

The Kinetics, Stoichiometry And Thermodynamics Evaluation Of The Reduction Of Nacn By Brilliant Green (BG⁺) In Aqueous Sulphuric Acid Medium

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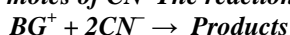
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Abstract: The kinetics and stoichiometry of the reduction of NaCN by Brilliant Green (BG⁺) in aqueous sulphuric acid medium have been studied under the following conditions: temperature of $29 \pm 1^\circ \text{C}$; ionic strength, $\mu = 0.196 \text{ mol dm}^{-3}$ (Na_2SO_4), $[\text{H}^+] = 2.00 \times 10^{-4} \text{ mol dm}^{-3}$ (H_2SO_4). In the stoichiometry, one mole of brilliant green was consumed by two moles of CN⁻. The reaction showed a stoichiometry of 1:2, which conforms to the equation:



The reaction was insensitive to changes in acid and ionic strength of the reaction medium. The Michaelis-Menten plot of $1/k_1$ versus $1/[\text{oxidant}]$ was linear without intercept which suggested absence of intermediate complex. Also, the activation enthalpy ($\Delta H^* = +19.22 \text{ kJ mol}^{-1}$) and entropy ($\Delta S^* = -0.168 \text{ KJ K}^{-1}\text{mol}^{-1}$) were determined. The entropy of activation shows a more ordered activated complex relative to the reactants species. A reaction mechanism via an outer-sphere pathway is proposed for this reaction

Keywords: Mechanism; Outer-sphere; Brilliant green; Thermodynamic; Stoichiometry Activation.

I. INTRODUCTION

Oxidation reactions are very important in nature and in organic synthesis. Reduction-Oxidation (Redox) reaction is the transfer of electrons between two Redox species like ions, molecules, biological systems etc. The reaction usually involves rearrangement and transfer of outermost shell electrons of reacting species in order to gain stability. Thus, oxidation is the loss of electrons while reduction is the gain of electrons (Wong *et al.*, 2002). Many reactions in inorganic and biological systems involve transfer of electron, thus, electron

transfer reaction plays a key role to various physical and biological systems (Ahmed *et al.*, 2018).

Brilliant green (BG⁺) is a triphenylmethane dye of the malachite green series, and it is chemically known as 4,4-bisdiethylaminotriphenylmethyl-sulphate (Kobiraj *et al.*, 2012). among the commonly recognized cationic dyes used for various purposes such as dyeing silk, cotton, biological stain, dermatological agent, wool, leather, jute, veterinary medicine, green ink manufacture, intestinal parasites, paper printing, and Fungus textile dyeing (Agarwal *et al.*, 2017). Brilliant green apart from being a dye of biological interest has a major use in

the dye industry for dyeing and printing all types of fibre (Baird *et al.*, 2000).

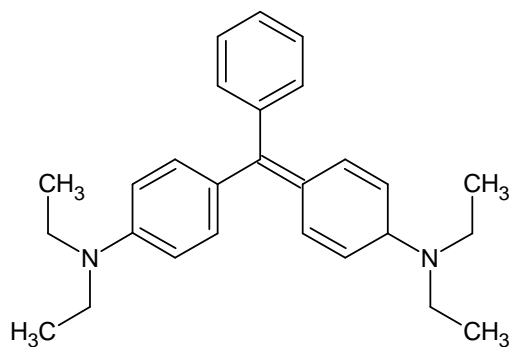


Figure: 1 Structure of Brilliant Green.

Brilliant green (BG⁺) dye is among the different classes of the available, cationic dyes which are considered to be the brightest and readily water soluble dyes (Ishaq *et al.*, 2017). The removal of BG⁺ dye is necessary before their discharge because the dye is hazardous when contact with the skin and when ingested and it is considered toxic to the lungs, through inhalation (El-Chaghaby *et al.*, 2018).

II. EXPERIMENTAL

MATERIALS

All chemicals and reagents used in the work were analar grade and were used without further purification. H₂SO₄ was used to furnish H⁺ to the reaction, BG⁺ was used as the oxidant, NaCN as the reductant and Na₂SO₄ was used to maintain a constant ionic strength for each run. Methanol was used to vary the dielectric constant of the reaction medium (Mohammed *et al.*, 2009).

STOICHIOMETRY DETERMINATION

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method (Yusuf *et al.*, 2004). The concentration of brilliant green was kept constant while that of cyanide ion was varied, keeping [H⁺] and ionic strength, μ, constant at 2.0 x 10⁻⁴ mol dm⁻³ and 0.196 mol dm⁻³ respectively. The reaction was allowed to go to completion and the absorbance of the solutions monitored at 620 nm, characteristic of malachite green (Thakare and Jathav, 2013). The values obtained were plotted against the individual mole ratios of the reactants. The stoichiometry of this reaction was determined from the plot of absorbance versus the mole ratio.

KINETIC MEASUREMENT

All kinetic measurements were carried out under pseudo-first order conditions with respect to [CN⁻] in at least 30-fold excess over [BG⁺]. The reaction was measured using UV Visible 721 spectrophotometer, by following the decrease in absorbance of the BG⁺ at λ_{max} = 620 nm, characteristic of BG⁺. The ionic strength was maintained constant at 0.196 mol dm⁻³ (Na₂SO₄), [H⁺] at 2.0 x 10⁻⁴ mol dm⁻³ (H₂SO₄) and T = 29 ± 1°C. Pseudo-first order plots of log(A_t - A_∞) against time

were made (where A_t and A_∞ are the absorbance at time, t and at the end of the reaction respectively) and the slopes of the plots gave the pseudo-first order rate constants, k_{obs}.

INFLUENCE OF ACID AND IONIC STRENGTH

The effect of changes in [H⁺] on the reaction rate was investigated by keeping [BG⁺] and [CN⁻] constant while varying [H⁺] between (0.4 – 4.0) x 10⁻⁴ mol dm⁻³. Ionic strength, μ, was maintained at 0.196 mol dm⁻³ (Na₂SO₄) and reaction was carried out at 29 ± 1°C. Order of reaction with respect to [H⁺] was obtained as the slope of the plot of log k₁ against log [H⁺]. Variation of acid dependent second order rate constant with [H⁺] was obtained by plotting k_{H+} against [H⁺].

The ionic strength of the reaction mixture was varied between 0.116 and 0.476 mol dm⁻³ and maintaining [BG⁺], [CN⁻] and [H⁺] constant. Reaction temperature was maintained at 29±1 °C. Relationship of reaction rate with changes in the ionic strength was determined by plotting log k₂ against μ.

Effect of changes in dielectric constant of the reaction medium on the reaction rate was investigated adding 0.10 – 0.80 cm³ (accounting for 2 – 16%) acetone to the reaction mixture, keeping [BG⁺], [CN⁻] and [H⁺] constant. The ionic strength of 0.196 mol dm⁻³ and temperature of 29 ± 1°C were maintained. A plot of log k₂ against 1/D gives the relationship between the second order rate constant and the total dielectric constant of the reaction medium, D.

FREE RADICAL TEST

Presence or otherwise of free radical species in the reaction was checked by addition of about 5.0 cm³ of acrylamide to a partially oxidized reaction mixture. This was followed by a large excess of methanol. Formation of polyacrylamide evidenced by gel formation would provide information for the presence of free radicals in the reaction mixture. Kinetic evidence as indicated by Michaelis-Menten plot of 1/k₁ versus 1/[CN⁻] also could give an idea on the presence or absence of intermediate complex.

ACTIVATION PARAMETERS

Activation parameters (ΔS* and ΔH*) were calculated from the intercept and slope of the plot of ln(k/T) versus 1/T using Eyring equation (Atkins and de Paula, 2006) given in below.

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k}{h}\right) + \left(\frac{\Delta S^*}{R}\right) + \left(\frac{\Delta H^*}{RT}\right) \dots\dots\dots 1$$

Where, k = reaction rate constant, T = Kelvin temperature, κ = Boltzmann's constant, h = Planck's constant, ΔS* = entropy of activation, ΔH* = enthalpy of activation, R = gas constant.

III. RESULTS AND DISCUSSION

The result of spectrophotometric titration showed that two moles of the reductant were consumed by one mole of

the oxidant. The plot of the titration from which the stoichiometry was determined is presented in (Figure 2). Based on this result, the overall stoichiometric equation for the reaction can be represented by:

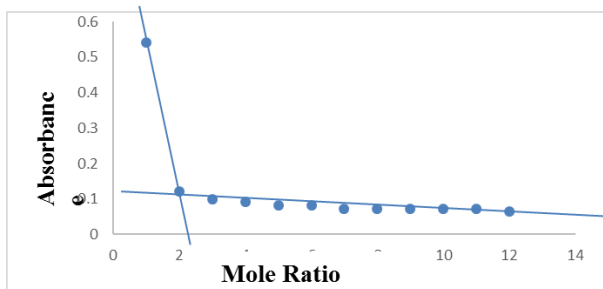
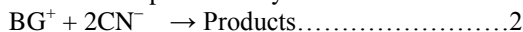


Figure 2: Plot of absorbance versus mole ratio for the determination of stoichiometry of the reduction of BG^+ by CN^- at $[BG^+] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[H^+] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.196 \text{ mol dm}^{-3} (\text{Na}_2\text{SO}_4)$, $T = 29.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$.

ORDER OF REACION

The pseudo – first order plot (Figure 3) was linear to more than 70 % extent of reaction which suggests a first order dependence of rate on $[BG^+]$. Also the slope (1.001) of the logarithmic plot of k_1 versus $[CN^-]$ showed that the reaction is first order with respect to $[CN^-]$ in figure (4). Hence, the reaction is second order overall. The second order rate constants, k_2 were fairly constant (Table 1.0) and equation (2) give the rate law for the reaction.

$$-\frac{d[BG^+]}{dt} = k_2[BG^+][CN^-] \dots\dots\dots 3$$

Where $k_2 = (2.55 \pm 0.05)$

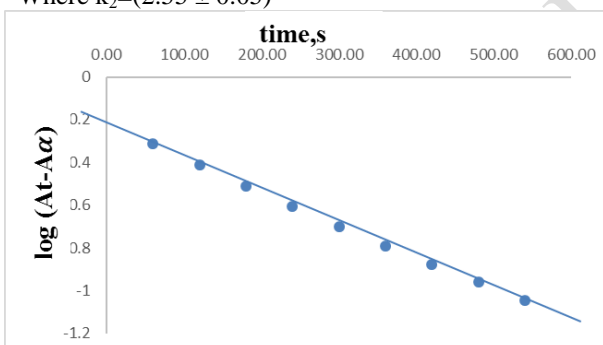


Figure 3: Pseudo-first order plot for the oxidation of CN^- by BG^+ at $[BG^+] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[CN^-] = 21.6 \times 10^{-3} \text{ mol dm}^{-2}$, $[H^+] = 2.0 \times 10^{-4}$, $\mu = 0.196 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, $T = 29.0 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$.

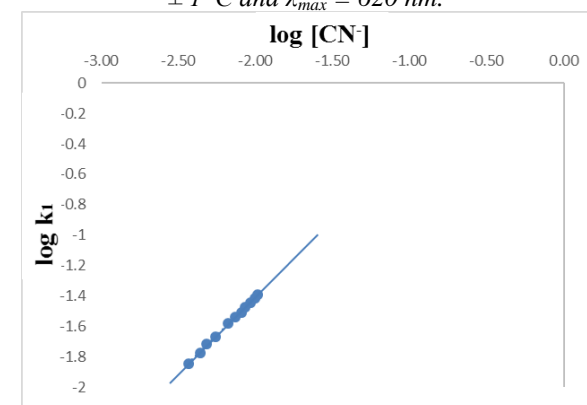


Figure 4: plot of $\log k_1$ versus $\log [CN^-]$ for the reaction of BG^+/CN^- at $[BG^+] = 2.0 \times 10^{-5} \text{ mol/dm}^3$, $[H^+] = 2.0 \times 10^{-3} \text{ mol/dm}^3$, $\mu = 0.196 \text{ mol/dm}^3$, $T = 29 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$.

$10^3 [CN^-]$ mol/dm ³	$10^4 [H^+]$ mol/dm ³	$10[\mu]$ mol/dm ³	$10^3 k_1$, s ⁻¹	$10k_2$, mol /dm ³ /s
14.4	2.0	1.86	3.6848	2.55
16.8	2.0	1.86	4.3757	2.60
21.6	2.0	1.86	5.5272	2.55
26.4	2.0	1.86	6.6787	2.52
28.8	2.0	1.86	7.3696	2.55
31.2	2.0	1.86	8.0605	2.58
33.6	2.0	1.86	8.5211	2.53
36.0	2.0	1.86	9.2120	2.55
38.4	2.0	1.86	9.9021	2.57
40.8	2.4	1.86	10.364	2.54
21.6	0.8	1.86	5.5272	2.55
21.6	1.2	1.86	5.5272	2.55
21.6	1.6	1.86	5.5272	2.55
21.6	2.0	1.86	5.5272	2.55
21.6	2.4	1.86	5.5272	2.55
21.6	2.8	1.86	5.5272	2.55
21.6	3.2	1.86	5.5272	2.55
21.6	3.6	1.86	5.5272	2.55
21.6	4.0	1.86	5.5272	2.55
21.6	2.0	1.06	5.5272	2.55
21.6	2.0	1.26	5.5272	2.55
21.6	2.0	1.46	5.5272	2.55
21.6	2.0	1.66	5.5272	2.55
21.6	2.0	1.86	5.5272	2.55
21.6	2.0	2.06	5.5272	2.55
21.6	2.0	2.26	5.5272	2.55
21.6	2.0	2.46	5.5272	2.55

Table 1: Pseudo-first order and second order rate constants for the reaction of BG^+ and CN^- at $[BG^+] = 2.0 \times 10^{-5} \text{ mol/dm}^3$, $\mu = 0.196 \text{ mol/dm}^3$, $T = 29 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$.

EFFECT OF CHANGES IN ACID, IONIC STRENGTH AND DIELECTRIC CONSTANT ON REACTION RATE

The reaction rate neither showed dependence on the concentration of acid $[H^+]$ nor significant effect on change in ionic strength (Tables 1) of the reaction medium. However, the rate of the reactions increased mildly with dielectric constant medium within the range investigated as shown in (Table 2).

D	$10^2 \frac{1}{D}$	$10^3 k_1 \text{ s}^{-1}$	$10k_2 \text{ dm}^3/\text{mols}$
0.00	0	5.5272	2.55
23.99	4.169	5.9878	2.77
26.98	3.707	6.4484	2.99
29.96	3.337	7.1393	3.30
32.95	3.035	7.5999	3.52
35.94	2.783	8.2908	3.84

Table 2: Effect of Changes in Total Dielectric Constant of the Reaction Medium on the Reaction of Brilliant Green and Cyanide Ion $[BG^+] = 2.0 \times 10^{-5} \text{ mol/dm}^3$, $[CN^-] = 21.6 \times 10^{-3}$, $[H^+] = 2.0 \times 10^{-4} \text{ mol/dm}^3$, $\mu = 0.196 \text{ mol/dm}^3$, $T = 29 \pm 1^\circ\text{C}$.

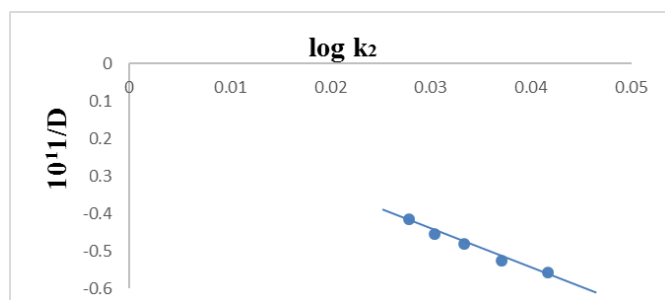


Figure 5: Plot of $\log k_2$ against $1/D$ for the reduction of BG^+ by CN^- at $[BG^+] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[CN^-] = 21.6 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.196 \text{ mol dm}^{-3} (\text{Na}_2\text{SO}_4)$, $T = 29.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$.

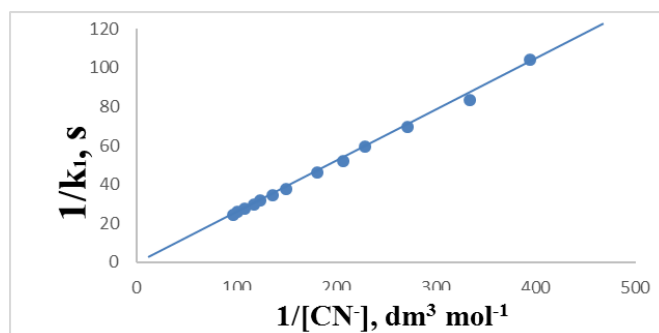


Figure 7: Michaelis-Menten plot of $1/k_{\text{obs}}$ versus $1/[\text{oxidant}]$ for the reaction of BG^+ with CN^-

The spectra of cyanide ion and that of the reaction mixture were taken over the wavelength 400 – 700 nm range, and the spectra were compared. Spectroscopic studies indicate that there was no clear shift from the wavelength of maximum absorption of CN^- studied. This indicates absence of formation of intermediate complex during the course of the reactions.

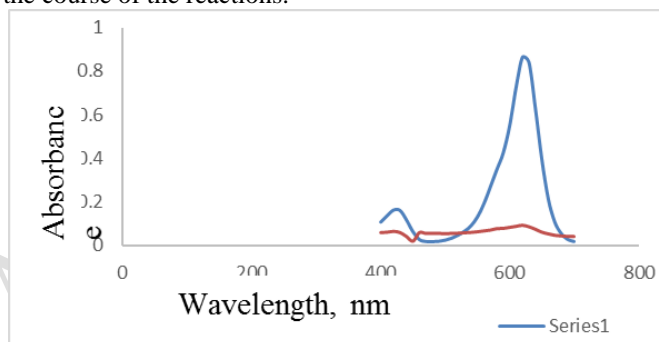


Figure 8: Spectra of the redox reaction mixture of BG^+ and CN^- after 2 minutes of reaction

ACTIVATION PARAMETERS

From the temperature dependent study (Table 3) and Eyring plot (Fig.6), the enthalpy, $\Delta H^* = +19.122 \text{ kJ mol}^{-1}$ and entropy, $\Delta S^* = -168.1672 \text{ JK}^{-1}\text{mol}^{-1}$ of activation were obtained. The temperature effect showed that the reaction rate increased slightly with increase in temperature and the negative entropy implies that the reaction is in favour of an endothermic reaction pathway.

Temperature, K	$10^3 k_{\text{obs}}, \text{ s}^{-1}$	$10K_2 \text{ dm}^3 / \text{mol/s}$
303	4.375	2.025
313	6.218	2.878
323	6.370	2.940

$$\Delta H^* = +19.122 \text{ kJ/mol}^{-1} \quad \Delta S^* = -168.1672 \text{ JK}^{-1}\text{mol}^{-1}$$

Table 3: Activation parameters of the reaction of BG^+ with CN^- at $[BG^+] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[CN^-] = 21.6 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.196 \text{ mol dm}^{-3}$, $[H^+] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $T = 29 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 620 \text{ nm}$.

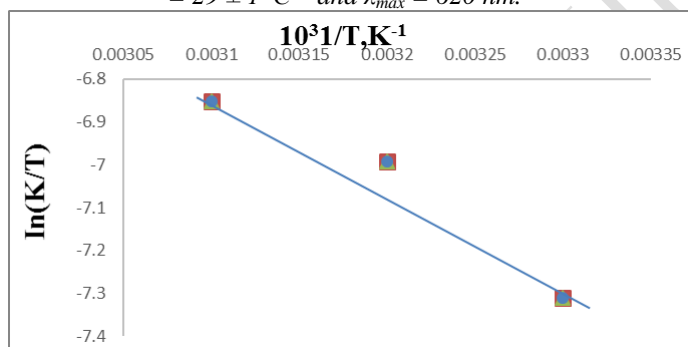


Figure 6: Plot of $\ln(K_2/T)$ versus $1/T$ for the reaction of BG^+ with CN^-

Michaelis - Menten plot of $1/k_{\text{obs}}$ versus $1/CN^-$ (figure 7) 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 operation. The free radical species was not detected as the reaction progresses evidenced by absent of gel formation upon addition of about 5.0 cm^3 of acrylamide.

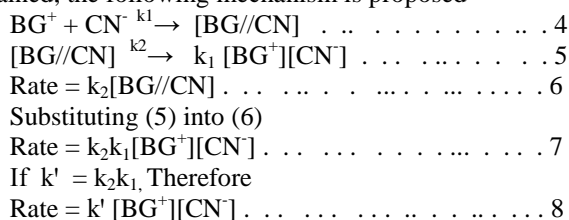
IV. DISCUSSION

The stoichiometry of 2:1 obtained in this study. The results of the kinetic study showed first order dependence with respect to both $[BG^+]$ and $[CN^-]$.

Variation of hydrogen ion concentration showed no effect on the reaction rate implying that protonation or deprotonation of any of the reactant species was unimportant during the course of the reaction. The non-dependence of this reaction on $[H^+]$ is in accord with the fact that neither the oxidant nor the reductant undergo significant protonation or deprotonation under the given reaction conditions Edokpayi *et al.* (2010).

The rate of the reaction surprisingly also showed no significant effect with change in ionic strength of the reaction medium in the concentration range investigated (Table 1) suggesting a zero Bronsted-Debye salt effect (Benson, 1969). Such salt effect can be occasioned when the activated complex is composed of either one or both neutral reactant partners (Atkins and de Paula, 2002) or due to ion pair effect. This tendency is further supported by the negative value of activation entropy ($\Delta S^* = -168.1672 \text{ JK}^{-1}\text{mol}^{-1}$) which is indicative of a more ordered activated complex. Free radical test was positive which indicated the presence of free radical species in one of the reaction steps. Michaelis - Menten plot of $1/k_{\text{obs}}$ versus $1/[CN^-]$ had zero intercept which suggests the

absence of an intermediate complex in the rate determining step. Also spectrum of the reaction mixture taken 2 minutes after the initiation of the reaction showed no shift from the λ_{max} of 620 nm characteristics of Brilliant green. Rationalizing the above results therefore, the reaction is possibly occurring through the outer-sphere mechanism. Based on the results obtained, the following mechanism is proposed



V. CONCLUSION

The Stoichiometric study showed that two moles of the reductant were consumed by one mole of the Oxidant. The rate of reaction was independent on the concentration of acid. The reaction displayed zero salt effect within the range investigated which was rationalized in terms of ion-pair effect, but increased mildly with increase in total dielectric constant of reaction medium. The Michaelis-Menten's plot gave zero intercept indicating the absence of intermediate complex. Also the activation parameters calculated are: $\Delta H^* = +19.122 \text{ kJmol}^{-1}$, $\Delta S^* = -168.1672 \text{ JK}^{-1} \text{ mol}^{-1}$.

Based on the experimental evidences the reaction is proposed to occur by the outer-sphere mechanism via an ion pair route.

REFERENCES

[1] Agarwal, S., Gupta, V. K., Ghasemi, M. and Azimi-Amin, J. (2017). Peganum Harmal-l Seeds Adsorbent for the Rapid Removal of Noxioud Brilliant Green Dyes from Aqueous Phase. *Journal of Molecular Liquid*. 231, 296 – 305.

[2] Ahmed, Y., Onu, A.D., Idris, S.O., Iliyasu, S.S., Abiti, Y.B. and Bello, U. (2018). Kinetics and Mechanism of the Oxidation of Ethylenediamine-N,N,N',N'-tetraacetatocobaltate(II) Complex by Hypochlorite ion in Aqueous Nitric Acid Medium. *Abubakar Tafawa Balewa University, Journal of Science, Technology and Education (JOSTE)*. 6 (4), 316-320.

[3] Atkins, P.W. and de Paula, J. (2002). *Physical Chemistry* (7th ed.). Oxford: Oxford University

[4] Press. p. 962.

[5] Babatunde, O.A. (2005) Kinetics and mechanism of electron transfer reactions of mixed-valence di- μ -oxo tetrakis (1,10-phenanthroline) di manganese (iii,iv) ion and rosaniline hydrochloride with some reducing agents. An unpublished Ph.D Thesis of Ahmadu Bello University, Zaria, Nigeria. p.962.

[6] Baird, R. M., Hodges, N. A. and Denyer, S. P. (Tailor and Francis, London 2000). *Handbook of Biological Quality Control. Pharmaceuticals and Medical Device*. 100.

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

[8] Ekdopayi, J.N., Iyun, J.F. and Idris, S.O. (2010). Kinetics and Mechanism of the Electron Transfer Reaction between Sulphite ion and Indigo Carmine in Aqueous Acidic Medium. *World Journal of Chemistry*, 5(1): 62-66.

[9] El-chaghaby, G. A., Eman, S. R. and Abeer, F. A. (2018). Rice Straw and Rice Straw Ash for the Removal of Brilliant Green Dye from Wastewater. *Asian Journal of Applied Chemistry Research*. 1(2), 1 – 9.

[10] Isahq, M., Siraj S., Intiaz, A. and Khalid, S. (2017). Removal of Brilliant Green Dye from Aqueous Medium by Unreacted Acid Treated and Magnetite Impregnated Bentonite Adsorbents. *Journal of Chemical Society Pakistan*. 39, 05.

[11] Kobiraj, R., Neha C., Atul, K. K. and Chattopadhyaya, M.C. (2012). Determination of Equilibrium, Kinetic and Thermodynamic parameters for the Adsorption of Brilliant Green Dye from Aqueous Solution onto Egg Shell Powder. *Indian Journal of Chemical Technology*. 19, 26 – 31.

[12] Mohammed, Y., Iyun, J.F. and Idris, S.O. (2009). Kinetics Approach to the Mechanism of the Redox Reaction of Malachite Green by Permanganate Ion in Aqueous Acidic Solution. *African Journal of pure and Applied Chemistry*. 3(12): 269-274.

[13] Thakare, Y. D., and Jadhav, S. M. (2013). Degradation of Brilliant Green Dye Using Cavitation Based Hybrid Techniques. *International Journal of Advance Engineering Technology*. 31 – 36.

[14] Wong, Y.C., Wong, C.T., Onyiruka, S.O. and Akpanisi, L.E.S. (2002). *University General Chemistry, Inorganic and Physical*. Onitsha-Nigeria: Africana-Fep Publishers Limited. pp. 452-453.

[15] Yusuf, U.F., Iyun J.F. and Ayoko G.A. (2004). Oxidation of hypophosphorus acid by poly (pyridine) iron (III) complexes. *Chemical Class Journal*. pp.118 – 122.