (II) Complex in Aqueous Medium. Open Journal of Inorganic Chemistry, 5, 75-82. https://doi.org/10.4236/ojic.2015.54009.

[7] Onu, A.D., Iyun, J.F. and Idris, S.O. (2008). Reduction reaction of [CoHEDTAOH2]- with NO2- in aqueous perchloric acid medium: Kinetics and Mechanisms, CHEMCLASS Journal Zaria.

[8] Onu, A.D., Iyun, J.F. and Idris, S.O. (2016). Oxidation of ethylenediaminetetraacetatocobaltate (II) complex by hydrogen peroxide in aqueous acid- ic medium: A Kinetics study, J. Chem. Soc. Nigeria, 41(2) 81 – 86.

[9] Naik, R. M., Srivastava, A., Tiwara, A. K., Yadav, S.B. S. and Verma, A. K. (2007). Kinetic and mechanism studies of amine-n-polycarboxylates complexes of cobalt (II) by periodate ions in aqueous mrdium. J. Iran. Chem. Soc., 4(1): 63 – 71. https://doi.org/10.1007/BF03245804.

[10] Naik, R.M.; Kumar, B.; Rai, J.; Rastogi, R. and Yadav S.B.S. (2010). Kinetics and mechanism of oxidation of hexamethylenediaminetetraacetato- cobaltate(II) complex by periodate ion in aqueous medium. E-journal of chemistry, 7(51), 5391 – 5399. https://doi.org/10.1155/2010/180576.

[11] Mansour, A.M. (2003) Kinetics and Mechanism of the Oxidation of [N-(2-Hydroxyethyl) Ethylenediamine-N',N',N'-Triacetatocobalt(II) by Vana- date Ion. Transition Metal Chemistry, 28, 276-279. https://doi.org/10.1023/A:1022966528585.

[12] Mohammed, Y., Iyun, J.F. and Idris, S.O. (2010). Silver – catalyzed proxydisulphate oxidationof malachite green in aqueous acidic medium: Kinet- ic and mechanistic approach.International Journal of Chemistry, 20(2), 105 – 112

[13] Perumareddi, J.R., Ramachandra, V.R., Rayudu, G.V.S., Bunzli, J.C.G. and Vinny, R.S. (2003). Modern Aspects of Rare Earths and their Com- plexes. (1st Ed.). Burlington Elsevier. p. 38. ISBN 0080536689

[14] Abdel-Khalek, A.A., Khalil, M.M. and Khaled, E.S.H. (1993) Kinetics of Oxidation of [N-(2-hydroxyethyl)-Ethylene-Diamine-N, N', N'- Triacetato] Cobalt (II) by N Bromosuccinimide. Transition Metal Chemistry, 18, 153-157. https://doi.org/10.1007/BF00139946.

[15] Perveen, A.; Nezemoleslam, T. and Naqvi, I.I. (2013). Preparation of cobalt(III) complexes with trans-1,2-diaminocyclohexane-N,N,N',N'- tetraacetic acid (CDTA) and ethylenediamminetetraacetic acid (EDTA), African Journal of Pure and Applied Chemistry.7(6).218-224.

[16] Jiann-Kuo W. (1987). Kinetics of the Reduction of hypochlorite ion. Journal of Electrochemical Society Volume 134, Issue 6, 1462-1467. https://doi.org/10.1149/1.2100690.

[17] Idris, S.O., Tanimu, A., Iyun, J.F. and Mohammed, Y. (2015). *Kinetics and mechanism of malachite green oxidation by hypochlorite ion in aque- ous acidic medium. American Chemical Science Journal, 5(2): 185-193. https://doi.org/10.9734/ACSJ/2015/12705.*

[18] Wilkins R.G. (2002): *Kinetics and mechanism of reactions of transition metal complexes, 2nd Ed., Wiley-VCH Verlag GmbH &Co., pp. 65-130.*

[19] Benson, D. (1969). *Mechanism of inorganic reactions in solution. McGraw- Hill U.K., pp. 153.*

[20] Atkins, P.W. and de Paula, J. (2002). *Physical Chemistry. 7th Ed., Oxford University Press, p.962.*

Evaluation of Retardant Property of Green Hair Growth Retardant Formula

Joel Ogboji *

Chemistry Department Abubakar Tafawa Balewa University Bauchi, Bauchi State, Nigeria. 2019
*Corresponding author E-mail: joel4chm@gmail.com

A B S T R A C T

Background: *The relevance of depilatory creams has appreciated significantly in recent time and their demand is on the increase. However most commercial depilatory creams contain chemicals with questionable health safety. These synthetic chemicals cause scaring, itching and burns on the skin.*

Objectives: *The study attempted to formulate green hair growth retarding cream, testing the formula for phytochemicals, hair growth retarding property and toxicity.*

Methods: *the cream was formulated from extracts of Tumeric (Curcuma longa), Aloe vera (Aloe barbadensis miller), Guava (Psidium guajava) and Neem (Azadirachta indica), evaluated for its phytochemical constituents and tested for its hair growth retardant property and toxicity on mice.*

Results: *The results show the presence of phytochemicals like tannins, phenols, flavonoids, terpeniods, alkaloids, volatile oil, anthroquinone, glycosides, saponins and a 25% hair growth retarding efficiency on tested mouse, no signs of itching, redness, swelling and topical injuries on the mouse.*

Conclusion: *overall, the research therefore provide convincing evidence of the safety of the formula over the conventional ones and also exhibit satisfactory hair regrowth retarding property.*

Keywords: Depilatory Cream; Extracts; Phytochemicals; Retarding Property; Toxicity.

1. INTRODUCTION

The average number of human hair is about 135000 and each grows and falls through the various cycles of hair growth which include anagen, catagen and telogen. The life cycle of hair are affected by factors such as nutrition, medical history, hereditary, physical constitution, hormone, secretion and aging (Schlossman 2008, Schueller 2009 and Postajian 2011).

Hair growth is a natural process that needs to be control by regular shaving to prevent excess body and facial hair. Hair removal from certain location on the human body has received much attention as the growth of hair on other parts of the body. Getting rid of hair on areas of the body where it is not desired is a problem applicable to all human (Nanda et al, 2006). In Nigeria and the world over, having facial hair happen to not only men but to women too. Today most women worry about their facial hair and will do anything to get rid of it. Facial hair is quite embarrassing and may reduce self-esteem, especially when it

becomes obviously unhidden even in the best of makeups (Nwalsial 2013). Thioglycolic acids whose calcium and potassium derivatives (calcium and potassium thioglycolate) are the main active ingredients in hair removal products cause skin irritation and severe skin burns. Additionally, the thioglycolates class has been shown to be rapidly absorbed through the skin in experimented animals, resulting in systemic toxicity.

Hair growth retardant is a substance that establishes and maintains a long-term and stable reduction in the frequency of hair regrowth. Although the action of hair growth retardant on hair is too slow to be studied, the rapid reaction of hair removal creams is a representative of hair growth retardant acting at an accelerated rate. The constituents of hair are primarily 88% keratin, a hard fibrous type of protein. The cytoskeleton of all epidermal cells is formed from keratin. The amino acid found in the keratin protein is cysteine. Disulphide (S-S) chemical bond firmly hold together the sulphur in cystine molecule and therefore making the cystine molecule difficult to break. The durability and resistance of hair fibre to degradation under environmental stress is a consequence of these disulphide chemical bonds. In an acidic environment, the hair fibre demonstrate great resistance to breakage, however the sulphide bond are susceptible to breakage under alkaline condition. (Depilatories 2006).

Forming the S-S bond require removal of two hydrogen atoms, each from a cysteine molecule.

Fig. 1: S-S Bond Formation in Cysteine Molecule.

This is an oxidation process and therefore an oxidizing agent [O] is required. The reaction can be reverse by using a suitable reducing agent, resulting to loss of hair from the skin. That is, the key to chemical hair removal is breaking the S-S bond in cystine molecule using suitable reducing agent such as thioglycolic acid.

Fig. 2: Thioglycolic Acid.

Thioglycolic salt (especially K salt) is contain in most hair removal products, potassium thioglycolate react with hydroxide ions in KOH or NaOH (also a component of hair removal products) to form a dianion.

$$H\text{-}S\text{-}CH_2COO^- + OH^- \longrightarrow {}^-SCH_2COO^- + H_2O$$

The dianions is the active reducing agent. It is the S end of the dianion that is active in the S-S bridge breaking, thus $^-SCH_2COO^-$ can be simplify as RS^- ($R = CH_2COO^-$).

The chemical reactions that lead to complete removal of hair follicle are represented in the figure below. These reactions occur at a low pH.
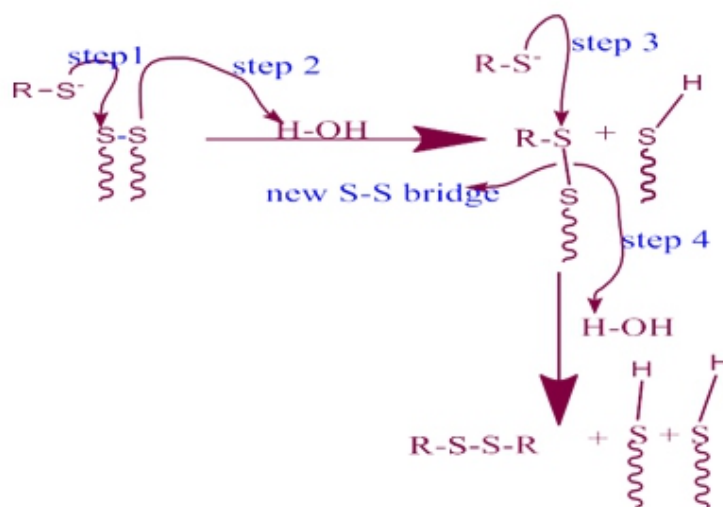
Fig. 3: Mechanism of Disulfide Bridge Breakage in Cysteine.

Step1; nucleophilic attack by S in RS on an S atom in cystine molecule breaks the S-S bridge and generate a new one between a cysteine molecule and the thioglycollate ion.

Step2; the anions formed in step1 strips a proton off water to generate a cysteine molecule.

Step3; a second thioglycollate molecule attack the first to break the newly formed S-S bridge and remake it between the thioglycollate molecules.

Step4; the anion generated in step3 strip a proton off water to form the second cysteine molecule (chemistry in your cupboard 2013).

2. MATERIALS AND METHODS

Materials

The different plant materials were gotten from Muda-Lawal market in Bauchi, the chemical reagents and mice were gotten from Abubakar Tafawa Balewa University, Bauchi State, Nigeria. Deionised water was used throughout the study.

Table 1: Formula for Preparing the Hair Growth Retardant Cream

Components	Amount
Tumeric extract	5 g
Aloe-vera extract	1 g
Guava extract	1 g
Neem extract	1 g
Calcium carbonate 2 g	2 g
Cetyl alcohol 3 g	3 g
Honey	4 ml
Deionized water	2 ml
Paraffin oil	2 ml

Methods

Cold extraction

The leaves of the plants were washed lightly to remove dirt, dried for four weeks in the shade to avoid chemical degradation due to sunlight. The dried leaves and dried turmeric tuber was separately pulverized using electrical blender. 150 g of powdered plant were separately subjected to cold extraction in 70% ethanol at ambient temperature with occasional agitation for five days. The mixture was filtered and the filtrate concentrated by evaporation at 45°C. The extracts were dried and stored in air-tight containers in the refrigerator at 4oC until later use.

Preliminary phytochemical screening

The preliminary phytochemical tests were performed to identify different chemical groups present in the extract in each plant.

Alkaloid test (dragendorff's test)

An extract (0.1 g) from each plant was treated with few drops of dragendorff's reagent (potassium bismuth iodide solution). The appearance of an orange brown precipitate indicates the presence of alkaloid (Seema 2008).

Flavonoid test

An extract (2 ml) from each plant was treated with few drops of NaOH solution. The appearance of intense yellow coloration which turns colourless on addition of few drops of dilute sulphuric acid solution indicates flavonoids presence (Alupuli et al, 2009).

Cardiac glycosis test

An extract (2 ml) of extract from each plant was treated with 0.4ml of glacial acetic acid containing few drops of FeCl3, concentrated sulphuric acid will be added along the test tube wall to settle at the bottom. The appearance of reddish brown colour changing to bluish green colour at the junction of the two reagents indicates the presence of cardiac glycosides (Alupuli et al, 2009).

Saponin test

About 2 ml of extract from each plant was shaken with 1ml of lime water. The formation of semi-permanent foam (15min) indicates the presence saponins (Ashutush 2003).

Tannin test

About 1ml of extract from each plant was treated with few drops of 1% FeCl3. The appearance of blue colour indicates the presence of hydrolysable tannins, while the appearance of green colour indicates the presence of condensed tannins (Ashutush 2003).

Anthraquinone test (borntrager's test)

About 2 ml of extract from each plant was boiled with 1ml of dilute HCl in a test tube. The content would be cooled and extracted with chloroform. The chloroform layer would be separated and ammonia solution added. The appearance of a rose-pink colour indicates the presence of anthraquine glycoside (Bartram 1995).

Terpenoids test

An extract (0.2 ml) from each plant was mixed with 2ml of chloroform followed by the addition of 3ml of concentrated H2SO4. A reddish brown colouration of the surface indicates presence of terpenoid (Trease and Evans 1989).

Phenols

Few drops of 1% FeCl3 was added to 2 ml solution of extracts. A violet colour indicates the presence of phenol (Lecture Demostration manual general chemistry).

Hair growth retardant procedure

The procedure adopted is a modified version of Neelam, 2011 in which

- Accurate weight of calcium carbonate, cetyl alcohol, unadulterated Honey and liquid paraffin were measured and mixed thoroughly. This mixture forms the base of the cream.
- Measured deionised water was added to the base.
- Accurate weight of turmeric powder was incorporated into the above mixture
- 1 g each of neem, aloe vera and guava extract were added and mixed well into a cream like texture.

Hair growth retarding test using mice

A modified version of the method described by (Wakisaka et al, 2009) was adopted in which two albino mice A and B, back were shaved 3x4cm2 with a clipper (to lower the density of the hair). The formula was applied topically the following day to the shaved portions of mouse A, daily topical application of the formula continued for 10 days. The same procedure was observed using 50% ethanol on the control mouse B. In order to observe the retarding effect of the cream on hair growth, pictures of the shaved portion was taken at an interval of 7days for 2 weeks beginning from the day of last application of the formula.

Evaluation of hair growth retarding efficiency

In this model, cello tape was adhered to and pulled off from the shaved portion of the back of each treated mice two weeks after last treatment. The hair density was calculated in accordance with equation A and the hair growth retarding efficiency was calculated according to equation B

Equation A:

Hair density = number of hair on cello tape/ unit area of shaved portion of mice

Equation B:

Retarding efficiency = (density of hair on control mice - density of hair on experimental mice/density of hair on control mice) x 100%.

Toxicity test of the hair growth retardant

During the 10 days of topical application of formulated hair regrowth retardant on the mice, the mice were observed for itching, swelling, redness, and topical injuries.

3. RESULTS AND DISCUSSION

Results

Table 2: Percentage Recovery of Ethanol Extract from 150 G Powder of Plants

	Guava	Neem	Aloe Vera	Tumeric	Balsam Fruit
Amount of Extract(g)	9.6	7.8	5.4	7.2	10.2
Recovered (%w/w)	6.4	5.2	3.6	4.8	6.8
Appearance	Dark Green	Green	White	Yellow	Dark brown

Table 3: Phytochemical Screening of Extracts

Phytochemicals	Guava	Aloe V.	Neem	Tumeric
Alkaloids	+	+	-	+
Saponins	+	-	-	-
Glycosides	-	-	+	+
Anthroquinone	-	+	+	+
Tanins	+	-	+	+
Flavonoid	+	+	+	+
Terpenoid	+	-	+	+
Phenol	+	+	-	+

(+): Present, (-): Absent.

Hair Growth Retardant Test

The effect of the formulated hair retardant on body surface of mice A and B is shown in plate I-III. Hair regrowth began 14-21 days after the last dose of the retardant cream (plates II-III)
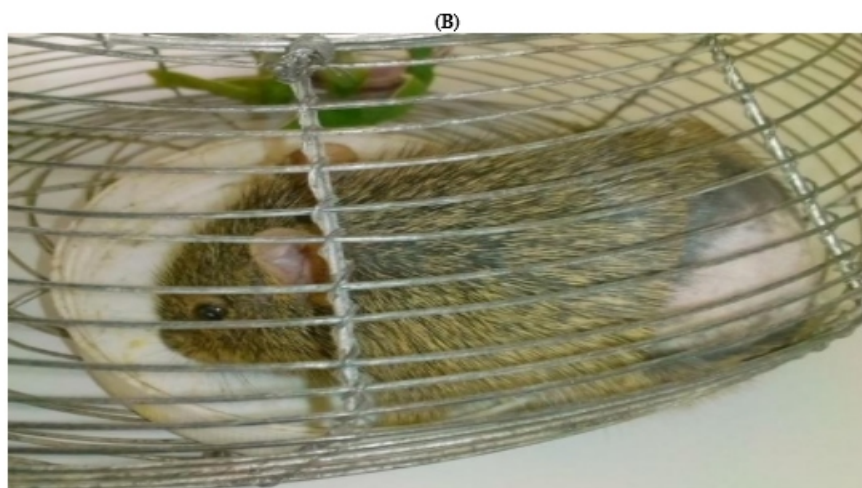
20th March

(A)

Fig. 1: 1st Day after Last Application of Hair Growth Retardant.

27th March

Fig. 2: 7 Days after Last Application of Hair Growth Retardant.
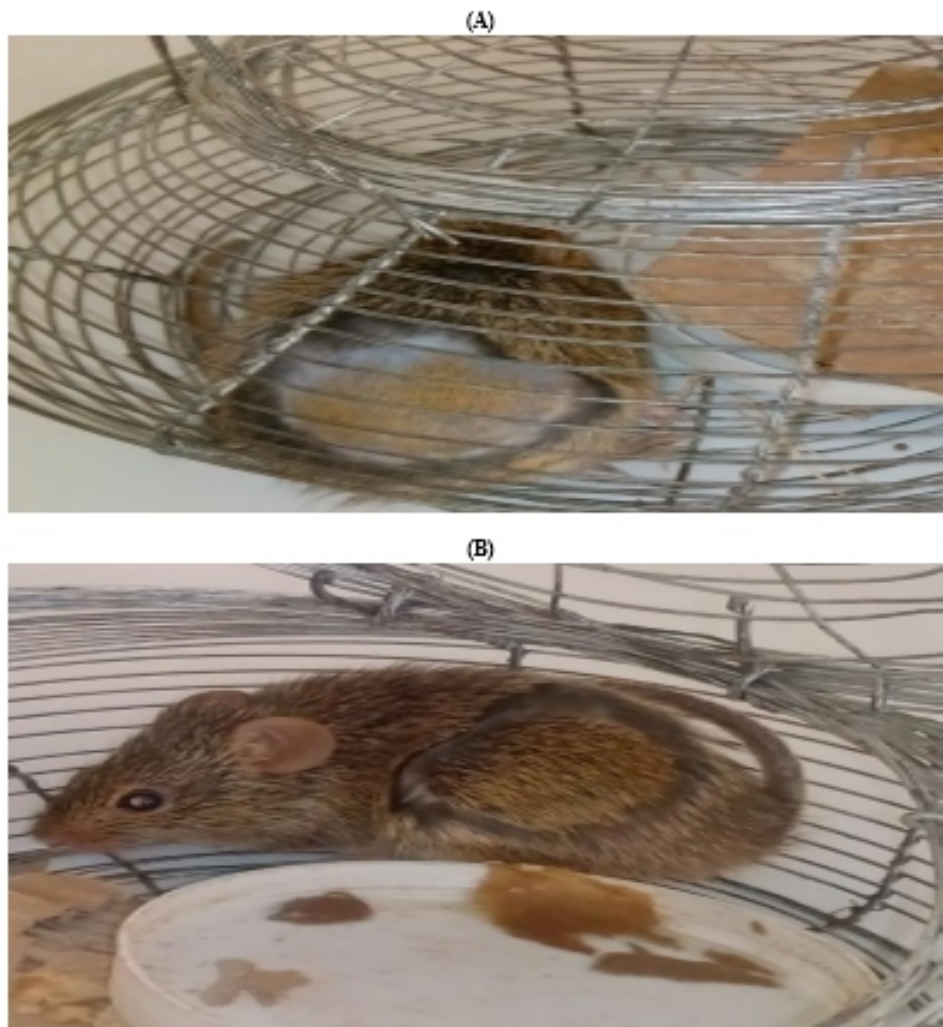
3rd April

Fig. 3: 14 Days after Last Application of Hair Growth Retardant.

Hair Growth retarding efficiency

Table 4 show that the formula has significant potential of retarding hair regrowth after shaving**.**

Table 4: Hair Growth Retarding Efficiency

Mice	Hair density	Retarding efficiency (%)
A	2.1	25
B	2.8	

Discussion

Percentage recovery

The percentage recovery of plant extracts shows that Ethanol extract exhibit 5.36% recovery. This constitute a very small portion of the plants indicating that the concentrations of these bioactive components in plants are very low.

Phytochemical tests

The result from the tests shows phytochemicals such as in table 3. The presence of these bioactive compounds in the extracts makes them medicinal especially as antimicrobial, anti-inflammatory and antioxidative agents. According to Igbinosa et al., 2009, tannins interfere with bacteria cell protein synthesis and are vital in treating ulcerated and inflamed tissues and also intestinal disorder. Alkaloids have been reported also to ease pains and saponin to manage inflammation (Igbinosa et al, 2009 and Hussain et al, 2009). Studies have also shown that flavonoids have greater potential benefit to human health. A study reveals a significant inverse relationship between flavonoid intake and myocardial infection (Jouad 2001).

Hair growth retardant test

The Hair growth Retardant showed evidence of slowing down hair growth. Significant regrowth of hair on mouse A started two weeks after the last application of the formulated hair retardant (plate III) while regrowth of hair started one week in the control, mouse B (plate II) after the last application (plate I). This result is in agreement with that of Neelam (2011). Hair growth inhibition is a reduction process involving the breaking of the S-S bond in the cystine molecule of the hair follicle. Some herbaceous plants extracts contain components with hydroxyl -OH, carbonyl –CO and carboxylic –COOH functional groups which act as reducing agent in an alkaline environment.

Curcumin contained in the Tumeric used in the formula contain four reduction sites that could facilitate the reduction process and consequently slow down hair growth.

Toxicity test

There were no signs of itching, swelling, redness and topical injuries (plate I-III).

Evaluation of hair growth retarding efficiency

It has been noticed that Mouse A treated with the formula showed a 25% significant reduction in the density of hair in the tested area of the mouse (table 4). This implies that the formula has hair growth retarding property

4. CONCLUSION

Overall, the result of the research provides convincing evidence of the hair growth retarding property of the herbal formula. The research proffers an alternative way forward on how safe natural materials can replace the synthetic ingredients in depilatory creams.

ACKNOWLEDGEMENTS

REFERENCES

[1] Postajian M. (2011): Cold wax depilatory composition and related process. United State Patent, US 7 867, 289, B2

[2] Schlossman M. (2008) chemistry and manufacture of cosmetics, Science, 4th edition, Allure Publishing. 724

[3] Schueller R. (2009): Beginning Cosmetic Chemistry, second edition. Allure Publishing. 531

[4] Nanda S, Nanda A, Khar K. R. (2006): Cosmetic Technology, Birla Publication Pvt. Ltd., 388

[5] Laura Nwalsial. (2013): Say Goodbye to Annoying Hair & Hello to Smooth Skin!. What You Need to Know About Hair Removal. Bella naija, Retrieved 13th March, 2016 from http://www.bellanaija.com/2013/07/say-goodbye-to-annoying-hair-hello-to-smooth-skin-what-you-need-to-know- about-hair removal/

[6] Depilatories, Cosmetics and Toiletories. (1990): (105), 87-89.

[7] Chemistry in your cupboard/ veet. Nucleophilic attack by S in RS on an S atom in cystine. 2013. Retrieved 21st December 2016 from http://www.rsc.org/learn-chemistry/resources/chemistry-in-your-cupboard/veet/1

[8] Seema, E. (2008): Isolation and Identification of Cyaniding Pigment from Allium Cepa L. and its Application as Antioxidant. M.Sc Thesis. University of Basra.

[9] Alupuli, A., Calinescu, I., Lavric, V. (2009): Ultrasonic vs Microwave Extraction Intensification of Active Principles from Medicinal Plants. AIDIC Conference Series, 09; 1-8DOI: 103303/ACOS0909001.

[10] Ashutush Kar. (2003): Pharmacognosy and Pharmacobiotechnology. New age international, K. K. Gutpa: New Delhi.

[11] Bartram, T. (1995): Encyclopedia of Herbal Medicine, 1st ed; Grace Publishers'Bournemouth.

[12] Trease, G. E. Evans, W. C. (1989): Pharmacognosy, 11th ed; Brailliar Tirideland Mac Millian Publisherss' London.

[13] Lecture Demostration manual general chemistry. Identification of phenols-ferric chloride test. University of Colorado

[14] Neelam V, Rupinder K. Sohal, Rajiv Gupta, Shubbini A. Saraf. (2011): Formulation and Evaluation of Herbal Depilatory Cream. Pharmacologyonline. 3, 674-683.

[15] Wakisaka, E. Kitahara, T. Tsuji, N. Kusuoku, H. (2009). Herbal hair growth inhibitor and depilation accelerator. United State Patent US 7,488,499B2.

[16] Igbinosa, O. O. Igbinosa, E. O. Aiyegoro, O. A. (2009). Antimicrobial activity and Phytochemical screening of stem bark extracts from jatropha curcas (linn). African Journal Pharm. and pharmacol. 3(2): 058-062.

[17] Hussain, J. A. L. Khan, N. Rehman, M. Hamayun, Z. K. Shinwari, W. Malik, I. J. L. (2009). Assessment of herbal products and their composite medicinal plants through proximate and micronutrients analysis. Journal. Med. Pl. Res. 3(12): 1072-1077.

[18] Jouad, H. Lacalle-Duboi, M. A. Lyoussi, B. Eddouks, M. (2001): Effect of flavonoids extracted from Spergularia purpurea pers on arterial blood pressure and renal function in normal and hypertensive rats. J. ethnopharmacol, 76(2): 159-163. https://doi.org/10.1016/S0378-8741(01)00209-4.

Estimation of Samarium in Nuclear Fuel Reprocessing Streams by Fiber Optic Aided Spectrophotometry

S. Ganesh[1*], N. K. Pandey[1]

[1]Reprocessing Group, Indira Gandhi centre for Atomic Research, Kalpakkam 603102
[*]Corresponding author E-mail:nkpandey@igcar.gov.in

A B S T R A C T

A simple analytical procedure is developed and validated for the estimation of traces amount of samarium in aqueous streams of nuclear waste. In this method, the formation of chelation of samarium ion with 3, 6-bis [(2-Arsonophenyl) azo]-4,5dihydroxy-2,7-naphtalene disulphonic acid (Arsenazo III) to produce a reddish purple colour complex which has maximum absorption at 654 nm at pH 2.6-2.8. The intensity of the colour is proportional to the amount of Sm(III). Linear calibration graphs were obtained for 0.31 to 2.78 µg/mL of Sm(III) with a relative standard deviation (RSD) of 1.32 % and correlation coefficient of R2 = 0.999 (n=10). Its molar absorptivity and Sandell's sensitivity are found to be 4.88x104 L.Mol-1.cm-1 and 2.05x10-5 µg/cm2 respectively. The stoichiometric composition of the chelate is 1:1. The reaction is instantaneous, and absorbance remains stable for over 24 hrs. The system allowed for the determination of samarium with a limit of detection (LOD) (3.3σ/S) of 0.314 µg/mL, the limit of quantitation (LOQ) (10σ/S) of 0.952 µg/mL. A systematic study of the influence of different parameters like pH, the concentration of the complexing agent, the stability of the colour, the volume of the buffer and interference of other competing metal ions. Results of the present method are in good agreement with those obtained by the standard procedure. It is directly applicable for the determination of samarium in environmental, industrial, water and waste streams of the nuclear plant.

Keywords: Samarium; Arsenazo III; Spectrophotometry; Molar Absorptivity.

1. INTRODUCTION

Trivalent lanthanides and actinides exhibit similar chemical behaviour are the same in solid and aqueous phase under PUREX process conditions. The lanthanides particularly Nd, Sm and Eu have almost identical ionic radii with actinides such as Am and Cm in the M(III) oxidation state. The significant advantages of the lanthanides are non-radioactive and can handle without special safety precautions even at higher concentrations. Samarium has familiar in the nuclear industry (soluble neutron poison and control rod) [1], and its oxide is used mainly as shielding and fluxing devices. Criticality is a significant challenging issue to be addressed at each stage of the reprocessing of high plutonium content spent fuel from the Fast Breeder Reactor [2]. Generally, the criticality safety precautions are taken by either controlling the geometry of equipment, mass or concentration of plutonium or combination of both may use. It is found to be the best possi- ble choice as soluble neutron poison due to its high neutron absorption cross-section, adequately high solubility in nitric acid and chemi- cal compatibility in the PUREX solvent extraction process conditions. For the determination of Sm(III), inductively coupled plasma

mass spectrometry [3], inductively coupled plasma mass and atomic emission spectrometry [4], polarography [5], radiochemical [6], voltam- metry [7], neutron activation analysis [8], potentiometry [9] and spectrophotometry [10-22] are available in the literature. Most of the methods required costly equipment and needs special care during the analysis. Therefore, a simple, fast and reliable based on the colour formation of Arsenazo III and samarium, describes the development of an analytical procedure for the determination of samarium with- out sacrificing precision. It is adaptable for on-site or at-line monitoring.

2. EXPERIMENTAL

Instrumentation

Indigenously developed fibre optic aided spectrophotometer coupled with the dip type probe has 1 cm path length was employed for measurement of absorbance. pH/mV meter coupled with the glass electrode was used for pH measurements of studied solutions and buffer solutions from Chemlabs, Bangalore, make Micro-07. For the production of deionised water with specific conductivity < 0.054 µScm-1 was used pure water system from MilliQ, India.

Chemicals and reagents

All the chemical and reagents used in the present study were of analytical grade. Stock solution of samarium (III) nitrate of 99.9% purity (obtained from M/s Alfa Aesar Chemicals) were prepared and standardised by EDTA titration using xylenol orange as an indicator [16]. From this stock solution, different concentrations of samarium standards are made with proper dilution. Prepared the buffer solution of pH 2.6-2.8 by dissolving 28.5 g of mono chloroacetic acid and 12.3 g of sodium acetate together in 500 mL of double distilled water. 0.05% of Arsenazo (III) (obtained from Merck, India) solution is prepared in distilled water. EDTA stock solution (0.01W/v) made by 10 mg of ACS grade of disodium dihydrogen ethylenediamine tetraacetate dehydrate in 100 mL of distilled water.

Developed procedure

To suitable aliquots of Sm(III) (0.1-3.0 µg) solution, 0.5 mL of 0.2% Arsenazo III solution and 1.0 mL of the buffer solution with pH 2.8 was added to each flask and made up to 10 mL standard flasks with double distilled water and the absorption spectrum was recorded from 700-380 nm against a reagent blank prepared.

3. RESULTS AND DISCUSSION

Free Arsenazo III molecule (Fig. 1a), is symmetrical and both the chromophore systems are identical resulting in only one absorption band due to coincident absorption spectra. The appearance of two absorption bands in the complex of Arsenazo III with Sm(III) ions is indicative of a symmetry breakdown in the complex molecule (Fig. 1b). The fact that these two peaks correspond to two electronic transi- tions in the same molecule is indicated by their simultaneous decrease upon successive additions of samarium in the solution. The ab- sorption band in the curve at 538 nm due to free Arsenazo III disappears on the adding up of Sm(III) solution, and two sharp peaks at 610 nm and 654 nm appear, which are characteristic of Arsenazo III–Sm(III) complex is represented in Table 1.
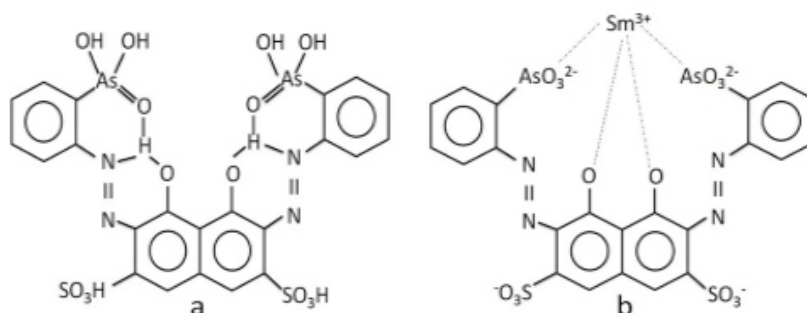
Fig. 1: Structure of Arsenazo III in (A) Uncomplexed and (B) Complexed with Sm3+ [22].

Table 1: Spectral Characteristics of Sm-AR III Complex

Parameter	Sm-Arsenazo III complex	
λ max, (nm)	654	610
Beer's law limit ((μg/mL)	0.31-2.768	0.53-4.76
Molar absorptivity, (L.Mol^{-1}.cm^{-1})	4.88x 10^4	2.84x 10^4
Sandell's sensitivity (μg/cm^2)	2.05 x 10^{-5}	3.52 x 10^{-5}
Detection Limit (μg/mL)	0.314	0.393
Quantitation Limit (μg/mL)	0.952	1.192
Regression equation	Y=0.327x	Y=0.193x
Correlation coefficient (r)	0.9993	0.996
Linear Range (μg/mL)	0.31-2.78	0.52-4.76
Stability formation region (pH)	2.6-2.8	2.6-2.8
Monochloro acetic acid & sodium acetate buffer (mL)	1	1
Arsenazo III (0.05%) (mL)	0.5	0.5

Spectral characteristics

Arsenazo III forms a stable reddish purple colour complex with Sm(III) in the aqueous medium at pH 2.6-2.8. The complex is stable for 24 hours. Fig. 2, which shows the typical absorption spectrum is a symmetric curve with maximum absorbance at λmax = 654 nm against a reagent blank.
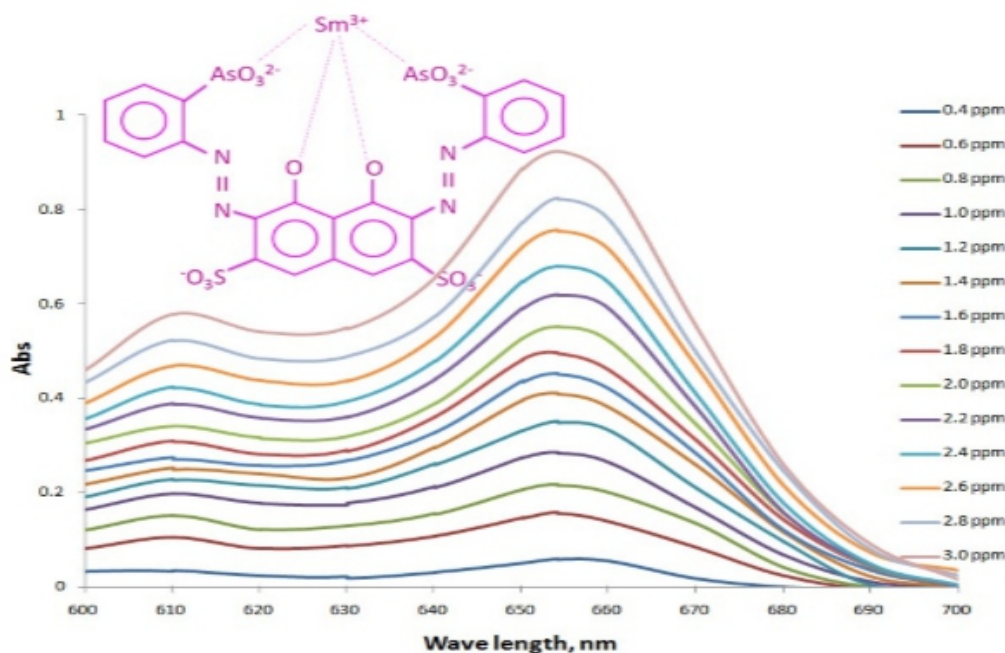
Fig. 2: Typical Absorption Spectrum of Sm(III)-Arsenazo III Complex at the Ph 2.6-2.8 Solutions; Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5 Ml, [Sm(III)] = 0.2-3 µg/Ml.

Calibration graph, beer's law and sensitivity

A calibration curve is made with fixed concentrations of Arsenazo III (0.5 mL, 0.2%) and variable concentrations of Sm(III) (0.31-2.78 µg/mL) (in presence of buffer pH = 2.8, 1 mL) at 654 and 610 nm and given in Fig.3. At these wavelengths, the system obeys Lambert- Beer's law in the concentration range of 0.31-2.78 µg/mL for 654 nm and 0.53-4.76 µg/mL for 610 nm. Fitting of the obtained data gives a linear regression equation at 654±0.5 nm obtained was: A = 0.327 x C, Sm (µg/mL), with a good correlation coefficient (R^2) equals 0.999. The slope of the relation verifies Beer's law in the equation mentioned above and gives the molar absorptivity (e). Since the sensi- tivity of the spectrophotometric method is often expressed in terms of the expression 'sensitivity index' given by Sandell [23], the sensi- tivity of the present method for determining samarium (atomic mass: 150.36 g.mole[-1], λmax of 654±0.5 nm)in the aqueous medium. The molar absorptivity and Sandell's sensitivity (concentration for 0.001 absorbance unit) are found to equal $4.88\pm0.2\times10^4$ L.Mole[-1].cm^{-1} and 2.05×10^{-5} µg.cm^{-2} respectively. To detect the optimum concentration ranges for maximum precision employ the Ringbom's plot [24]. The transmittance plotted against the logarithm of metal concentration. The linear portion of the curve indicates that the range was 0.1 to 0.5 ppm of Sm(III) (Fig.4) and slope of Ringbom's plot was 0.483.
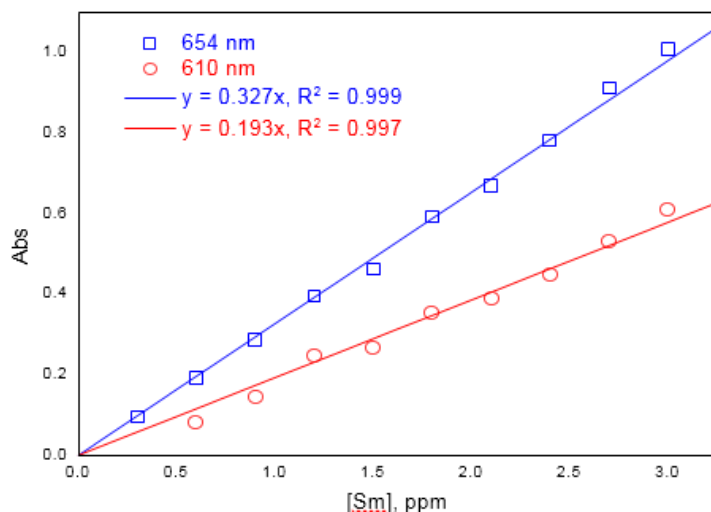
Fig. 3: Typical Calibration Graph For Determination of Sm (III) Nitrate with Arsenazo III at 654 and 610 Nm, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5 Ml, [Sm (III)] = 0.2-3 µg/Ml.
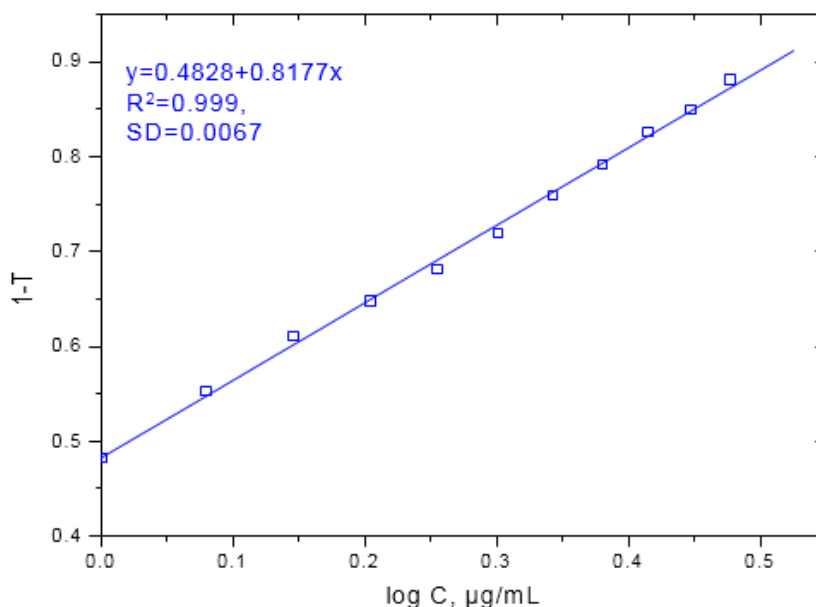

Fig. 4:Ringbom'sPlot for Determination of Sm(III) Nitrate with Arsenazo III at 654, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5 Ml, [Sm(III)] = 0.2-3 µg/Ml.

Effect of buffer solutions

Fig 5 shows the influence of the concentration of the buffer solution on the absorbance of Sm(III)-Arsenazo III complex. And there is a considerable effect of the buffer solution on the system. 1 mL of a buffer solution is sufficient for maximum absorbance. No significant change observed if more than one mL. Thus, 1 mL of buffer solution is adequate for all studies.
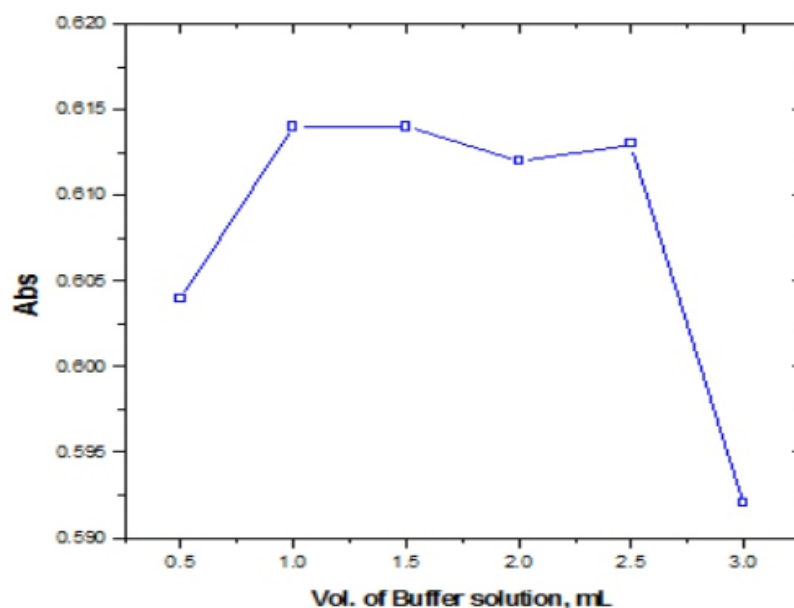
Fig. 5:Effect of Volume of Buffer Solution on the Absorbance of Samarium Estimation at 654 Nm, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5-3 Ml, [Sm(III)] = 2 μg/Ml.

Effect of pH solution

The pH of the solution has a significant influence on the absorbance of the Sm (III)-Arsenazo III Complex. To vary the pH of the reaction mixture was varied from 2 to 12 and the absorbance was found to be maximum, in the pH range 2.8 (Fig.6). Hence pH 2.8 was found to be most suitable for maintaining pH and mono chloroacetic acid /sodium acetate buffer solution employed as optimum for all subsequent work.
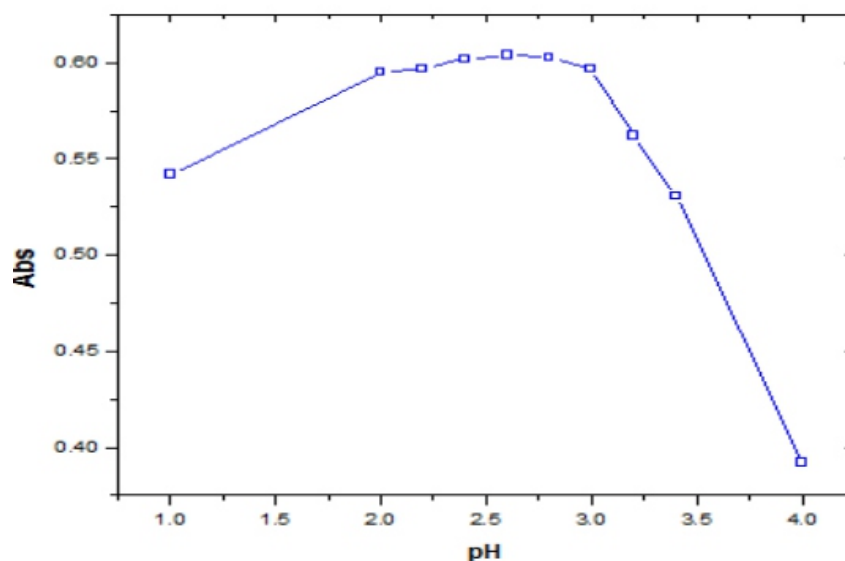

Fig. 6:Effect of Volume of Ph Solution on the Absorbance of Samarium Estimation at 654 Nm, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5-3 Ml, [Sm(III)] = 2 μg/Ml.

Effect of arsenazo III dye concentration

The study of Arsenazo III dye concentration was essential for the optimum complex formation and its stability. In general dye concentra- tion, less or higher than the required amount, would cause deviation from Beer's law and overlapping of dye spectra with other ion-dye complexes. To optimise the 0.2% Arsenazo III, a series of the solution containing fixed Sm(III) concentration, fixed buffer solution and different volume of Arsenazo III from 0.1 to 1 mL to form Sm(III)-Arsenazo III complex at pH 2.8. From Fig. 7, it indicates that the maximum absorbance was the most obvious when adding one mL dye at 654 nm, once it exceeds this volume, absorbance would remain constant. So one mL of Arsenazo III is favourable and used in subsequent experiments.
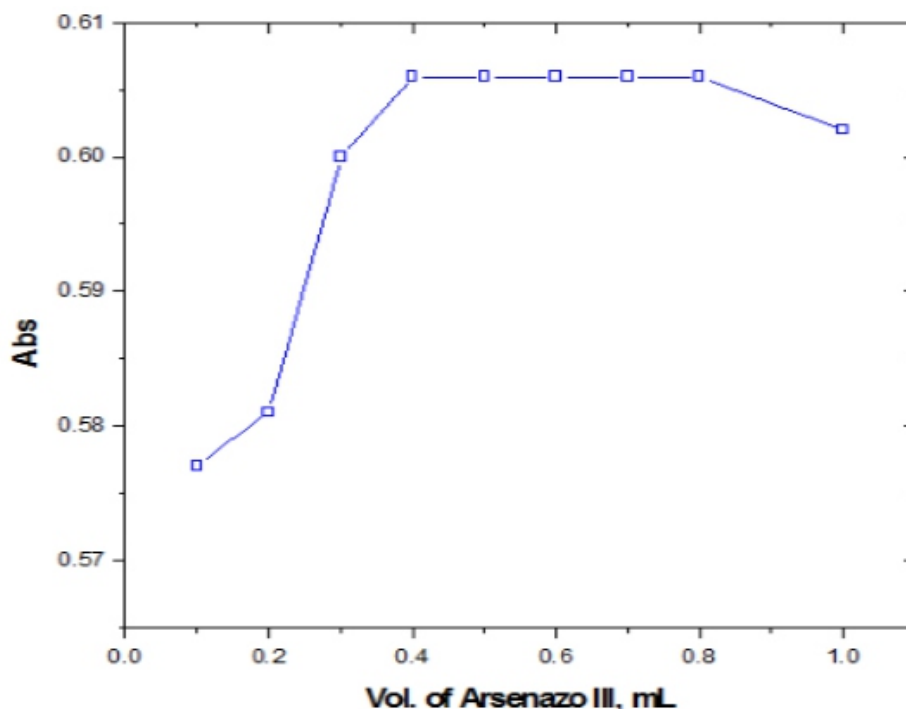

Fig. 7:Effect of Arsenazo III on the Absorbance of Samarium Estimation at 654 Nm, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5-3 Ml, [Sm (III)] = 2 µg/Ml.

Stability

The formation of the coloured complex of Sm(III) with Arsenazo III was instantaneous. Measurement of the absorbance was carried out immediately after mixing the Sm(III) and Arsenazo III, and the complex was found to be stable for 24 hours (Fig. 8). Freshly prepared buffer solution used for the measurement of absorbance.
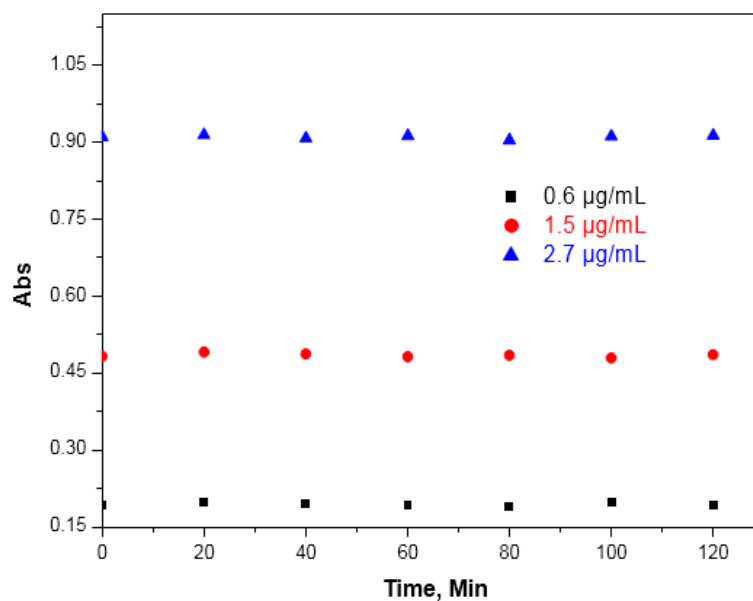
Fig. 8: Time Dependence of Absorbance for Sm(III)-Arsenazo III Complex; Blank Corrected.

(•) – 0.6 μg/Ml; (•) – 1.0 μg/Ml; (•) – 2.7 μg/Ml.

Composition of the complex

To investigate the composition of Sm(III)-Arsenazo (III) using the mole ratio method [25] and Job's method of continuous variation [26]. In the mole ratio method (Fig.9) a break was observed when the Sm(III)-Arsenazo(III) ratio was 1:1, indicating an ML type complex formation. The plot of Job's method also confirms the same pattern of an ML type composition of the complex which represented in Fig. 10.
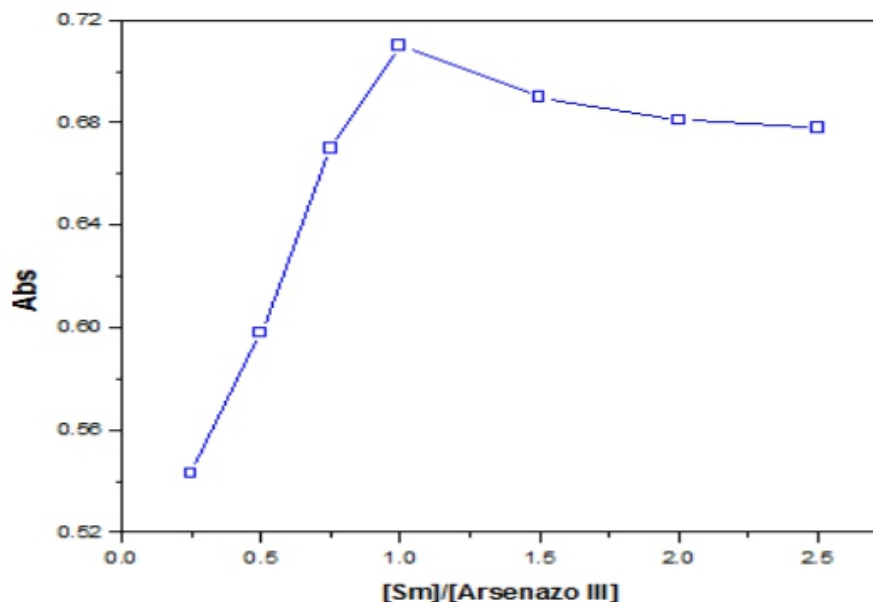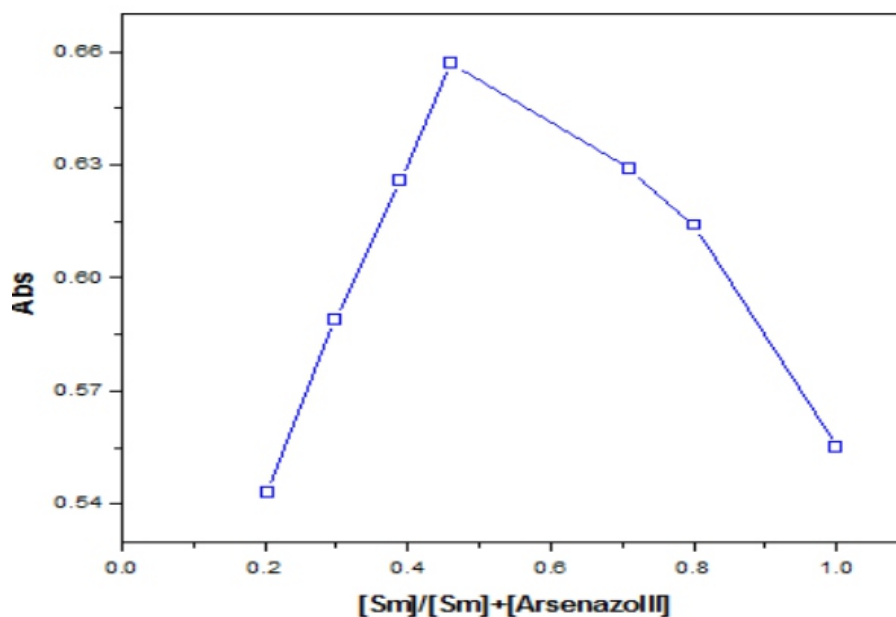

Fig. 9:Mole Ratio Method.

Fig. 10:Job's Continuous Variation Method.

Effect of foreign ions

AbsTo investigate the influence of various metal ions in the present method by complexation or ion exchange separation process. It is no selective, but minimum interference leading to improved selectivity using complexation and results compiled in Table 2. The most severe interferences were from Nd(III) ions. Interference from those ions is probably due to complex with arsenazo (III). To achieve the higher tolerance limits of trivalent metal ions by using several masking agents such as 1% tartaric acid, 1% citric acid, 0.5% EDTA, 1% thiocy- anate and thiourea. During the interference studies, any precipitate formed was removed by centrifugation. Interference from these metal ions Eu(III), La(III), Nd(III), Y(III) and U(VI) have been removed by a short single-step ion-exchange separation process using cation- exchange resin (ex) AG50 W-X8 [27].
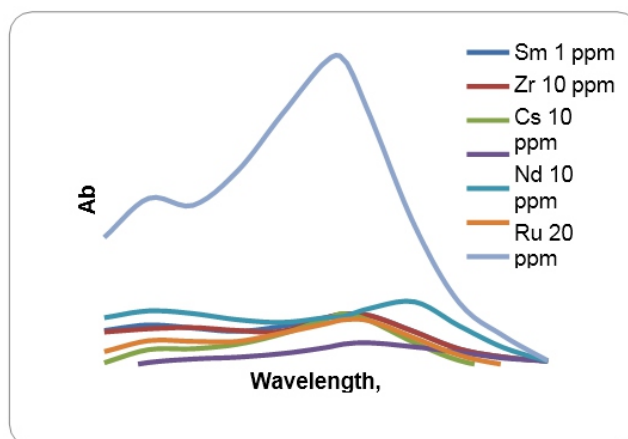

Fig. 10:Effect of Arsenazo III on the Absorbance of Samarium Estimation at 654 Nm, Blank Corrected. Buffer Solution V = 1 Ml, Arsenazo III Solution V = 0.5-3 Ml, [Sm(III)] = 2 μg/Ml.

Table 2:Interference of Metal Ions during the Determination of Samarium

Interference of metal ions			Concentration of Samarium (µg/mL)		% error
Metal	Conc. Taken (µg/mL)		Taken	Obtained	
CsNO3	10		0.725	9.398	1.34
Zr(NO3)4	10		0.725	9.351	0.13
UO2(NO3)2	10		0.725	9.378	514.01
Gd(NO3)3	10		0.725	8.744	11.45
Nd(NO3)3	10		0.725	8.492	61.48
Ru(III)	10		0.725	Peak shifted	-
Y(NO3)3	10		0.725	7.834	17.3

Masked with 1 mL 1% aqueous thiocyanate solution, Anions are effectively masked by the addition of 0.3 mL 0.5% EDTA, ii. Eu(III), La(III), U(VI) interfering ions are effectively separated by convenient type cation -exchange resin (ex) AG 50 W-X8.

Removal of arsenazo III

Chromogenic reagents create the main problems associated with the treatment of chemical and radiochemical laboratories. So disposal of waste required special treatment. Arsenazo III is hazardous and contains arsenic, which is a very toxic element. It was used in acidic medium and widely applicable for the determination of many metal ions. Arsenazo based analytical waste generated during the estimation of samarium, which introduced a new toxic metal ion like arsenic and acidic medium. After analysis, the waste solution was passed through the activated charcoal column for removal of arsenazo III from the waste solution [28].

4. VALIDATION OF THE PROPOSED PROCEDURE

To validate the developed procedure under the experimental conditions by the guidelines from the international conference for Harmonization (ICH) [29] like linearity, accuracy, precision and specificity.

Precision and accuracy

To evaluate the accuracy and precision of the present method by determining different concentration levels of samarium (each analysis replicate at least five times). The relative standard deviation (n = 5) was 1.32% for 0.5 to 500 µg of samarium in 10 mL, indicating that this method is highly precise and reproducible. Five sample solutions of each concentration were analyzed under the same experimental conditions within one day (intra day precision) and in five consecutive days (inter day precision). The % RSD and data summarised in Table.3. Hence, the precision and accuracy of the method were found to be excellent.

Table 3:Accuracy and Precision of Proposed Method

Parameters	Intraday			Inter day assay		
[Sm] taken, ppm	1	1.5	2.8	1	1.5	2.8
[Sm] found, ppm	0.991	1.499	2.808	1.008	1.509	2.746
Standard deviation* (SD), ppm	0.006	0.008	0.037	0.158	0.195	0.271
RSD (%)	0.604	0.532	1.315	1.06	0.898	0.46
Standard analytical error (%)	0.084	0.078	0.12	0.105	0.071	0.121
Confidence limit#						0.333
*Mean for five independent determinations.						
# Confidence limit at 95% confidence level and four degree of freedom (t=2.776).						

Detection limit and quantitation limit

The detection limit has been calculated as $(3.3\sigma/S)$, where σ denotes the standard deviation for blank (n=10) and S stands for the slope of the analytical curve from the calibration graph. The limit of detection (LOD) was found to be 0.314 µg/mL, whereas the limit of quantita- tion (LOQ) $(10\sigma/S)$ was 0.952 µg/mL with precision (was evaluated by determination of the different concentration of samarium) ex- pressed as relative standard deviation (RSD) of 1.32%. The obtained results indicate that this method is highly precise and reproducible. Calculations were made the recommendations by IUPAC [30]. The best agreement between theoretically computed and practically verified values of LOD and LOQ was approached namely at significance level $\alpha = 0.05$.

Robustness and ruggedness

To examine the robustness of the developed procedure by the influence of a small variation like the concentration of analytical reagent and the pH of the solution. It showed that a slight difference in these variables did not affect the procedure significantly. The ruggedness was tested by applying the proposed method of analysis of samarium under the same experimental conditions by two different analysts. Results obtained from inter-day RSD and within-day RSD were found to be reproducible and between 0.45 and 1.32% (Table.4).

Table 4:Reproducibility of the Method by Two Different Analysts

	[Sm], ppm Taken	Obtained	% RSD
Analyst 1	1.2	1.216	0.85
Analyst 2	1.2	1.197	
Analyst 1	0.44	0.447	0.45
Analyst 2	0.44	0.413	

Range and linearity

The precision and accuracy of the method were tested by taking known two different trace amounts of samarium. As shown in table 5, mean values were obtained with Student's t-values at 95% confidence level and the variance ratio F-values calculated (p=0.05) for 5 degrees of freedom. The results showed comparable accuracy (t-test) and precision (F-test) and did not exceed the theoretical values, indicating that there was no significant difference in accuracy and precision. The performance of the proposed

method was verified with other existing UV-Vis spectrophotometric method using Chrome azurol S as chromogenic reagent reported in the literature [13].It is clear from table 5 that the calculated t value is less than the tabulated t value at the 95% confidence level for four degrees of freedom is 2.776. Therefore, tcal< ttable, and there is no significant difference between the two methods at this confidence level. The proposed method is simple and requires less time to complete the analysis. The proposed procedure is simple, fast, less time, versatile, accurate and useful due to high tolerance limits from cations and anions.

Table 5:Evaluation Data of Accuracy and Precision Calculation for Sm-Arsenazo III Complex

	Variable 1		Variable 2	
	Present Method	**Reference Method [13]**	**Present Method**	**Reference Method [13]**
Mean	1.852	1.848	2.402	2.406
Standard Deviation	0.0193	0.022	0.0192	0.0358
Variance	0.00037	0.0004	0.0004	0.0013
RSD	1.041	1.164	0.8008	1.488
Degree of freedom	4	4	4	4
f-Test cal	1.256		1.661	
f-Test table	2.298			
p (Probability)	0.05		0.05	
fcal? ftable	No significant different		No significant different	
Confidence level	95%		95%	
t-Test cal	0.99		1.859	
t-Test table	2.228		2.228	
tcal? ttable	No significant different		No significant different	

5.APPLICATIONS

To utilize the proposed method for the determination of samarium concentration during the solvent extraction behaviour of it with the TBP-HNO3 system at conditions prevalent in FBR fuel reprocessing. Figure 11 is the schematic diagram of at-line monitoring setup. A suitable aliquot of Sm(III) sample was put into the reactor, which is mixed thoroughly with the continuous flow of buffer and arsenazo III solutions. Both solutions were allowed continuously through the isocratic pump with a flow rate of 0.5 ml/min. A dip type probe in- serted into the column and consistently run the spectrum of the colour complex of Sm-Arsenazo III. During this exercise, the arsenazo III based analytical waste generated. This waste processed separately passed through the activated carbon and removed the arsenazo based complex and sent back to the process streams.

6. CONCLUSIONS

The developed method for the determination of Sm(III) ions in the aqueous medium is simple, sensitive, selective and applicable for all the range of nitric acid and heavy metal ion concentration relevant to PUREX process for continuous monitoring. The accuracy and selectivity concerning relative standard

deviation of the present method are reliable for the determination of samarium in real samples to microgram levels in the aqueous medium at room temperature (25 ± 5)oC. The obtained results by the developed procedure compared with those derived from neutron activation analysis method [8] and one more spectrophotometry [13]. The results are found to be a good agreement. The removal of arsenazo (III) is 98%. It also applicable for at-line monitoring of samarium.

REFERENCES

[1] Natarajan, R., (2017), Reprocessing of spent nuclear fuel in India: Present challenges and future programme, Progress in Nucl. Energy, 101, pp. 118-132. https://doi.org/10.1016/j.pnucene.2017.03.001.

[2] Ganesh, S., Desigan, N., Pandey, N.K., Mallika, C., KamachiMudali, U., (2017), Extraction studies of gadolinium relevant to its use as neutron poison in the PUREX process, Progress in Nucl. Energy, 98, pp 234-238. https://doi.org/10.1016/j.pnucene.2017.03.027.

[3] Li, B., Sun, Y., Yin, J., (1996), Determination of cerium, neodymium and samarium in biological materials at low levels by isotope dilution induc- tively coupled plasma mass spectrometry, J. Anal. Atomic Spectrometry, 14(12), pp1843-1848. https://doi.org/10.1039/a905346h.

[4] Paama, L., Pamoja, E., Must, M., Peramaki, P., (2001), Optimal conditions for europium and samarium determination in cathodoluminophors by inductively coupled plasma atomic emission spectrometry, J. Anal. Atomic Spectrometry, 16(11), pp1333-1336.

[5] T.M. Florence, L.E. Smythe, (1960), Polarographic determination of lanthanides by means of azo dye stuffs, U. S. At. Energy Comm, TID- 7606, p. 14.

[6] R.G. Monk, J. Herrington, (1961), Microchemical methods in radiochemical analysis, Anal. Chim. Acta, 24, pp. 481. https://doi.org/10.1016/0003- 2670(61)80100-1.

[7] M. Servigne, Detection and micro chemical determination of rare elements by luminescence, (1940), Bull. Soc. Chim. Biol, 7, pp. 121

[8] Orvini, E., Speziali, M., Salvini, A., Herbog, C. (2000), Microchem. J, 67, pp.97-104. https://doi.org/10.1016/S0026-265X(00)00104-1.

[9] Gupta, V. K., Goyal, R.N., Sharma, R.A. (2009), Anal.Chimica Acta, 647, pp 66-71. https://doi.org/10.1016/j.aca.2009.05.031.

[10] Pushpa Ratre, P., Devendra Kumar, (2001), Spectrophotoemtric determination of trace amounts of samarium in environmental samples, Am. Int. J. Res. In formal, applied & Natural Science, 3(1), pp 110-118.

[11] Mathew, A.V., Kumar, K., Rao, I.M., Satyanarayana A, and Shyamala, P., (2012) Spectrophotometric determination of neodymium (III), Samari- um (III) in micellar medium - An alternative to solvent extraction procedures., Indian J. Chem. Tech, 19, pp. 331-336.

[12] Dey, A.K., and Munshi, N.K., (1971), Spectrophotometric determination of lanthanides using 4-(2-Pyridyl azo) resorcinol, Microchimica acta, 59, pp 751-756. https://doi.org/10.1007/BF01217100.

[13] Soyalk, M., Orhan, T., (2000), Spectrophotometric determination of samarium (III) with chrome azurol s in the presence of cetylpyridinium chlo- ride, Talanta, 53, pp 125-129. https://doi.org/10.1016/S0039-9140(00)00386-6.

[14] Ujrovcik, J., and Leny, J. (2014), Extractive spectrophotometric determination of samarium with chloroph osphonaso III, Acta TechnicaJourinensis, 7(1), pp 62-70. https://doi.org/10.14513/actatechjaur.v7.n1.218.

[15] Mohammed, M.T., Hafezand and Zaki, M, (1986) Application of 8-hydroxyquinoline sulfonic acid in the spec trophotometric determination of some lanthanides, Microchem, J., 34, pp.258-261. https://doi.org/10.1016/0026-265X(86)90118-9.

[16] Agrawal, Y.K., and Thomaskutty, P.T., (1987), Separation and micro determination of rare earth metals with N-phenylbenzohydroxamic acid and xylenol orange", J. Radioanal. Nu. Chem., 116, pp.365-374. https://doi.org/10.1007/BF02035781.

[17] Alaa, A., and Ibrahim, A.S., (2010), Complexation and spectrophotometric study of samarium (III) using pyrimidine azo derivatives in the presence of cetyltrimethyl ammonium bromide, Anal.Lett. 43, pp2598-2608. https://doi.org/10.1080/00032711003726910.

[18] Gadzhieva, S.R., Chyragov, F.M., and Guseinov, F.E., (2005), Spectrophotometric study of the complexation of samarium (III) with disodium 2- (2-hydroxy-3-sulpho-5-nitrophenylazo)naphthalene-1,8-dihydroxy-3-6-disulphonate in the presence of cetyltrimethylammonium bromide, J.Anal.Chem, 60, pp 819-821. https://doi.org/10.1007/s10809-005-0188-5.

[19] Dik, T.A., Kostyuk, N.N., and Trebnikov, A.G., (2003), Spectrophotometric determination of Sm(III) content in hydrochloric acid solution, J. Appl. Spectro., 70, pp 729-732. https://doi.org/10.1023/B:JAPS.0000008870. 62153.93.

[20] Shah, V.L., and Sancal, S.P., (1969), A spectrophotometric study of the chelates of chromotrope 2R with praseodymium, neodymium, samarium and europium, Microchem. J., 14, pp 261-270. https://doi.org/10. 1016/0026-265X(69)90041-1.

[21] Bhagavathy V., Prasada Rao, T., Dhamodaran, A.D., (1988), Third order derivate molecular absorption spectrophotometric determination of traces of samarium with methyl thymol blue-CTAB or CPB, Anal Letters., vol. 21(5), pp.901-920. https://doi.org/10.1080/00032718808070868.

[22] Savvin, B., (1964), Analytical applications of arsenazo III-the mechanism of complex formation between arsenazo III and certain elements, Talan- ta, 11, pp.7-13. https://doi.org/10.1016/0039-9140(64)80004-7.

[23] Sandell, E.B., (1950), Colorimetric determination of traces of metal. Chapter III, 2nd Edition, Interscience publishers, New York. [24] Ringbom, A.Z., (1938), Anal Chem., 115, 332. https://doi.org/10.1007/BF01753937.

[25] Yoe, J.H., Jones, A.L., (1994), Ind.Eng.Chem.Anal.Ed. 16, pp. 111 [26] Job, P., Job plot, (1928), Ann Chim., 9, pp 113-203.

[27] Strelow, F.W.E., (1980), Anal. Chim. Acta, 120, pp.249-254. https://doi.org/10.1016/S0003-2670(01)84368-3.

[28] Ahmed, I.M., Aglan, R.F., Hamed, M.M., (2017), Removal of Arsenazo III and thorin from radioactive waste solutions by adsorption onto low- cost adsorbent, J.Radioanal.Nucl.Chem. 314, pp 2253-2262. https://doi. org/10.1007/s10967-017-5586-2.

[29] Currie, L.A., (1995), Nomenclature in evaluation of analytical methods including detection and quantification capabilities, IUPAC recommenda- tions, Pure and applied chem. 67(10), pp 1699-1723. https://doi.org/10.1351/pac199567101699.

[30] IUPAC: Analytical chemistry Division, (1978), Spectrochimica Acta. 33, pp. 242.

Corrosion Inhibition of Carbon Steel in Perchloric Acid by Potassium Iodide

Tarik Attar [1,2*], Abbes Benchadli [1], Esma Choukchou-Braham [1]

[1] Laboratory Toxicomed, University Abou Beker Belkaid Tlemcen, BP119, 13000 Tlemcen, Algeria
[2] Superior School of Applied Sciences of Tlemcen, BP 165, 13000 Bel Horizon, Tlemcen, Algeria
[*] Corresponding author E-mail: att.tarik@gmail.com

A B S T R A C T

Corrosion processes are responsible for numerous losses mainly in the industrial scope. It is clear that the best way to combat it is pre- vention. The effect of temperature on the corrosion behavior of carbon steel was studied by mass loss measurements in the temperature range 293–333 K. The inhibition efficiency increases with increasing temperature. The inhibitor showed 97.98 % inhibition efficiency at 1.10-3 M concentration of iodide potassium in 1 M perchloric acid solutions. The values of activation energy (Ea), enthalpy of activation (ΔHa) and entropy of activation (ΔSa), free energy of adsorption (ΔGads), enthalpy of adsorption (ΔHads) and entropy of adsorption (ΔSads) were calculated. The adsorption of this inhibitor on carbon steel surface obeys Langmuir adsorption isotherm.

Keywords: Corrosion Inhibition; Carbon Steel; Potassium Iodide; Weight Loss; Adsorption Isotherm.

1. INTRODUCTION

Carbon steels are the most commonly used construction materials and corrosion phenomena has become important particularly in acidic media because its employability are increased. Strong acids are widely used in industries for many purposes, especially in cleaning, de- scaling, pickling procedures, Oil Well acidizing and other applications isotherm (Abd El–Maksoud 2008). Therefore, protective measures should be required to reduce the corrosion rate in acids by using chemical and other means, among the different methods use of inhibitors is most commonly and economical (Al-Otaibi et al. 2014). A corrosion inhibitor is a chemical substance which, when added in small concentrations to an environment, minimizes or prevents corrosion (Riggs 1973; Uhlig et al. 1985). Inhibitors had great acceptance in the industries due to excellent anti-corrosive proprieties. The inhibition efficiency depends on the various parameters, corrosive medium, pH, temperature, duration of immersion, metal composition and on the nature of the inhibitor (Loto et al. 2012; Attar et al. 2014). Adsorption isotherms provide information about the interaction of the adsorbed molecules with the electrode surface (Bereket et al. 2002; attar et al. 2014). The adsorption of the inhibitors can be described by two main types of interaction: Physisorption and/or chemisorption (Xiumei et al. 2012; Zarrok et al. 2012): One is physical adsorption, which involves electrostatic forces between ionic charges or dipoles on the ad- sorbed species and the electric charge at the metal/solution interface. The heat of adsorption is low and therefore

this type of adsorption is stable only at relatively low temperatures. The other is chemical adsorption, which involves charge transfer or sharing from the inhibitor molecules to the metal surface to form a coordinate type bond. This type of adsorption is known to have much stronger adsorption energy compared to the other mode of adsorption. Thus, such bond is more stable at higher temperatures. The weight loss method (gravimetric) is known to be the most widely used method of monitoring inhibition efficiency (Obot et al. 2010).

The aim of the present work is to study the inhibition efficiency of iodide potassium for the corrosion of carbon steel in perchloric acid medium 1M and to evaluate thermodynamic parameters of corrosion inhibition process for the adsorption of inhibitor on carbon steel metal surface.

2. EXPERIMENTAL

Material preparation

The test solutions of 1 M of Perchloric acid were prepared by the dilution of analytical grade 72% $HClO_4$ with bi-distilled water in 50 mL. Steel XC38 containing in wt. %: 0.37 C, 0.68 Mn, 0.077 Cr, 0.059 Ni, 0.023 Si, 0.016 S, 0.011 Ti, 0.009 Co, 0.16 Cu, and iron is the remainder. The electrode was polished using different grades of emery papers after be polished, degreased and weighed. Each specimen was weighed using an analytical balance of 0.0001 g accuracy. All experiments are in triplicates and illustrated data are mean values of obtained results.

3. RESULTS AND DISCUSSION

Effect of immersion time

The weight loss measurements were performed in 1 M HClO4 in absence and presence of KI at 10-3 M concentration for 30 min to 24 h immersion time at temperature of 303 K.

The inhibition efficiency (IE%) of potassium iodide was calculated using the formula (1).

$$IE(\%)=100*(W_{corr}-W_{inh})/W_{corr} \qquad (1)$$

Where W_{corr} and W_{inh} are the corrosion rates of carbon steel samples in the absence and presence of potassium iodide compound, respectively.

The corrosion rate (w) was calculated from the formula (2):

$$W = (m_1-m_2)/S.t \qquad (2)$$

Where m_1 is the mass of the specimen before corrosion, m_2 the mass of the specimen after immersion in solution, S the total area of the specimen and t the corrosion.

The variation of the inhibition efficiency of this inhibitor is almost constant from the first 60 minutes of immersion, which allowed us to say that the immersion time has no significant effect on the corrosion inhibition of carbon steel in M HClO4, is shown in Figure 1. The weight loss of carbon steel is nearly varied linearly with immersion period in the absence and presence of inhibitor as seen in Figure 2.
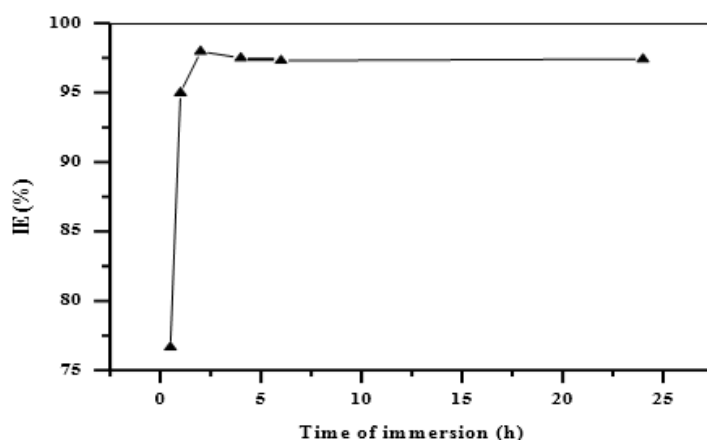

Fig. 1: Variation of the Inhibition Efficiency with Immersion Time for Carbon Steel 1M HClO$_4$ Containing 10^{-3}M of KI at 303 K.

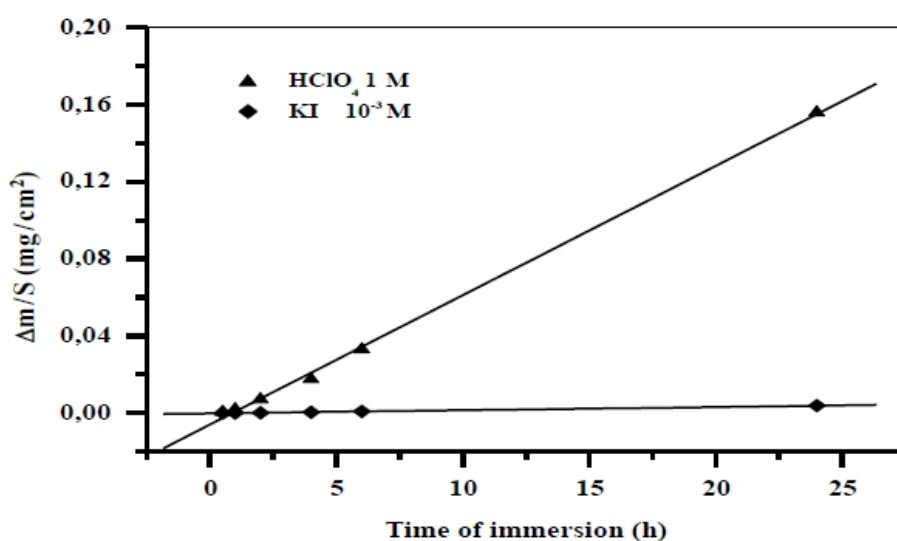**Fig. 2: Weight Loss Versus Immersion Time of XC38 in 1 M HClO4 Without and with 10-3 M of KI at 303 K.**

Effect of temperature

The effect of temperature on the inhibition effectiveness at various concentration of potassium iodide was studied in the temperature domain (293–333 K) at 2 h of immersion. The values of inhibition efficiency and corrosion rate obtained from weight loss method are showed in figure 3 and 4.
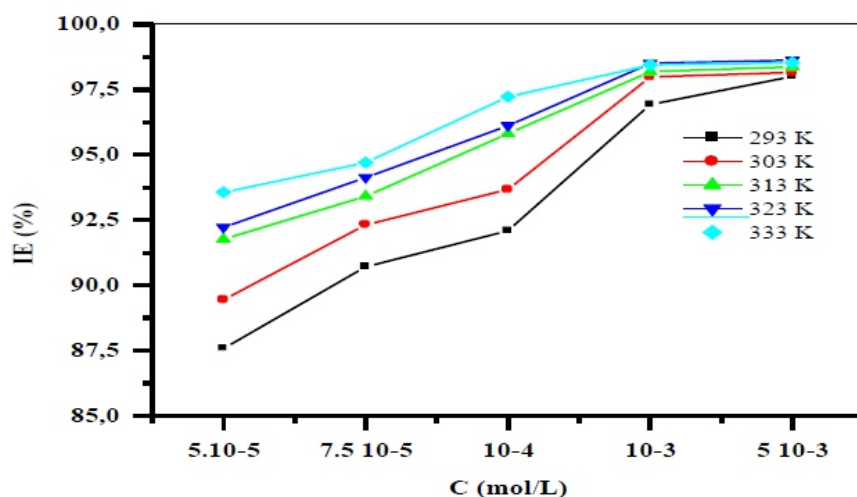
Fig. 3: Variation of Inhibition Efficiency (IE%) with Concentration of KI for Carbon Steel in 1 M HClO4 at Different Temperatures.

The inhibition was estimated to be superior to 87.59 %, even at concentrations as low as $5 \cdot 10^{-5}$ M, and the maximum efficiency of 97.98 % was recorded at 10^{-3} M. The same study was carried out in the Hydrochloric acid where the maximum efficiency at 10^{-3} M, was 59.37% and 6.25 % at low concentration ($5 \cdot 10^{-5}$ M) (Benchadli et al. 2018). From the graph it is evident that the concentration change had only marginal influence on inhibition efficiency. It was also observed that corrosion rate decreased with increase in inhibitor concentration.
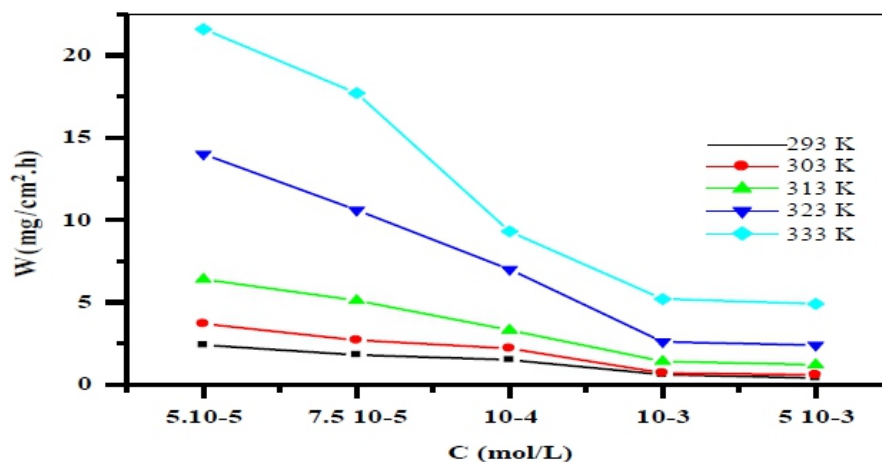

Fig. 4: Variation of Corrosion Rate with the Concentrations of KI for Carbon Steel in 1 M HClO4 at Different Temperatures.

The study of the effect of temperature on the inhibition efficiency and corrosion rate facilitates the calculation of kinetic and thermody- namic parameters for the inhibition and the adsorption processes.

Thermodynamic parameters and adsorption isotherm

The adsorption is also influenced by the structure and the charge of the metal surface, and the type of testing electrolyte (Obot et al. 2009). In acid environment, the inhibitor acts generally by chemisorption and/or physical adsorption at the metal surface (Elmsellem et al. 2014). The inhibition of the corrosion of carbon steel in 1 M HClO4 medium acid with addition of different concentrations of potassium iodide can be explained by the adsorption of the iodide ions on the metal surface. Inhibition efficiency was directly proportional to the fraction of the surface covered by the adsorbed molecules (θ). The values of the degree of surface coverage were evaluated at different concentrations of the inhibitors.

The degree of surface coverage (θ) was calculated using following equation (3):

$$\theta = 1-(w_{inh}/w_{corr}) \tag{3}$$

The Langmuir adsorption isotherm plot for the adsorption of various concentrations of the inhibitor was shown in Figure 5. According to the Langmuir isotherm model (Benabdellah et al. 2006).

$$C_{inh}/\theta = C_{inh} + 1/K_{ads} \tag{4}$$

Where K_{ads} is the equilibrium constant of the equilibrium adsorption process. This isotherm assumes that adsorbed molecule occupies only one site and it does not interact with other adsorbed species (Abdel Hameed et al. 2011). The linear regression parameters be- tween Cinh/θ and Cinh are listed in Table 1. The strong correlation (R2=1) showed that the adsorption of the inhibitor molecules in 1M HClO4 acid on the surface of electrode obeyed to the Langmuir's adsorption isotherm (Tang et al. 2003).

Table 1: Thermodynamic Parameters for the Adsorption of KI in HClO$_4$ Solution on Carbon Steel Electrodes at Different Temperatures.

T (K)	R2	10^4xKads (L/mol)	ΔHads (KJ/mol)	ΔGads (KJ/mol)	ΔSads (J/mol K)
293	1	12.966		-38,462	213.16
303	1	22.167	23.994 (eq.6)	-41,125	214.914
313	1	30.181		-43,286	214.952
323	1	33.24		-44,928	213.38
333	1	46.042	23,730 (eq.7)	-47,221	213.858

It can be observed that K_{ads} values increase with the increasing temperature. The high values of K_{ads} suggest that interaction between adsorbed molecules and the metal surface is strong, indicating that the inhibitor molecules are not easily removable from the surface by the solvent molecules (Desimone et al. 2011).

Adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG_{ads}) were calculated using the following relationship (Fekry et al. 2010):

$$\Delta G_{ads} = -RT_{ln} (55.5\ K_{ads}) \qquad (5)$$

Where, 55.5 is the concentration of water in solution in mol/L and R is the universal gas constant and T is the absolute temperature.
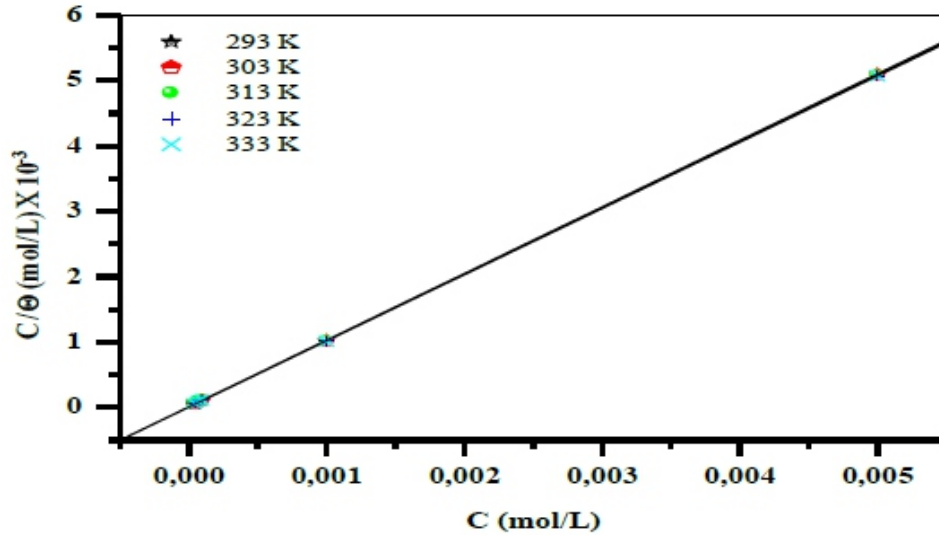
Fig. 5: Relationship between C_{inh}/Θ and Inhibitor Concentration C_{inh}.

To obtain the adsorption heat (ΔH_{ads}), the regression between Ln (K_{ads}) and 1/T (Figure 6) was dealt with and straight line obtained with slope equal to ($-\Delta H_{ads}/R$). The adsorption heat could be calculated according to the Van't Hoff equation (Tang et al. 2003).

$$lnK_{ads} = (-\Delta H_{ads}/RT) + Const \qquad (6)$$

Fig. 6: Relationship between Ln (K_{ads}) and 1/T for Carbon Steel Corrosion in 1M HClO$_4$ Solution with Potassium Iodide.

Generally, the values of adsorptive free enthalpy up to - 20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption), while those negative

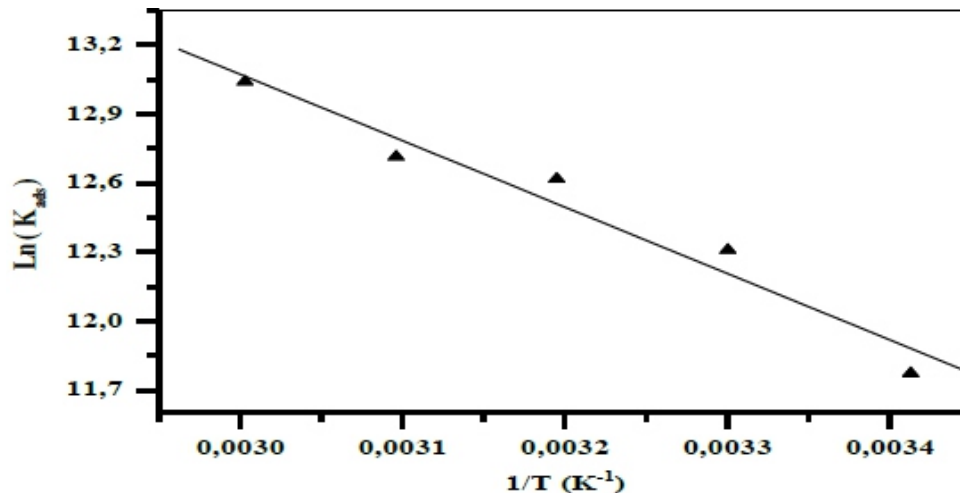values higher than - 40 kJ/mol involve sharing or transfer of electrons from the inhibitors to the metal surface to form a coordinate type of bond (chemisorption) (Bensajjay et al. 2003).
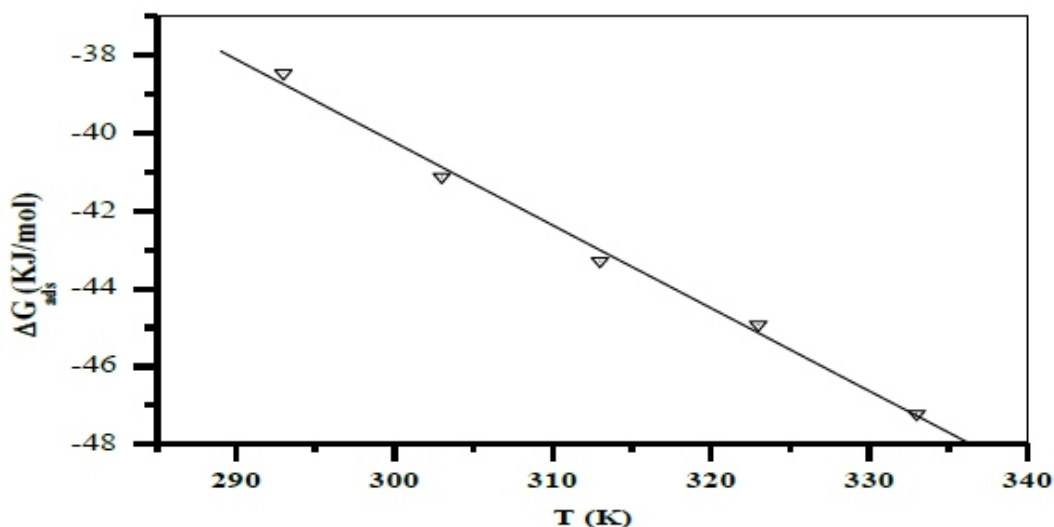

Fig. 7: Relationship between ΔG_{ads} and Absolute Temperature.

$\Delta Gads$ is related to the enthalpy change and entropy change of adsorption process, ΔH_{ads} and ΔS_{ads}, respectively by Gibbs equation

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (7)$$

Using the obtained values of ΔG_{ads} from the modified Langmuir isotherm, we can plot ΔG_{ads} versus T (Fig. 7). These plots give straight lines with slopes (-$\Delta Sads$) and intercepts ($\Delta Hads$) (Hassan et al. 2007). The endothermic adsorption process ($\Delta H_{ads} > 0$) is attributed unequivocally to chemisorption (Durnie et al. 1997). In the present case, the positive values of the enthalpy of adsorption indicate that the adsorption of the tested compounds is an endothermic process. The magnitude of ΔG_{ads} values obtained from weight loss measurements was in the range of -38 to -47 kJ/mol which also shows chemisorptions of the inhibitor. Moreover the ΔG_{ads} values increase with increasing temperature, which is due to the fact of strong chemisorption at higher temperatures. ΔS_{ads}=213.21 J/mol.K found by Gibbs equation. The value of ΔS_{ads} is positive in the adsorption process indicating that the presence of inhibitor increases the solvent entropy (Hameed et al. 2011). The value of the enthalpy and entropy of adsorption found by the two methods such as Van't Hoff and Gibbs relations are in good agreement.

Kinetic parameters of activation

The Arrhenius equation is employed to study the effect of temperature on the rate of corrosion of carbon steel in acid media containing various concentrations of inhibitor as expressed by equation (8) (Singh et al. 2012; Attar et al. 2014).

$$w = A + \exp(-Ea / RT) \qquad (8)$$

Where w is the corrosion rate of carbon steel, A is Arrhenius pre-exponential factor, Ea is the activation energy, R is the gas constant and T is the temperature.

The activation energy (Ea) at different concentrations of the inhibitor at various temperatures was determined by plotting ln(w) Versus 1/T (Figure 8).
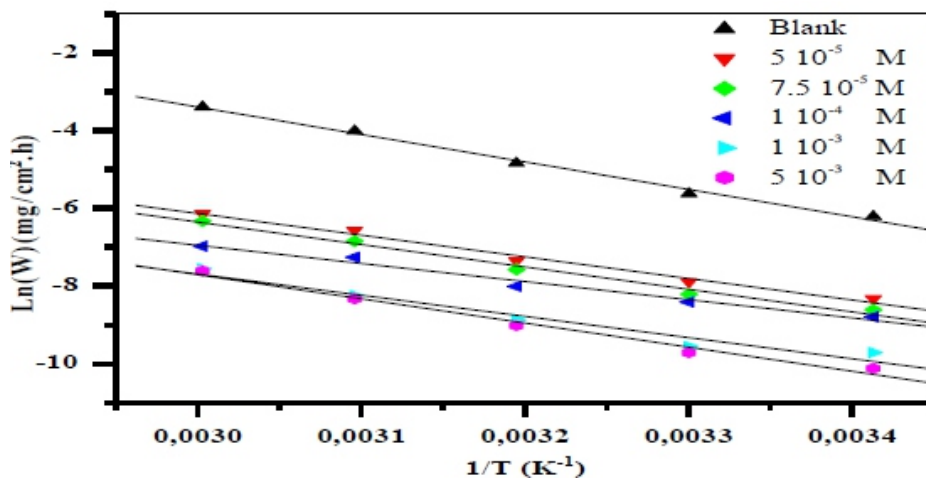
Fig. 8: Arrhenius Plot for the Dissolution of Carbon Steel in 1 M HClO₄ with and Without Inhibitor at Various Temperatures.

The enthalpy and entropy of activation for the metal dissolution process are determined using the transition state Eq. (9)

$$\ln(w/T) = -\Delta Ha/RT + \ln(RT/Nh) + (\Delta Sa/R) \qquad (9)$$

Where h is Plank's constant and N is Avogadro's number R is the universal gas constant, ΔH is the enthalpy of activation and ΔS is the entropy of activation. A plot of ln(w/T) versus 1/T gave a straight line (Figure. 9) with slope (-ΔHa/R) and intercept [ln(R/Nh) + (ΔSa/R] From the plot, the values of ΔHa and ΔSa were calculated and tabulated in Table 3, (Correlation (R^2>0.98).

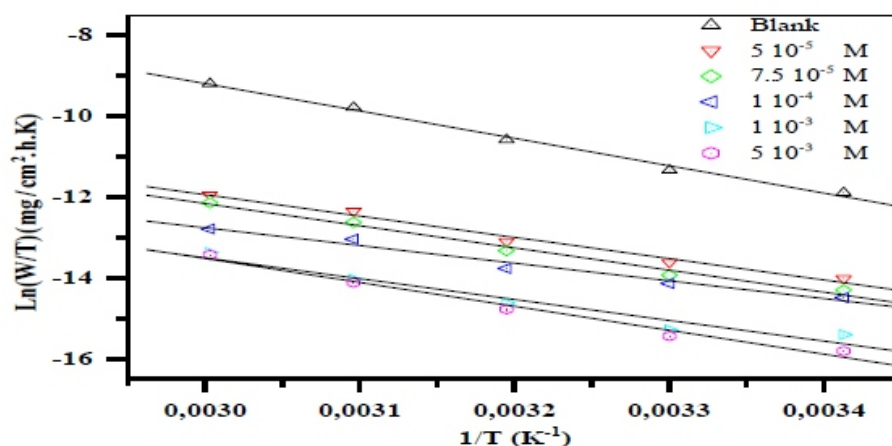**Fig. 9: Transition Arrhenius Plots of Carbon Steel in 1 M HClO4 with and without Inhibitor at Various Temperatures.**

Table 2: Activation Parameters for the Carbon Steel Dissolution in 1 M HClO$_4$ in Absence and Presence of Different Concentrations of KI

CInh (M)	Ea (KJ/mol)	ΔHa (KJ/mol)	ΔSa (J/mol.K)	?Ha313K(=Ea-RT KJ/mol)	△Ga 313 K (KJ/mol)
0	58.794	56.2	-1,05,437	56.191	89.201
5 10^{-5}	46.338	43.743	-1,65,622	43.785	95.582
7.5 10^{-5}	48.053	45.459	-1,62,304	45.45	96.26
10-Apr	38.914	36.32	-1,94,688	36.311	97.257
10-Mar	45.376	42.782	-1,81,468	42.773	99.581
5 10^{-3}	51.689	49.095	-1,62,677	49.086	100.012

Further, the values ΔHa obtained from the Eq. (9) and those values obtained from equation, ΔH=Ea-RT are in good agreement with each other.

The change in activation free energy (ΔGa) of the corrosion process can be calculated at each temperature by applying the equation:

$$\Delta Ga = \Delta Ha - T\Delta Sa \qquad (10)$$

The values of the apparent activation energy Ea for the inhibited solutions are lower than that for the uninhibited one, indicating a chemisorption process of adsorption (Dehri et al. 2006). The positive sign of the enthalpies ΔHa reflects the endothermic nature of the steel dissolution process and that mean the dissolution of steel is difficult (Mohamed et al. 2015). The negative values of ΔSa in the inhibited and uninhibited systems imply that activation complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease disorder takes place on going from reactants to the activated complex (Abd El-Rehim et al. 2001). In corrosion context, the activation Gibbs free energy is the excess energy needed to transform metal atoms at the metal surface into solvated metal ions (David et al. 2010).

4. CONCLUSION

On the basis of the experimental results obtained in the present study, the following conclusions can be drawn.

- The protection efficiency of the inhibitor depends on its concentration, immersion time and temperature.
- The efficiency (IE%) increase with increasing concentration and temperature.
- The corrosion process was inhibited by adsorption of the inhibitor molecule on the carbon steel surface.
- Adsorption of inhibitor on carbon steel surface from 1 M HClO$_4$ obeys Langmuir adsorption isotherm.

- The negative values of ΔGads showed the spontaneity of the adsorption.

- The inhibitor molecules adsorbed on the surface of carbon steel through chemisorption adsorption.

REFERENCES

[1] Abd El-Maksoud SA, Fouda AS (2005), *Some pyridine derivatives as corrosion inhibitors for carbon steel in acidic medium. Materials Chemistry and Physics, 93, 84-90. https://doi.org/10.1016/j.matchemphys.2005.02.020.*

[2] Al-Otaibi MS, Al-Mayouf AM, Khan M, Mousa AA, Al-Mazroa SA (2014), *Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media. Arabian Journal of Chemistry, 7, 340-346. https://doi.org/10.1016/j.arabjc.2012.01.015.*

[3] Riggs OL (1973), *Corrosion Inhibitors (2ndedn), CC. Nathan, Houston.*

[4] Uhlig HH, Revie RW (1985), *Corrosion and corrosion control. John Wiley & Sons, New York.*

[5] Loto RT, Loto CA, Popoola API (2012), *Corrosion inhibition of thiourea and thiadiazole derivatives: a review. Journal of Materials and Environ- mental Science, 3, 885-894.*

[6] Attar T, Larabi L (2014), *The Inhibition Effect of Potassium Iodide on the Corrosion of Pure Iron in Sulphuric Acid. Advances in Chemistry, 2014, 1-5. https://doi.org/10.1155/2014/827514.*

[7] Bereket G, Yurt A (2002), *Inhibition of the corrosion of low carbon steel in acidic solution by selected quaternary ammonium compounds. Anti- Corrosion Methods and Materials, 49, 210-220. https://doi.org/10.1108/00035590210431764.*

[8] Attar T, Larabi L (2014), *Corrosion inhibition of cold rolled steel in 0.5M H2SO4 by potassium iodide. Der Pharma Chemica, 6, 181-186.*

[9] Xiumei W, (2012), *The Inhibition Effect of Bis-Benzimidazole Compound for Mild Steel in 0.5 M HCl Solution. Int. J. Electrochem Sci, 7, 11149- 11160.*

[10] Zarrok H, Zarrouk A, Salghi A, Ramli Y, Hammouti B (2012), *Adsorption and Inhibition Effect of 3-Methyl-1-Propargylquinoxalin-2(1H)-One on Carbon Steel Corrosion in Hydrochloric Acid. Int. J. Electrochem. Sci, 7, 8958-8973.*

[11] Obot IB, Obi-Egbedi NO (2010), *Adsorption properties and inhibition of mild steel corrosion in sulphuric acid solution by ketoconazole: Experi- mental and theoretical investigation. Corros Sci, 52, 198-204. https://doi.org/10.1016/j.corsci.2009.09.002.*

[12] Benchadli A, Attar T, Choukchou-Braham E (2018), *Corrosion Inhibition of Carbon Steel (XC 38) in Hydrochloric Acid by Potassium Iodide. Journal of Advanced Research in Science and Technology, 5, 834-844.*

[13] Obot IB, Obi-Egbedi NO (2009), *Umoren, Antifungal drugs as corrosion inhibitors for aluminium in 0.1 M HCl. Corros. Sci, 51, 1868-1875. https://doi.org/10.1016/j.corsci.2009.05.017.*

[14] Elmsellem H, Basbas N, Chetouani A, Aouniti A, Radi A (2014), *Quantum Chemical Studies and Corrosion Inhibitive Properties of Mild Steel by Some Pyridine Derivatives in 1 N HCl Solution. Portugaliae Electrochimica Acta, 32, 77-108. https://doi.org/10.4152/pea.20140207.*

[15] Benabdellah M, Aouniti A, Dafali A, Hammouti B, Benkaddouret M (2006), *Investigation of the inhibitive effect of triphenyltin 2-thiophene car- boxylate on corrosion of steel in 2 M H3PO4 solutions. Applied Surface Science, 252, 8341–8347. https://doi.org/10.1016/j.apsusc.2005.11.037.*

[16] Abdel Hameed RE (2011), *Ranitidine Drugs as Non-Toxic Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Medium. Portugaliae Electro- chimica Acta, 29, 273-285. https://doi.org/10.4152/pea.201104273.*

[17] Tang LB, Mu GN, Liu GH (2003), *The effect of neutral red on the corrosion inhibition of cold rolled steel in 1.0 M hydrochloric acid,'' Corros. Sci, 45, 2251-2262. https://doi.org/10.3390/ma6062436.*

[18] Desimone MP, Gordillo G, Simison SN (2011), *The effect of temperature and concentration on the corrosion inhibition mechanism of an am- phiphilic amido-amine in CO2 saturated solution. Corrosion Science, 53, 4033–4043. https://doi.org/10.1016/j.corsci.2011.08.009.*

[19] Fekry AM, Ameer MA (2010), *Corrosion Inhibition of Mild Steel in Acidic Media Using Newly Synthesized Heterocyclic Organic Molecules. In- ternational Journal of Hydrogen Energy, 35, 7641–7651. https://doi.org/10.1016/j.ijhydene.2010.04.111.*

[20] Tang LB, Mu GN, Liu GH (2003), *The effect of neutral red on the corrosion inhibition of cold rolled steel in 1.0 M hydrochloric acid. Corros. Sci, 45, 2251-2262. https://doi.org/10.1016/S0010-938X(03)00046-5.*

[21] Bensajjay E, Alehyen S, El Achouri M, Kertit S (2003), *Corrosion inhibition of steel by 1phenyl 5mercapto 1,2,3,4tetrazole in acidic envi- ronments (0.5 M H2SO4 and 1/3 M H3PO4). Anti-Corros. Meth. Mater, 50, 402-409. https:// zdoi.org/10.1108/00035590310501558.*

[22] Hassan HH (2007), Inhibition of mild steel corrosion in hydrochloric acid solution by triazole derivatives: Part II: time and temperature effects and thermodynamic treatments. Electrochim. Acta, 53, 1722–1730. https://doi.org/10.1016/j.electacta.2007.08.021.

[23] Durnie W, De Marco R, Jefferson A, Kinsella B (1999), Development of a Structure-Activity Relationship for Oil Field Corrosion Inhibitors. J. Electrochem. Soc, 146, 1751-1756. https://doi.org/10.1149/1.1391837.

[24] Hameed RSA (2011), Aminolysis of polyethylene terephthalate waste as corrosion inhibitor for carbon steel in HCl corrosive medium. Adv. App. Sci. Res. 2, 483-499.

[25] Singh A, Ahamad I, Yadav DK, Singh VK, Quraishi MA (2012), The effect of environmentally benign fruit extract of shahjan (moringa oleifera) on the corrosion of mild steel in hydrochloric acid solution. Chemical Engineering Communications. 199, 63-77. https://doi.org/10.1080/00986445.2011.570390.

[26] Attar T, Larabi L, Yahia H (2014), Inhibition effect of potassium iodide on the corrosion of carbon steel (XC 38) in acidic medium. International Journal of Advanced Chemistry, 2, 139-142. https://doi.org/10.14419/ijac.v2i2.3272.

[27] Dehri I, Ozcan M (2006), The effect of temperature on the corrosion of mild steel in acidic media in the presence of some sulphur-containing or- ganic compounds. Materials Chemistry and Physics, 98,316–323. https://doi.org/10.1016/j.matchemphys.2005.09.020.

[28] Mohamed SM, Mahmoud AA (2015), Some pyrazole derivatives as corrosion inhibitors for carbon steel in hydrochloric acid solutions. J. eur. chem, 6, 342-349. https://doi.org/10.5155/eurjchem.6.3.342-349.1279.

[29] Abd El-Rehim SS, Refaey SAM, Taha F, Saleh MB, Ahmed RA (2001), Corrosion inhibition of mild steel in acidic medium using 2-amino thio- phenol and 2-cyanomethyl benzothiazole. Journal of Applied Electrochemistry, 31, 429–435. https://doi.org/10.1023/A:1017592322277.

[30] David E, Talbot J, James D, Talbot R (2010), Corrosion Science and Technology: Materials Science & Technology. CRC Press, 94-95.

Effect of Hydrogen ION Concentration and Adsorbent Dosage on the Removal of Heavy Metals from Metal Scrap Effluents using Activated Carbon from African Palm Fruit

Zalihat Abdullahi[1], Kamaludeen Hussaini[1], Sani Abdulrazak[2]*, Abdulwahab Hashimu Yau[3]

[1]Department of Chemistry, Faculty of Science, Federal University of Technology, Minna, Nigeria

[2]Department of Veterinary Physiology, Faculty of Veterinary Medicine, Ahmadu Bello University, Zaria

[3]Department of Veterinary Pharmacology and Toxicology, Faculty of Veterinary Medicine, Ahmadu Bello University, Zaria

*Corresponding author E-mail: sazzak175@gmail.com

A B S T R A C T

This study details the production of activated carbon from African palm fruit and subsequent treatment of heavy metals; Cadmium, Cop- per, Nickel, and Lead in wastewater effluent with the produced activated carbon from a metal scrap market in the heart of Kaduna state, Nigeria, which constitutes high level of pollution in the environment. Hydrogen ion concentration and adsorbent dosage were determined on water treatment quality using Atomic Absorption Spectrophotometer (AAS). The produced activated carbon showed a significant ability in removing heavy metals; Cadmium, Copper, Nickel, and Lead from samples of the wastewater. Higher efficiencies were observed with increase in adsorbent dosage (99.73 ± 0.265, 95.96 ± 0.053, 99.91 ± 0.085, and 95.12 ± 0.035 % at 2.5 g for Cadmium, Cop- per, Nickel, and Lead, respectively) and at a pH of 6 (99.61 ± 0.182 and 80.31 ± 0.015 % for Cadmium and Lead, respectively) and at a pH of 8 (99.79 ± 0.201 and 99.73 ± 0.252 for copper and nickel respectively). This findings show that African palm fruit can be utilized to produce activated carbon used in removal heavy metals from effluent water, representing an effective means of utilizing agricultural residues and also an alternative to the expensive commercial activated carbon.

Keywords: African Palm Fruit; Adsorbent Dosage; pH; Activated Carbon; Wastewater Effluent.

1. INTRODUCTION

Borassus aethiopum has a fan-like palm with a trunk of about 50 cm diameter and growing up to 30 m high. The trunk is considered as a good material for house construction as it appears to be very resistant to termites and fungi, and it is a very hard wood (Ouattara et al. 2015). Its shells are considered as agricultural waste in Northern Nigeria. Activated Carbon is a class of microporous materials that serve as adsorbents for the removal of gaseous and liquid pollutants as well as many other applications. They are amorphous and have an extensively developed internal pore structure. They are produced from a material rich in carbon, such as wood, coal, lignin and coconut shell (Gamby et al 2001; Gupta et al. 2004; El-said et al. 2010; Verla et al. 2012).

Recent study by Abdulrazak et al. 2016 showed higher percentage removal of heavy metals from wastewater effluent using activated carbon at a temperature of 80°C and at an optimum contact time of 60 minutes, after which the percentage removal decreases. Also, Khan et al.2001 reported that at an adsorbent dose of 0.8g /50ml is sufficient to remove 80–100% Cr (VI) from aqueous solution having an initial metal concentration of 20mg/L at a pH value of 1 but the efficiency reduced sharply to 15% at pH 3. (Halim et al. 2008) studied the removal of lead ions from industrial waste water by different types of natural materials. They reported that at lead concentration of 4mg/L and pH 6 the adsorption capacity was higher for Nile-rose plant powder at 80% removal and at the same Concentration and pH it was also reported that bone powder removed 98.8% of lead. (Abdulrazak et al. 2015) also studied the removal efficiency of chromium by produced activated carbon from moringa oleifera pods from tannery wastewater and reported higher removal efficiency at higher temper- ature. Iyagba and Opete (2009) reported that the removal of chromium and lead from drill cuttings using palm kernel shell and husk as adsorbents is possible. The removal and rapid decontamination of heavy metals becomes very important for the environmental remedia- tion. The primary parameter for choice of adsorbent materials is cost. The most effective method for heavy metal removal from water is adsorption through the use of activated carbon for heavy metal removal from waste water (Nwabanne et al. 2012). This is due to its good capacity for adsorption of heavy metals. However, high cost of activated carbon and 10-15% loss during the regeneration has limits its use in the utilization of activated carbon in the developing countries (Ho et al. 2005). Therefore, there is increasing research interest in using alternative low-cost adsorbents especially from low cost agricultural wastes in water treatment (Khan et al. 2003; Abdulrazak et al. 2015).

2. MATERIALS AND METHOD

Activated carbon preparation

African palm fruits were collected and sun-dried for six days. The seeds were then removed and the sample was pulverized using mortar and pestle. This was used for the analysis.

Activated carbon used as sorbent was prepared according to the method described by (Abdulrazak et al. 2015). Six grams (6g) of ground African palm fruits were soaked in 50 ml of 50% w/v phosphoric acid solution at 30°C for 48h. After filtration, the impregnated raw material was then carbonized in a muffle furnace at 300°C for 2 hours in nitrogen atmosphere. After cooling, each of the carbonized ma- terials was washed with 200 ml hot distilled water, and then dried for 2 hours at 120°C. The dried activated carbon was then weighed to determine percentage yield, which is mathematically expressed as;

$$Percentage\ yield\ (\%) = \frac{yield\ (g)}{mass\ of\ raw\ material\ (g)} \times 100 \qquad (1)$$

Physiochemical properties

Bulk density

The method described by Abdulrazak et al. 2016. A 25cm³ cylinder was filled to the mark with the produced activated carbon. The cylin- der was tapped for at least one to two minutes to compress the carbon to a steady volume. The compressed sample was poured out of the cylinder and weighed and the mass (m) was divided by the final volume occupied in the cylinder.

$$Bulk\ density = \frac{mass\ (g)}{final\ volume\ (cm3)} \qquad (2)$$

Conductivity

This was done as described by Abdulrazak et al. 2016. Exactly 0.5g of the activated carbon was placed into 100 cm³ beaker containing 50 cm³ distilled water. It was macerated using a glass rod and then allowed to stay for about 1 hour. The conductivity was determined using conductivity meter.

Effect of hydrogen ion concentration

The effect of Hydrogen ion concentration on the adsorption of heavy metals by the activated carbon from African palm fruit was studied over a pH range of 2, 4, 6, 8 and 10 respectively. Exactly 50ml of effluent was measured into five different 250ml conical flask. The pH of the flask was adjusted to 2, 4, 6, 8 and 10 for the 1st, 2nd, 3rd, 4th, and 5th flask respectively using 0.1M HCl or 0.1M NaOH solutions. A weight of 0.5g of the activated carbon was then added into the effluent in each flask and the mixtures were stirred for a period of 60 min. It was then filtered using filter paper,

Effect of adsorbent dosage

50ml of the digested effluents was added into five different 250ml conical flask. 0.5g, 1.0g, 1.5g, 2.0g, and 2.5g of the adsorbent was added into the 1st, 2nd, 3rd, 4th, and 5th flask respectively, and the mixtures were corked and stirred for 60 minutes. The content of each flask was filtered using filter paper.

Data analysis

Each procedure in the study was repeated five times and data was expressed as mean percentage ± Standard deviation.

2. RESULTS AND DISCUSSION

Table 1 shows the result of physiochemical properties of the produced activated carbon is represented below.

Table 1: Result of the Physicochemical Properties of the Adsorbent.

Parameters	Values
Bulky density (g/cm^3)	0.66
Electrical conductivity)	1.2 x10$_2$

Tables 2 and 3 shows the Effect of Hydrogen ion concentration on removal of Heavy metals; Cadmuim, Nickel, Lead and Copper. From the table below, there are higher treatment efficiencies at pH 6, except for Copper and Nickel, which shows higher treatment efficiency at pH 8. This is in agreement with similar work carried out by Mustaqeem et al. (2014a).

Table 2: Effect of Ph on Removal of Heavy Metals (Cadmium and Copper)

pH	Percentage removal of Heavy metals (%)									
	Cadmium			Standard Deviation		Copper			Standard Deviation	
	Minimum	Maximum				Minimum	Maximum			
	Level	level	Mean		Variance	Level	Level	Mean		Variance
2	89.17	89.29	89.22	0.061	0.004	86	86.2	86.12	0.108	0.012
4	92.84	93	92.92	0.08	0.006	90.4	90.5	90.44	0.055	0.003
6	99.4	99.73	99.61	0.182	0.033	96.5	96.58	96.53	0.044	0.002
8	95.5	95.78	95.64	0.14	0.02	99.6	100	99.79	0.201	0.041
10	92.8	92.9	92.85	0.05	0.003	95.5	95.61	95.55	0.057	0.003

Table 3: Effect of pH on Removal of Heavy Metals (Nickel and Lead)

pH	Percentage removal of Heavy metals (%)									
	Nickel			Standard Deviation		Lead			Standard Deviation	
	Minimum	Maximum				Minimum	Maximum			
	Level	Level	Mean		Variance	Level	Level	Mean		Variance
2	99	100	99.65	0.566	0.321	74	74.2	74.07	0.113	0.013
4	99.79	100	99.86	0.118	0.014	77.5	77.6	77.55	0.05	0.003
6	99	100	99.66	0.572	0.327	80.3	80.33	80.31	0.015	0.0002
8	99.5	100	99.73	0.252	0.063	80.25	80.3	79.34	0.055	0.033
10	99.7	100	99.87	0.153	0.023	79.3	79.4	79.34	0.04	0.002

Hydrogen ion concentration is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of metal ions. For this, the role of hydrogen ion concentration was examined at different pH. (Mustaqeem et al. 2014b) Hydrogen ion concentration affects protonation of functional groups on the adsorbents, as well as its solubility. The metal uptake was low at low pH, this is due to more Hydrogen ions that are in solution which compete with the metal ion for active site of the adsorbent. As the pH in- creases, there is increase in the percentage removal due to reduction of the H+ ion in solution. Highest removal of Copper and Nickel, Cadmium and Lead were highest at pH of 6. Apart from Nickel and Copper, the percentage removal for all metals decreases at pH of above 6. The decrease in removal may be due to the formation of metal hydroxide complex at higher pH and also due to weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent

which ultimately leads to the reduction in ad- sorption capacity (Baral et al. 2006). This is similar to what was reported by (Mulu 2013).

Tables 4 and 5 show the Effect of Adsorbent Dosage on removal of Heavy metals; Cadmuim, Nickel, Lead and Copper. The table below shows higher treatment efficiencies with increased dosage. That is, highest percentage removal of the heavy metals analyzed occurred at adsorbent dosage of 2.5g.

Table 4: Effect of Adsorbent Dosage on Removal of Heavy Metals (Cadmium and Copper)

Adsorbent Dosage (g)	Percentage removal of Heavy metals (%)									
	Cadmium					Copper				
	Minimum Level	Maximum Level	Mean	Standard Deviation	Variance	Minimum Level	Maximum Level	Mean	Standard Deviation	Variance
0.5	91.73	99.76	91.75	0.015	0.0002	85.6	85.85	85.75	0.132	0.0175
1	99.7	99.77	99.73	0.036	0.0013	87.65	87.73	87.69	0.04	0.0016
1.5	99.12	99.2	99.16	0.04	0.0016	90.3	90.5	90.37	0.1102	0.0121
2	99.3	100	99.73	0.379	0.1433	91.4	91.5	91.45	0.05	0.0025
2.5	99.5	100	99.7	0.265	0.07	95.9	96	95.96	0.053	0.0028

Table 5: Effect of Adsorbent Dosage on Removal of Heavy Metals (Nickel and Lead)

Adsorbent Dosage (g)	Percentage removal of Heavy metals (%)									
	Nickel					Lead				
	Minimum Level	Maximum Level	Mean	Standard Deviation	Variance	Minimum Level	Maximum Level	Mean	Standard Deviation	Variance
0.5	91.7	91.73	91.73	0.025	0.0006	89.01	89.17	89.11	0.09	0.008
1	99.6	99.75	99.68	0.074	0.0058	92.3	92.4	92.35	0.05	0.003
1.5	99.08	99.12	99.1	0.02	0.0004	93.3	93.4	93.36	0.053	0.003
2	99.6	100	99.83	0.2053	0.0421	95.1	95.15	95.12	0.026	0.001
2.5	99.83	100	99.91	0.085	0.0073	95.1	95.16	95.12	0.035	0.001

The availability and accessibility of adsorption site is controlled by adsorbent dosage (Rafeah., et al 2009). It can be seen that, as the dose of the adsorbent increased, there is increase in percentage removal. Highest removal of Cadmuim, Nickel, Lead and Copper, were at adsorbent dosage of 2.5g. The increase in percentage removal as adsorbent dosage increase is due to the increase or availability of more adsorption site of the adsorbent at higher dose and also increase in functional groups available on the adsorbent on which metals could interact (Meikap, 2005).

Organic contents of wastewater and the presence of microorganisms stimulate adsorption and, therefore, show that the produced activat- ed carbon can improve performance by developing different bacterial species (Jeong et al. 2016), which may also played a part in the whole study.

4. CONCLUSION

This results obtained shows that locally available materials such as low cost African palm fruit (Borassus aethiopum) could easily be sourced to produce activated carbon which can be used as efficient

adsorbents for Heavy metal removal from effluent water, representing an environmentally effective means of utilizing these agricultural residue and also high cost of commercial activated carbon.

REFERENCES

[1] Abdulrazak S, Hussaini K, & Sani HM (2016) Evaluation of removal efficiency of heavy metals by low-cost activated carbon prepared from Afri- can palm fruit. Applied water Science. 7, 3151-3155. https://doi.org/10.1007/s13201-016-0460-x.

[2] Abdulrazak S, Sulyman YI, Bello HI, Akanni AS, Oniwapele YA, & Muktari M, (2015) Tannery wastewater treatment using activated carbon from Moringa oleifera pods. Journal of Environmental Science Toxicology and Food Technology. 9(12), 96–99

[3] Baral S, Das SN, & Rath P (2006) Hexavalent Chromium Removal from Aqueous Solution by Adsorption on Treated Sawdust, Biochemical Engi- neering Journal, 31(3), 216– 222. https://doi.org/10.1016/j.bej.2006.08.003.

[4] El-Said AG, Badaway NA, & El Pasir AA (2010) Comparison of synthetic and natural adsorbents for sorption of Ni (II) ions from aqueous solu- tion. Journal of Nature and Science 8:86-94

[5] Gamby J, Taberna PL, Simon P, Fauvarque J, & Chesneau M (2001) Studies and characteristics of various activated carbons used for car- bon/carbon supercapacitors. Biodiversity and conservation. 101(1), 109-116. https://doi.org/10.1016/S0378-7753(01)00707-8.

[6] Gupta VK, Mittal A, Krishnan L, & Gabje V (2004) Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. Separation and Purification Technology. 40(1):87–96 https://doi.org/10.1016/j.seppur.2004.01.008.

[7] Halim SHA, Shehata AMA, & El-Shahat MF (2008) Removal of lead ions from industrial waste water by different types of natural materials. Wa- ter research. 37,1678-1683. https://doi.org/10.1016/S0043-1354(02)00554-7.

[8] Ho YS, Chiang TH, & Hsueh YM (2005) Removal of basic dye from aqueous solution using tree fern as a biosorbent. Process Biochemistry Jour- nal. 40(1), 119-124. https://doi.org/10.1016/j.procbio.2003.11.035.

[9] Iyagba ET, & Opete OSE (2009) Removal of chromium and lead from drill cutting using activated palm kernel shell and husk. African Journal of Environmental Science and Technology. 3(7), 17 -179.

[10] Jeong S, Kyungjin C, Hyokwan B, Torove L, Scott AR, Pejhman K, & Saravanamuthu V (2016) Effect of microbial community structure on or- ganic removal and biofouling in membrane adsorption bioreactor used in seawater pretreatment. Chemical Engineering Journal. 294. https://doi.org/10.1016/j.cej.2016.02.108.

[11] Khan NA, Ali SI, & Ayub S (2001) Effect of pH on the Removal of Chromium (Cr) (VI) by Sugar Cane Baggase. Science and Technology. 6, 13- 19. https://doi.org/10.24200/squjs.vol6iss2pp13-19.

[12] Khan NA, Shaaban MG, & Hassan MHA (2003) Removal of heavy metal using an inexpensive adsorbent. In: Proc. UM Research Seminar (2003) organized by Institute of Research Management & Consultancy (IPPP), University of Malaya, Kuala Lumpur.

[13] Meikap BC (2005) Removal of chromium (VI) from dilute aqueous solutions by activated carbon developed from Terminaliaarjuna nuts activated with zinc chloride. Chemical Engineering Journal. 60, 3049-3059. https://doi.org/10.1016/j.ces.2004.12.049.

[14] Mulu BD (2013) Batch Sorption Experiment, Langmuir & Freundlich Isotherm Studies for the Adsorption of Textile Metal ions onto Teff Straw (Eragrostis tef) Agricultural Waste. Journal of Thermodynamics. 13, 1-6. https://doi.org/10.1155/2013/375830.

[15] Mustaqeem M, Sharif M, Bagwan P, & Patil R (2014) Evaluation of removal efficiency of Cu (II) ion by activated carbon prepared from Nirgudi, Mudra and Gliricidia Sipium leaves from their aqueous solution. International Journal of Advanced Chemistry. 2(1) 44-48. https://doi.org/10.14419/ijac.v2i1.1863.

[16] Nwabanne JT, & Igbokwe PK (2012) Comparative study of Lead (II) removal from aqueous solution using different adsorbents. International Journal of Engineering Research and Applications. 2, 1830-1838.

[17] Outtara DH, Outtara HG, Goualie BG, Kouame LM, & Niamke SL (2015) Biochemical and Functional Properties of Lactic Acid Bacteria Isolated from Ivorian Cocoa Fermenting Beans. Journal of Applied Biosciences, 77, 6489-6499. https://doi.org/10.4314/jab.v77i1.9.

[18] Rafeah W, Zainab N, & Veronica U (2009) Removal of Mercury, Lead, and Copper from aqueous solution by activated carbon of palm oil empty fruit bunch. World Applied Science Journal 5; 84-91.

[19] *Sambou B, Goudiaby A, Ervik F, Diallo D, & Camara MC (2002) Palm wine harvesting by the bassari threatens Borassus aethiopum populations in north-western guinea. Journal of power sources. 11 (7), 1149-1161 https://doi.org/10.1023/A:1016005025090.*

[20] *Verla AW, Horsfall M, Verla EN, Spiff AI, & Ekpete OA (2012) Preparation and characterization of activated carbon from fluted pumpkin seed shell. Asian Journal of Natural and Applied Sciences 1: 39-50.*

Instructions for Authors

Essentials for Publishing in this Journal

1   Submitted articles should not have been previously published or be currently under consideration for publication elsewhere.

2   Conference papers may only be submitted if the paper has been completely re-written (taken to mean more than 50%) and the author has cleared any necessary permission with the copyright owner if it has been previously copyrighted.

3   All our articles are refereed through a double-blind process.

4   All authors must declare they have read and agreed to the content of the submitted article and must sign a declaration correspond to the originality of the article.

Submission Process

All articles for this journal must be submitted using our online submissions system. http://enrichedpub.com/ . Please use the Submit Your Article link in the Author Service area.

Manuscript Guidelines

The instructions to authors about the article preparation for publication in the Manuscripts are submitted online, through the e-Ur (Electronic editing) system, developed by **Enriched Publications Pvt. Ltd**. The article should contain the abstract with keywords, introduction, body, conclusion, references and the summary in English language (without heading and subheading enumeration). The article length should not exceed 16 pages of A4 paper format.

Title

The title should be informative. It is in both Journal's and author's best interest to use terms suitable. For indexing and word search. If there are no such terms in the title, the author is strongly advised to add a subtitle. The title should be given in English as well. The titles precede the abstract and the summary in an appropriate language.

Letterhead Title

The letterhead title is given at a top of each page for easier identification of article copies in an Electronic form in particular. It contains the author's surname and first name initial .article title, journal title and collation (year, volume, and issue, first and last page). The journal and article titles can be given in a shortened form.

Author's Name

Full name(s) of author(s) should be used. It is advisable to give the middle initial. Names are given in their original form.

Contact Details

The postal address or the e-mail address of the author (usually of the first one if there are more Authors) is given in the footnote at the bottom of the first page.

Type of Articles

Classification of articles is a duty of the editorial staff and is of special importance. Referees and the members of the editorial staff, or section editors, can propose a category, but the editor-in-chief has the sole responsibility for their classification. Journal articles are classified as follows:

Scientific articles:

1. Original scientific paper (giving the previously unpublished results of the author's own research based on management methods).

2. Survey paper (giving an original, detailed and critical view of a research problem or an area to which the author has made a contribution visible through his self-citation);

3. Short or preliminary communication (original management paper of full format but of a smaller extent or of a preliminary character);

4. Scientific critique or forum (discussion on a particular scientific topic, based exclusively on management argumentation) and commentaries. Exceptionally, in particular areas, a scientific paper in the Journal can be in a form of a monograph or a critical edition of scientific data (historical, archival, lexicographic, bibliographic, data survey, etc.) which were unknown or hardly accessible for scientific research.

Professional articles:

1. Professional paper (contribution offering experience useful for improvement of professional practice but not necessarily based on scientific methods);

2. Informative contribution (editorial, commentary, etc.);

3. Review (of a book, software, case study, scientific event, etc.)

Language

The article should be in English. The grammar and style of the article should be of good quality. The systematized text should be without abbreviations (except standard ones). All measurements must be in SI units. The sequence of formulae is denoted in Arabic numerals in parentheses on the right-hand side.

Abstract and Summary

An abstract is a concise informative presentation of the article content for fast and accurate Evaluation of its relevance. It is both in the Editorial Office's and the author's best interest for an abstract to contain terms often used for indexing and article search. The abstract describes the purpose of the study and the methods, outlines the findings and state the conclusions. A 100- to 250-Word abstract should be placed between the title and the keywords with the body text to follow. Besides an abstract are advised to have a summary in English, at the end of the article, after the Reference list. The summary should be structured and long up to 1/10 of the article length (it is more extensive than the abstract).

Keywords

Keywords are terms or phrases showing adequately the article content for indexing and search purposes. They should be allocated heaving in mind widely accepted international sources (index, dictionary or thesaurus), such as the Web of Science keyword list for science in general. The higher their usage frequency is the better. Up to 10 keywords immediately follow the abstract and the summary, in respective languages.

Acknowledgements

The name and the number of the project or programmed within which the article was realized is given in a separate note at the bottom of the first page together with the name of the institution which financially supported the project or programmed.

Tables and Illustrations

All the captions should be in the original language as well as in English, together with the texts in illustrations if possible. Tables are typed in the same style as the text and are denoted by numerals at the top. Photographs and drawings, placed appropriately in the text, should be clear, precise and suitable for reproduction. Drawings should be created in Word or Corel.

Citation in the Text

Citation in the text must be uniform. When citing references in the text, use the reference number set in square brackets from the Reference list at the end of the article.

Footnotes

Footnotes are given at the bottom of the page with the text they refer to. They can contain less relevant details, additional explanations or used sources (e.g. scientific material, manuals). They cannot replace the cited literature.

The article should be accompanied with a cover letter with the information about the author(s): surname, middle initial, first name, and citizen personal number, rank, title, e-mail address, and affiliation address, home address including municipality, phone number in the office and at home (or a mobile phone number). The cover letter should state the type of the article and tell which illustrations are original and which are not.

Address of the Editorial Office:

Enriched Publications Pvt. Ltd.
S-9,IInd FLOOR, MLU POCKET,
MANISH ABHINAV PLAZA-II, ABOVE FEDERAL BANK,
PLOT NO-5, SECTOR -5, DWARKA, NEW DELHI, INDIA-110075,
PHONE: - + (91)-(11)-45525005