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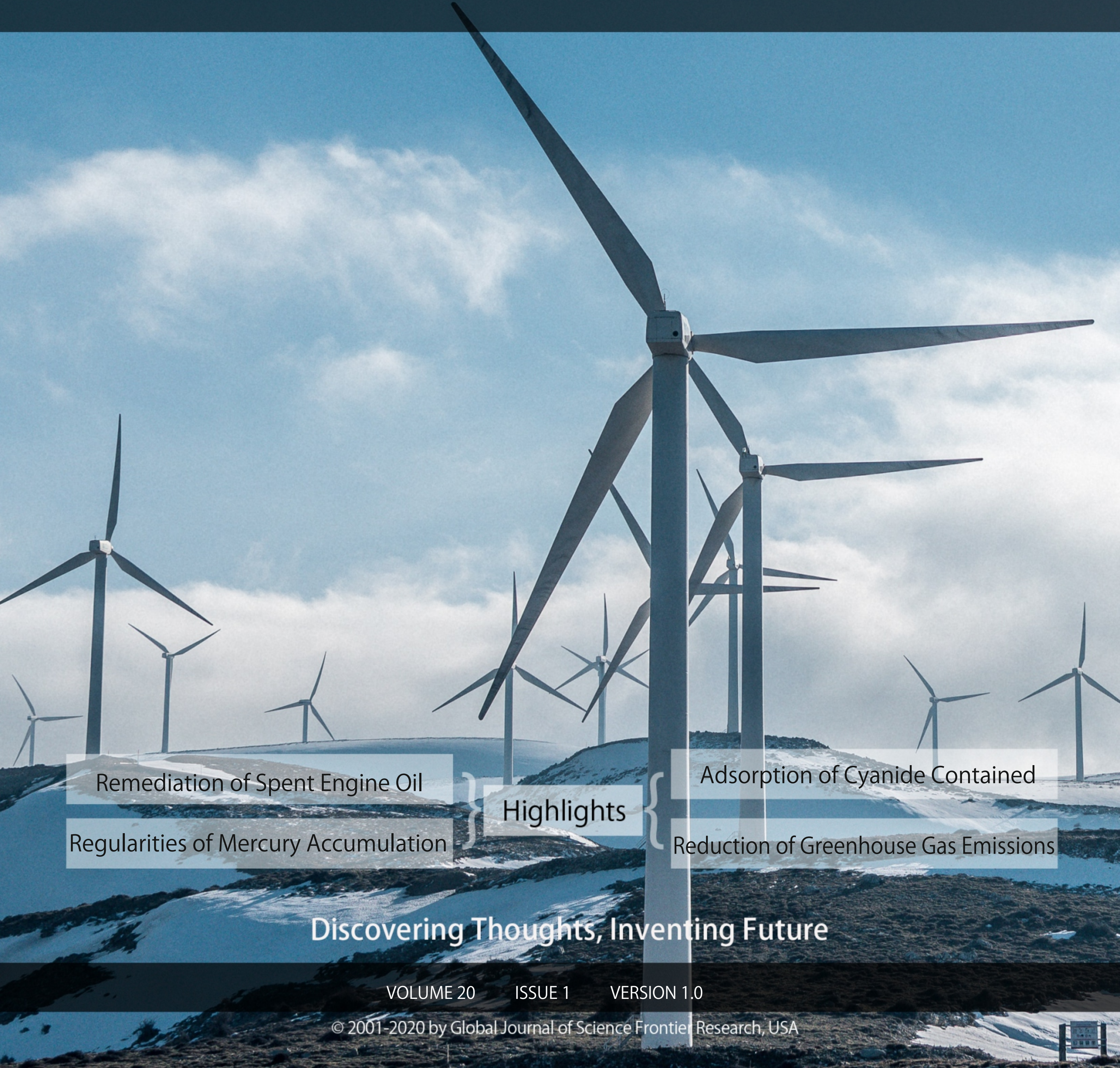

Highlights

Remediation of Spent Engine Oil

Regularities of Mercury Accumulation

Adsorption of Cyanide Contained

Reduction of Greenhouse Gas Emissions

Discovering Thoughts, Inventing Future

VOLUME 20 ISSUE 1 VERSION 1.0

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ENVIORNMENT & EARTH SCIENCE

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Kinetics and Thermodynamics of β- Endosulfan Pesticide 1 Adsorption in Jordan Valley Soils

By Nader Mahmoud Sadeq

Alexandria University

Abstract- Knowledge of the β- endosulfan adsorption characteristics of soil is necessary for predicting its mobility and fate in soil environments. To examine the characteristics of β-endosulfan retention, sorption batch experiments were performed on three Xeropsamments soils having different properties. The sorption data were applied to various kinetics models. The results reveal that the tested models fitted the adsorption data in the order: first-order~modified Freundlich > parabolic diffusion >Elovich. The energy of activation (Ea) and enthalpy (ΔH#), entropy (ΔS#), and free energy of activation (ΔG#) related to β- endosulfan sorption were calculated using the Arrhenius equation. The activation energy (Ea) values (18.57 - 38.18 kJ mol^{-1}) and the positive ΔH# values characterize β-endosulfan adsorption process onto the sorbents studied as physisorption with an endothermic nature. The negative values of $\Delta S^{\#}$ (-23– -17 J mol^{-1}) obtained in this study suggest that the β-endosulfan sorption process involves an associative mechanism.

Keywords: *equilibrium isotherm models• kinetic models • associative mechanism• physisorption.*

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Nader Mahmoud Sadeq

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I. Introduction

The increasing use of pesticides in the modern agricultural practices leads to several environmental problems in soil and water. Transport of pesticides sorbed onto soil particles can represent a significant pathway from the original land application to receiving water bodies (Sen and Khilar 2006).Identifying and understanding the mechanisms controlling the fate of pesticides in the soil environment are vital for both maintaining environmental quality and optimizing sustainable agriculture practices (Soulas and Lagacherie 2001). Endosulfan(6,7,8,9,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9- methano-2,3,4 enzodioxa-thiepin-3-oxide)is a broad spectrum contact insecticide and acaricide that is used throughout the world on a wide variety of fruits, vegetables, cereals, and cotton, and ornamental plants in commercial agricultural settings. Endosulfan is classified in the U.S. Environmental Protection Agency toxicity category I. Technical grade endosulfan is composed of two stereo chemical isomers: "α-endosulfan and β-endosulfan, in concentrations of approximately 70% and 30%, respectively (Herrmann2002).The α-isomer is more volatile and dissipative, while the β- isomer is generally more adsorptive and persistent (Rice et al.1997). The moderately adsorptive and persistency properties of β-isomer enable it to stay in the environment for an extended period (US EPA2007). Endosulfan has been detected in the atmosphere, soils, sediments, estuaries, surface, ground and rain waters, and food stuffs (Spark and Swift 2002). Once endosulfan is applied to crops, it can either persist in soil as a sorbed phase or be removed through several physical, chemical, and biological processes (Siddique et al.2003).Because elevated endosulfan concentrations could result in both acute and chronic risks of concern for terrestrial and aquatic organisms, knowledge of the endosulfan adsorption characteristics of soil is necessary for predicting their mobility and fate in soil environments. Extensive use of endosulfan more than a decade to control insects in Jordan Valley, east of west bank is of great concern regarding the potential transport in the environment. The use of uncontrolled and large amount of endosulfan may deteriorate the soil and groundwater quality. The fate of endosulfan as an insecticide has not been examined yet thoroughly in Palestine and specifically in the Jordan Valley which is considered the main vegetable production area in the country. The main objective of this study was to determine sorption kinetics and thermodynamics from batch experiments for β-endosulfan and to ascertain sorption characteristics in representative soils of Jordan valley. Such information is necessary for understanding the mechanisms involved in the adsorption of endosulfan and the prediction of its movement in Jordan valley soils in order to establish risk assessment and remediation strategies for endosulfan contaminated soils (Kumar and Philip2006; Krishna and Philip2008).

II. Materials and Methods

a) Study area

Soil samples were taken from three locations intensely cultivated with vegetable and extended from northern part to southern part of the Jordan valley. These locations represent Jordan valley soils and included Bardaleh in northern part of Jordan Valley, Al-Zubeidate in middle part of Jordan valley, and Al-Nwueimeh in southern part of Jordan Valley. The study area has 5654 ha of irrigable land and is located between 31° 46 – 32° 24 North latitudes and 35° 27 – 35° 34 East longitudes. The Jordan valley has semi-arid climate with almost no precipitation between April and September. The long-term mean annual precipitation is about 166 mm, the mean annual atmospheric temperature is about 29.6C° and the evaporation is 1500

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mm. The soils of the Jordan valley are mainly sandy loamy, slightly alkaline (pH 7.2- 7.8)and classified as Xeropsamments according to the USDA system. The farmers in these locations usually apply large quantities of endosulfan (Thionex® 35) for insect and pests control. The study area contains more than 125 wells, distributed from northern part of Jordan valley to southern part of Jordan valley mostly used for irrigation only 12 wells are used for drinking.

b) *Soil samples*

Three different soils were chosen to represent the most common types in Jordan valley, Bardaleh in northern part of Jordan valley, Al-Zubeidate in middle of Jordan Valley and Al-Nwueimeh in southern part of Jordan valley. Three surface samples (0 – 30 cm) were collected from each location, air-dried, ground, sieved (< 2 mm). and preserved in air tight polyethylene bags before use. Selected physical and chemical properties of these samples were determined (Table 1).

c) *Adsorption kinetic study*

Kinetic retention using the batch method was used to quantify adsorption isotherms for β-endosulfan by the three studied soils at three different temperatures 298, 308 and 318K. Triplicate 2-g samples of each soil were placed in Teflon centrifuge tubes and mixed with 40-mL solution of 15 and 30 mg L^{-1} initial β-endosulfan concentrations. The mixtures were continuously shaken on a temperature-controlled shaker at 120 rpm and then centrifuged at 5,000×g for 10 min prior to sampling. After 0.5, 1, 2, 4, 8 and 24 h hours of reaction time, a 5-mL aliquot was taken, extracted with n-hexane solution and filtered through anhydrous sodium sulphate to remove moisture content and analyzed using HPLC, model (Perkin Elmer, USA). Amounts of endosulfan sorbed by the soil matrix were determined by the difference between the concentrations of the supernatant and that of the initial solutions.

d) *Analysis of β-endosulfan*

The extracted samples were analyzed using high-performance liquid chromatochraphy model (Perkin Elmer Series 200). Analyses were performed in isocratic system using a 325 reverse phase C18 column (25 cm x 4.6 mm id). For separation of endosulfan, a 70:30 mixture of methanol and water was passed through the column at a flow rate of 0.7 ml/min and the wavelength of the UV/visible detector was fixed at 214 nm (Siddique et al., 2003). Column temperature was ambient and injection was made with a 50-μl SGE syringe and a manual loop injector (20-μl). Sample filtration was carried out with solvent compatible Gellman syringe filter of 0.20-μm GHP membrane. The eluent was degassed by purging with helium. Laboratory and instrumental blanks were frequently analyzed to ensure the absence of contaminants, or interference arising from samples or laboratory handling. Recoveries, calculated from spiked matrixes, were greater than 90%.Detection limits (LOD), ranged between 0.08 and 0.33 ng mL^{-1} in agreement with values reported in the literature (Keith et al., 1983).

e) *Kinetics Modeling*

Four kinetic models were applied to the sorption data:

First-order rate [Elkhatib et al. 2013] $\ln(q_o - q) = a - k_a t$ (1)

Elovich (Elkhatib et al.1992) $q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t$ (2)

Parabolic Diffusion (Elkhatib and Hern 1988) $q = a + k_d t^{1/2}$ (3)

Power Function (Elkhatib and Hern 1988) $q = k_a C_o t^{1/m}$ (4)

Where

q or q_t = β-endosulfan adsorbed (mg kg^{-1}) at time t, q_o = β-endosulfan adsorbed (mg kg^{-1}) at equilibrium, k_a = apparent sorption rate coefficient, **α** = the initial adsorption rate (*mg g^{-1} min^{-1}*), ***β*** = a constant related to the extent of surface coverage (mg g^{-1}) , a = a constant; k_d = apparent diffusion rate coefficient, q = adsorbed β-endosulfan (mg kg^{-1}), c_o= initial β-endosulfan concentration (mg l^{-1}), t = reaction time (min), k_a= sorption rate coefficient (min^{-1}), and 1/m = constant.

f) *Statistical analysis*

The linear least-squares optimization program provided by SAS PROC LIN (SAS Institute 2000) was utilized to obtain best-fit parameters which provide the best description of the adsorption data.

III. RESULTS AND DISCUSSION

a) *β-endosulfan Sorption vs. time*

Sorption of β-endosulfan on the three studied soils versus time at two initial concentrations and a temperature of 298K are illustrated in Fig.1. In the three studied soils the sorption of β-endosulfan kinetics exhibited an immediate rapid sorption by which about 73% -92% of initially β-endosulfan sorbed in the first hour followed by a slow sorption at 298K. The initial sorption rate for β-endosulfan was high as a large number of adsorption sites were available at the onset of the process. Adsorption slowed down in later stages because after some time the remaining vacant surface sites may be difficult to occupy due to the repulsive forces between β-endosulfan molecules on the solid and liquid phase (Anirudhan and Ramachandran 2007). When initial β-endosulfan concentrations were changed (15 and 30 mg/L) at temperature 298K; the amount sorbed per unit mass showed an increase with rise in initial β-endosulfan concentrations (Fig.1). This is due to the increase in the mass driving force which allows more β-endosulfan molecules to pass from the solution to the adsorbent surface. At low initial β-endosulfan concentration, the ratio of β- endosulfan in solution to the available sorption sites is small and consequently the sorption is dependent of the initial concentration, but as the concentration of the β-endosulfan increase, the competition for sorption sites becomes fierce (Sarvanane et al. 2002). Similar results were reported by Ismail et al. (2002) when studying adsorption of β-endosulfan on soils, they found that sorption of β-endosulfan increased with increasing solution concentrations.

b) *Kinetics Modeling*

The kinetics of β-endosulfan sorption on the three studied soils were analyzed using various kinetic models; first-order, Elovich, intraparticle diffusion model, and, modified Fruendlich. The conformity between experimental data and the model predicted values was expressed by the coefficient of determination (R^2) values and the standard error of estimate (SE).Based on $R^2$and SE values (Table2), the modified Freundlich and the first-order models best described β- endosulfan sorption on the three studied soils. The parabolic diffusion law described the adsorption data of β-endosulfan satisfactorily as the R^2 values were quite high and SE values were low (Table 2). The empirical Elovich model did not describe the β-endosulfan reaction as the R^2 values were lower and SE values were quite high for this model (Table 2). The order of application of various kinetic models to describe β-endosulfan adsorption data was first-order ~ modified freundlich> parabolic diffusion >Elovich Sorption processes in soil systems are complex and often involving some changes taking place during it, e.g. (1) An increase in vacant site numbers as sorption progress act. (2) Changes in solution conditions such as ionic strength. Therefore, careful selection of appropriate rate models capable of describing the inherently complex and system-specific dynamics of sorption processes is necessary for accurate fate and transport modelling (Elkhatib et al.1992; Xie et al.2011; Saha et al.2013).

c) *Effect of initial concentrations and temperatures on β-endosulfan sorption*

First-order equation was among the best kinetic equations studied to describe the rate of β-endosulfan sorption as evidenced by the overall high values of R^2 and low SE values (Table 2). Therefore, the first order rate equation was employed (Table3 and Fig.2) to analyze the sorption rate of β-endosulfan onto the soils studied. To ascertain that a reaction is a first order, a change in only one parameter (e.g., initial concentration) should generate parallel kinetic plots resulting from similar apparent rate coefficients. Fig.3 shows the first order kinetic plots for β-endosulfan sorption at initial concentrations of 15 and 30 mg L^{-1} on Al-Zubeidate soils at 298K. The slopes (apparent rate coefficients) correspond well and are nearly equal confirming that the reactions are first order. For example, at 15 and 30 mg β-endosulfan L^{-1} concentrations, β-endosulfan sorption on Al-Zubeidate soil at 298 K resulted in apparent rate coefficients of 0.0032 and 0.0035 respectively (Table 3).

Effect of temperature on β-endosulfan sorption was studied in all the three soils in the range of 298–318K at 15 and 30 mg L^{-1} initial β-endosulfan concentrations. The β-endosulfan sorption rate on the studied soils, from greatest to least, at all three temperatures was as follows: Al-Zubeidate, Al-Nwueimeh and Bardaleh soils (Table 3). As the temperature of the reaction increased from 298 to 318K, with all other reaction conditions remaining constant, the β-endosulfan sorption increased on all soil sorbents. Elshafei et al. (2009) observed that the adsorption rate of cadusafos on soil at 298, 308 and 318K increased with increasing temperature. This work shows that at a low temperature (298K), β-endosulfan sorption is relatively slow, compared with sorption observed at 318K in the laboratory. The enhanced adsorption with temperature may be attributed to either increase in the number of active binding sites available for adsorption on the adsorbent surface or due to the decrease in the boundary layer thickness surrounding the adsorbent, and thereby decreased boundary layer mass transfer resistance owing to the decrease in the viscosity of the solution. Often soil temperatures can rose above 318K in arid soils, indicating that sorption rates in the field can be even faster than reported here and thus allow higher soil surface loading levels.

d) *Activation Energy and Thermodynamic Parameters of β-endosulfan adsorption*

By applying first order kinetic model and plotting lnka vs. 1/T for each soil concentration studied (Fig.4), where "T" is the temperature in Kelvin and "ka" is the apparent sorption rate coefficient, the following linear relationship is obtained:

$$\ln k_a = (-E_a/RT) + \ln A$$

Where
R= gas constant (8.314 kJ/mol),
A= universal frequency factor.

It can be seen that the slope is given by –Ea/R and the intercept by ln A. Therefore, the thermodynamic parameters can be obtained using the following equations:

$$\Delta H^{\#} = Ea - RT$$

$$(\Delta S^{\#}/R) = \ln A - 1n\ (BTe/h)$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

Where

$\Delta H^{\#}$ = enthalpy of activation
$\Delta S^{\#}$ = entropy of activation
$\Delta G^{\#}$ = free energy of activation
B = Boltzman's constant
h = Planck's constant
e = electronic charge

The values of Ea for β-endosulfan sorption on the studied soils followed the range 21.25 to 22.47, 18.57 to 20.67 and 38.07 to 38.18 kJ mol^{-1} for Al-Nnuweimeh, Al-Zubeidate and Bardaleh soils, respectively (Table 4).The energy of activation measures the magnitude of the forces to be overcome during the process of sorption reactions and may give an idea about the type of sorption. The activation energy for physical adsorption is usually less than 42 kJ mol^{-1}, and higher values represent chemical reaction process as chemical adsorption is specific and involves forces much stronger than in physical adsorption (Elkhatib et al. 1993; Sparks2003). In the present study, the values of activation energy confirm that the nature of β-endosulfan sorption onto studied soil is physical adsorption. The finding is in accordance with the observations of previous studies by Gulen et al. (2005) .They found that, the value of activation energy (Ea) for azinphosmethyl sorption onto pyrolyzed Horse shoe sea crab shell was about 1.52 kJ mol^{-1} , this value is within the range of physical adsorption.

In order to get an insight whether the sorption process follows an activated complex, it is necessary to consider the thermodynamic activation parameters of the process. Values of enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), and free energy of activation ($\Delta G^{\#}$) were computed and presented in Table 4. The values of enthalpy of activation ($\Delta H^{\#}$) followed the range 18.77-19.99, 16.10-18.19 and 35. 60- 36.82 KJ mol^{-1}, for Al- Nuweimeh, Al-Zubeidate and Bardaleh soils, respectively. Data in Table 4 showed that enthalpy of activation values decrease with increasing initial concentration signifying less energy requirements for the reaction system as a result of increasing initial β-endosulfan concentration in to the studied soils. The positive values of $\Delta H^{\#}$ imply that the β-endosulfan adsorption process is endothermic and the magnitude of $\Delta H^{\#}$ may indicate the type of binding mechanism involved, i.e., physical and/or chemical sorption. The heat evolved during physical adsorption is in the range 2.1–< 40 kJ mol^{-1}, while the heats of chemisorptions is about 40 kJ mol^{-1}, a value that has been recognized in the literature as the transition boundary between both types of sorption processes (Liu and Liu, 2008).The calculated values of $\Delta H^{\#}$ for β-endosulfan sorption were lower than40 kJ mol^{-1}, indicative of physical adsorption mechanism. This observation agrees with results reported by Memon et al. (2007) for the adsorption of methyl parathion onto chestnut shells. The values of ΔG were in the range 87.59 to 87.79, 86.99 to 87.22, and 89.34 to 89.61 kjmol^{-1}, for Al- Nnuweimeh, Al-Zubeidate and Bardaleh soils, respectively (Table 4).The positive values of ($\Delta G^{\#}$) indicate that sorption reactions require some energy from an external source to convert reactants into products and the nonspontaneous nature of β-endosulfan sorption onto the studied soil. The values of $\Delta S^{\#}$ were in the range -23.08 to-22.74, -23.77 to -23.15 and -18.02 to-17.88jmol^{-1}k^{-1}, for Al- Nuweimeh, Al-Zubeidate and Bardaleh soils, respectively (Table 4).The negative $\Delta S^{\#}$ values (i.e., entropy decreases as a result of sorption) suggests the stability of sorption process with no structural change at solid–liquid interface. This occurs as a result of redistribution of energy between the sorbate and the sorbent. Before sorption occurs, the β-endosulfan molecules near the surface of the sorbent will be less ordered than in the subsequent sorbed state. As a result, the distribution of rotational and translational energy among a small number of molecules will decrease with increasing sorption by producing a negative value of $S^{\#}$. Additionally, the magnitude and sign of $\Delta S^{\#}$ gives an indication whether the sorption reaction is an associative or dissociative mechanism. Entropy values $\geq$10 J mol^{-1} generally imply a dissociative mechanism (Atwood, 1997). Therefore, the negative values of $\Delta S^{\#}$ (-23– -17 J mol^{-1}) obtained in this study suggest that the β-endosulfan sorption process involves an associative mechanism. Similar results were reported by Yedla and Dikshit (2001) for endosulfan sorption onto wood charcoal.

IV. CONCLUSION

The results of the present study showed that The Al-Zubadate soil had the highest affinity for β-endosulfan sorption while the Bardaleh soil exhibited the lest affinity; β-endosulfan sorption on Al-Nuweimeh soil was intermediate between that observed for Al-Zubadate and Bardaleh soils. Adsorption rate constant of β-endosulfan were highest for Al-Zubadate soil whereas, it was the least for Bardaleh soil, these suggest that the β-endosulfan have affinity to calcium carbonate and organic matter. Adsorption of β-endosulfan in all soils followed Freundlich isotherm model and it is inferred that the sorption was monolayer. The influence of temperature on β-endosulfan sorption onto the soils were observed that an increase in the temperature for 298K to 318K led to an increase in percentage sorption for all studied soils the increase in sorption could be due to changes in pore size or an increase in kinetic energy of the sorption with increase in temperature suggests endothermic nature. The activation energy (E_a) for sorption of β-endosulfan onto studied soils was determined using the Arrhenius equation, the values of activation energy for β-endosulfan sorption less than 42 kJ mol^{-1} , Since E_a values < 42 KJ mol^{-1} indicates that diffusion controlled process, it is concluded that β-endosulfan adsorption for the studied soils is a diffusion controlled reaction. The positive values of $(\Delta H^{\#})$ suggest that the sorption reactions are energy consuming process. The enthalpy $(\Delta H^{\#})$ of sorption reaction were positive suggest that sorption process were endothermic reaction. The small negative values for $(\Delta S^{\#})$ suggesting that β-endosulfan sorption for the studied soils is associative mechanism. The positive values of $(\Delta G^{\#})$ which are an indication of a nonspontaneous sorption process that is, due to the endothermic character. The magnitude of $(\Delta G^{\#})$ increased with the rise in temperature.

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Table 1: Selected physical and chemical characteristics of the three different soils used for the present study

Characteristics	Al-Nwueimeh soil	Al-Zubeidate soil	Bardaleh soil
pH $^{\#}$	**7.76±0.2**	**7.28±0.007**	**7.64±0.05**
EC$^{\#}$ (dsm^{-1})	**2.25±0.02**	**21.41±0.01**	**3.49±0.007**
Total carbonate $^{\#}$ (%)	**39.14±0.3**	**35.74 ±0.4**	**12.43±0.3**
Sand (%)	**75.55± 1.2**	**71.27 ± 1.3**	**69.61±0.98**
Silt (%)	**10.4 ±1.5**	**11.38 ± 1.2**	**18.34±0.86**
Clay (%)	**14.05± 1.9**	**17.35±1.5**	**12.05±1.3**
Texture§	**sandy loam**	**sandy loam**	**sandy loam**
Organic matter$^{¥}$ (%)	**1.37±0.04**	**3.25±0.06**	**1.04±0.04**
CEC§§ cmol(+).kg^{-1}	**13.755 ±0.4**	**35.815±0.3**	**14.651±0.2**

$^{\#}$ Soil: water ratio 1:2 $^{\#\#}$ Nelson,1982 § Day, 1965 §§ Rhoades ,1982 $^{¥}$ Nelson and Sommers,1982

Table 2: Range and mean values of coefficient of determination (R^2) and standard error of estimates (SE) for different kinetics models fitted to the β-endosulfan sorption o n the three studied soils

Model	R^2		SE	
	Range	Mean	Range	Mean
Kinetics Models				
Modified Freundlich	0.962-986	0.978	0.035-0.093	0.065
First order	0.922***-988	0.948	0.001-0.13	0.075
Elovich	0.882**-984	0.937	0.33-0.79	0.498
Parabolic Diffusion	0.939-987	0.971	0.11-0.65	0.313

***, *** significant at $p < 0.01$ and $p < 0.001$respectively*

Table 3: Calculated first order equation parameters β-endosulfan sorption for the three studied soils under isothermal conditions

Initial Conc. (mg L^{-1})	**Al-Nuweimeh soil**		**Al-Zubeidate soil**		**Bardaleh soil**	
	ka min^{-1} x 10^3	**a µg g^{-1}**	**ka min^{-1} x 10^3**	**a µg g^{-1}**	**ka min^{-1} x 10^3**	**a µg g^{-1}**
			298K			
15	**2.61**	**2.28**	**3.22**	**2.11**	**1.21**	**2.47**
30	**2.82**	**2.47**	**3.54**	**2.33**	**1.31**	**2.59**
			308K			
15	**3.42**	**1.28**	**4.43**	**1.07**	**2.22**	**1.12**
30	**3.71**	**2.41**	**4.71**	**2.25**	**2.64**	**2.59**
			318K			
15	**4.63**	**1.26**	**5.4**	**1.35**	**3.24**	**1.17**
30	**4.81**	**2.40**	**5.6**	**2.18**	**3.43**	**2.56**

Table 4: Thermodynamic parameters of β-endosulfan sorption on the three studied soils at two β-endosulfan initial concentrations

Initial Conc. mg L^{-1}	***Ea kJ mol^{-1}***	***$\Delta G^{\#}$ (kJ mol^{-1})***	***$\Delta S^{\#}$ J mol^{-1}***	***$\Delta H^{\#}$ (kJ mol^{-1})***
		Al-Nuweimeh soil		
15	22.47±0.04	87.79±0.002	-22.74±3.88	19.99±0.001
30	21.25±0.04	87.59±0.42	-23.08±0.69	18.77±0.21
		Al-Zubadate soil		
15	20.67±0.002	87.22±0.004	-23.15±7.14	18.19±0.002
30	18.57±0.002	86.99±0.004	-23.77±7.71	16.10±.002
		Bardaleh soil		
15	38.18±0.004	89.61±0.008	-17.88±0.014	36.28±0.004
30	38.07±0.001	89.34±0.0002	-18.02±0.38	35.60±0.0001

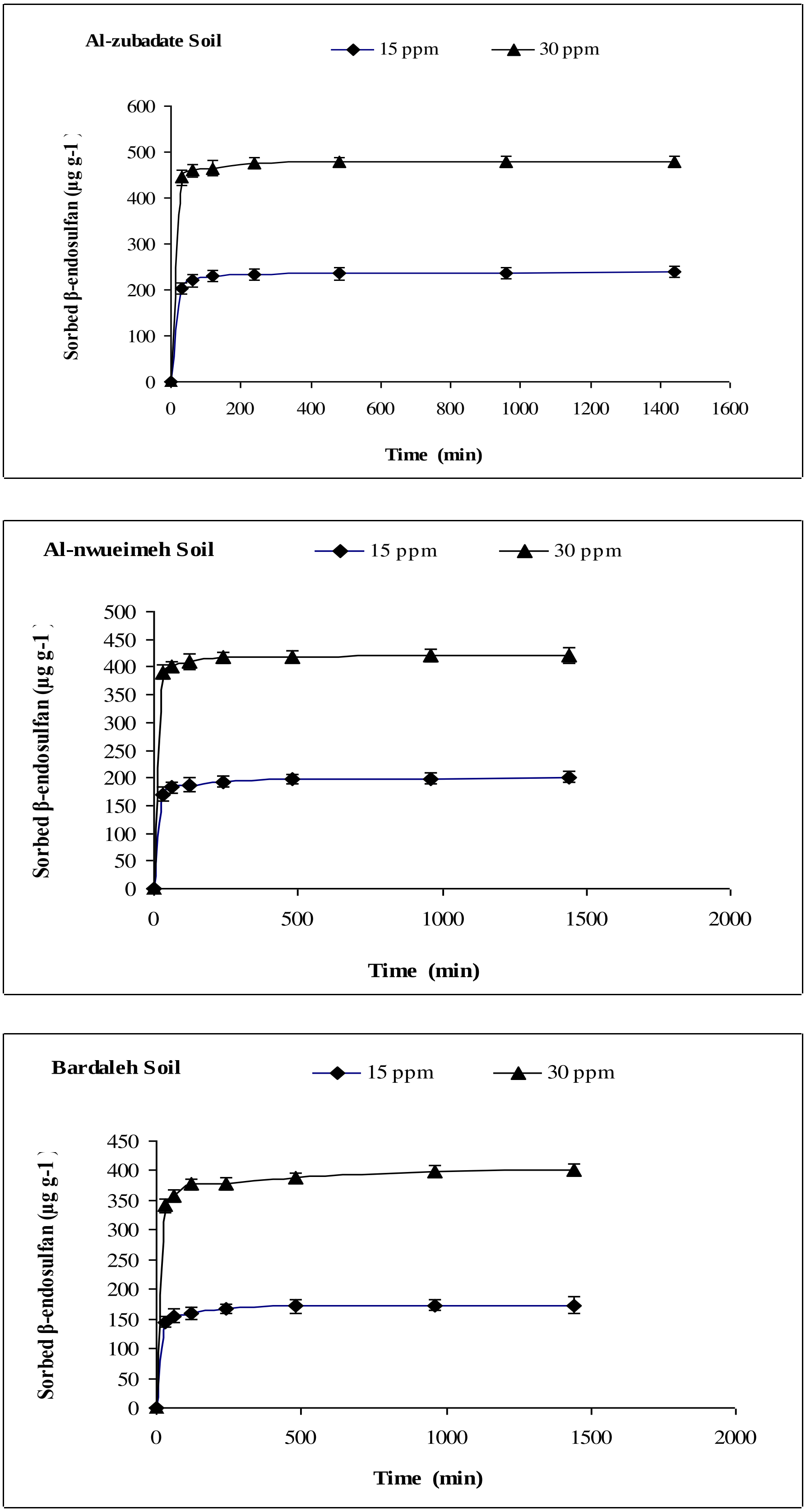

Fig. 1: Macroscopic sorption of β-endosulfan sorbed on three studied soils at 298K and two different initial β-endosulfan concentrations vs. time

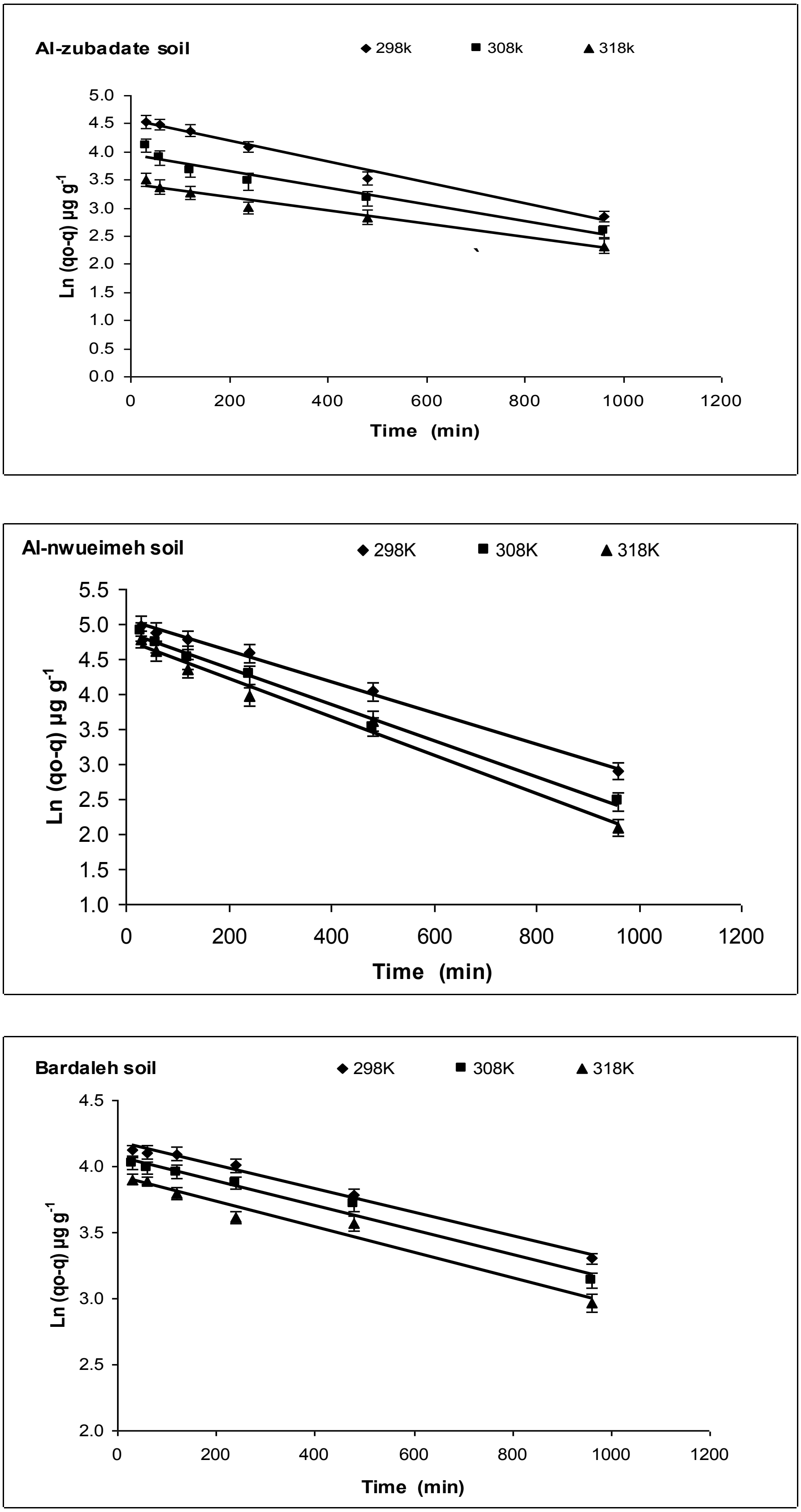

Fig. 2: First order equation plots of β-endosulfan sorption on the three studied soils at 3 temperatures and 30 mg ml^{-1} initial β-endosulfan concentration

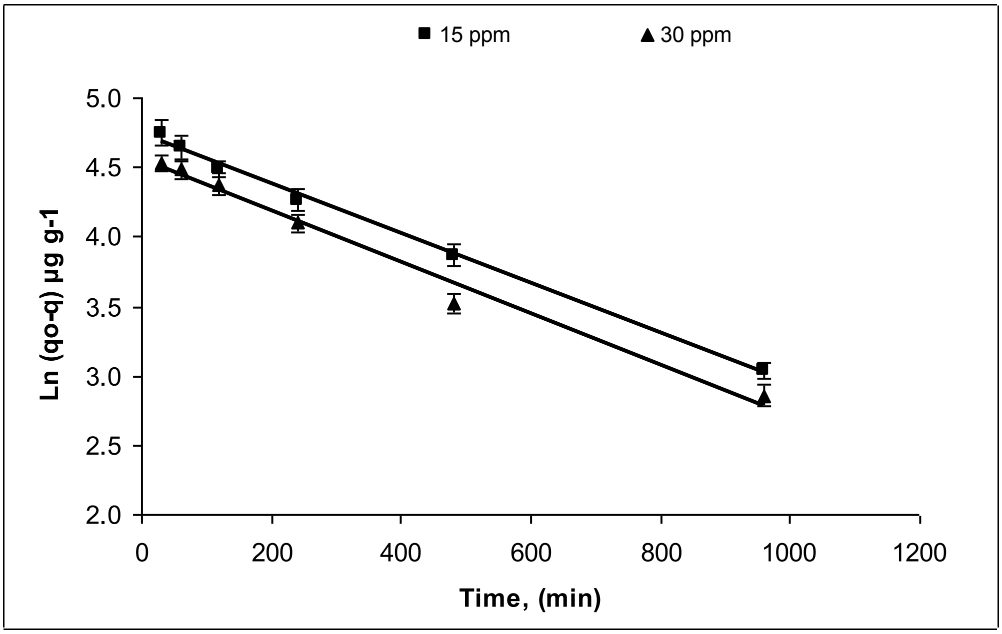

Fig. 3: Parallel relationship of the first order kinetic model with Al-Zubeidat soils at 298K and changing initial concentration while all other reaction parameters remained constant

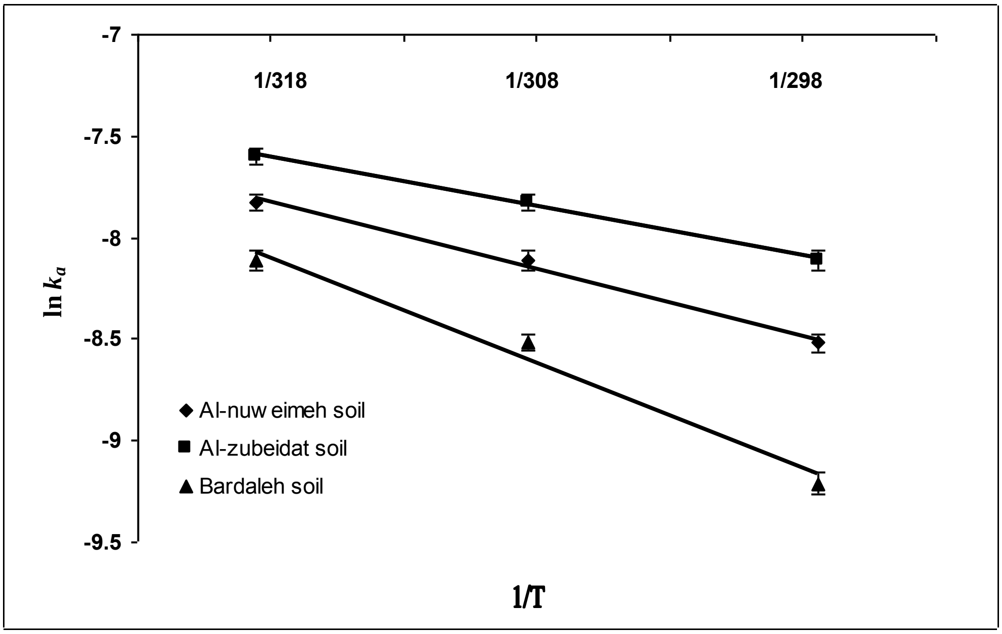

Fig. 4: Arrhenius plots of β-endosulfan sorption for three studied soils in Jordan Valley at three different temperatures

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Some Regularities of Mercury Accumulation in the Muscles of Freshwater Fish

By Anatoly V. Gorbunov, Sergey M. Lyapunov, Marina V. Frontasyeva & Sergey S. Pavlov

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Abstract- The Volga river basin is characterized by a high degree of industrial development and the presence of natural sources of mercury. The 400 issue samples of the main species of commercial fish were collected. The analysis of the selected material was carried out by the method of atomic absorption with "cold steam." The levels of mercury accumulation in the muscles and caviar of the main species of commercial fish were estimated. The graphs of the distribution of mercury concentration in the muscles of roach, bream, walleye, pike, and perch depending on the area of fish caught are given. The dependence of mercury accumulation in the muscles of perch, bream and pike on the mass of fish in the absence of human-made impact was estimated. The concentration of mercury in the fish eggs is minimal and does not depend on the concentration of mercury in fish muscles. It is shown that the maximum concentration of mercury in fish muscles is typical for the Rybinsk reservoir, and the minimum is for the upper Volga. It was found that the concentration of mercury in the muscles of perch with a high degree of confidence is directly proportional to the weight, in the muscles of pike-inversely proportional to the weight of the fish. For bream, dependence is not detected.

Keywords: mercury, food chain, fish tissue, especially accumulation of the river volga.

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Anatoly V. Gorbunov [α], Sergey M. Lyapunov [σ], Marina V. Frontasyeva [ρ] & Sergey S. Pavlov [Ѡ]

Abstract- The Volga river basin is characterized by a high degree of industrial development and the presence of natural sources of mercury. The 400 issue samples of the main species of commercial fish were collected. The analysis of the selected material was carried out by the method of atomic absorption with "cold steam." The levels of mercury accumulation in the muscles and caviar of the main species of commercial fish were estimated. The graphs of the distribution of mercury concentration in the muscles of roach, bream, walleye, pike, and perch depending on the area of fish caught are given. The dependence of mercury accumulation in the muscles of perch, bream and pike on the mass of fish in the absence of human-made impact was estimated. The concentration of mercury in the fish eggs is minimal and does not depend on the concentration of mercury in fish muscles. It is shown that the maximum concentration of mercury in fish muscles is typical for the Rybinsk reservoir, and the minimum is for the upper Volga. It was found that the concentration of mercury in the muscles of perch with a high degree of confidence is directly proportional to the weight, in the muscles of pike-inversely proportional to the weight of the fish. For bream, dependence is not detected.

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I. Introduction

The main anthropogenic sources of mercury are the chemical industry (production of chlorine, caustic, vinyl chloride, etc.), energy (the use of natural coal, oil, fuel oil), the electronics industry and metallurgy, the use of toxic chemicals and fungicides. One of the most significant sources of freshwater fish in the European part of Russia is the Volga River. It should be noted that for areas related to the entire flow of the river. The Volga is characterized by the presence of both natural and anthropogenic sources of mercury. The anthropogenic source of mercury can be considered the entire industrial agglomeration located on the banks of the Volga River. In these agglomerations, almost the entire line of industrial production is represented, including the sources of mercury listed above. Also, some mercury enters the natural environment when burning fossil fuels and its derivatives in boiler and heating systems.

The natural sources of mercury include the Astrakhan gas condensate field, located in the lower reaches of the. Volga river. It is confined to the intersections of the Karpinsky lineament and is characterized by deep, transverse faults. Here, the flow of mercury emanations is pulsating in nature and forms a similar character of atmochemical anomalies. A study of atmospheric air conducted in Astrakhan [1] revealed a fairly high concentration of mercury: 100–150ng/m^3 ($MPL_{avdaily}$ = 300 ng/m^3).

The concentration of total mercury in the water of the Volga reservoir chain varies from 0.02 to 0.42 μg/m3, the average concentration of mercury in surface water in the lower Volga reaches 0.05 μg/l (0.03–0.09 μg / l in depending on the time of year) [2,4]. In bottom sediments, which are the main storage of mercury in freshwater systems, the concentration of mercury ranges from 0.03 to 0.18 mg/kg (in the Rybinsk reservoir to 0.75 mg/kg) [3,4]. In the Astrakhan region, the mercury concentration in bottom sediments is 0.08-0.4 mg/kg. The above concentrations of mercury do not create a critical situation in the natural environment but can have a decisive influence on the accumulation of mercury in biota.

The accumulation of mercury in fish is directly dependent on its receipt in water. Mercury enters aquatic ecosystems, mainly with storm flows in the form of solutions and suspensions. After entering the reservoir, the conversion of mercury occurs in three main directions: it is restored to an elemental state and disappears into the atmosphere; forms strong, insoluble compounds (sulfides) and deposits in the bottom sediments; sorbed on the surface of bacterial membranes and goes into organic mercury compounds - methyl mercury and dimethyl mercury. Methyl mercury, methyl mercury hydroxide CH_3HgOH (MMHg), is the most stable form of methyl mercury in freshwater environments and is the most common organic compound of mercury in freshwater systems [5,6,7].

Methyl form of mercury is a potent neurotoxin, easily accumulated by aquatic biota, accumulates in plants, benthos, and animals, and ultimately concentrates in the upper links of the trophic food chain – fish. In the human body, methylmercury is well absorbed from the gastrointestinal tract, is spread by erythrocytes throughout the body.

The methylated form of mercury, due to its high solubility in fats, easily passes through biological membranes and penetrates the placenta as a result of which it can affect the developing embryo. The intake of mercury in the human body in the absence of intensive

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external sources is mainly determined by the level of fish consumption (up to 60% of the total intake) [8]. According to statistics [9, 10], in the Volga region regularly consume up to 32% of the respondents on average, and 58% consume fish at least 1–2 times a week. It should be noted that this is official data based on sales of fish and fish products through commercial networks.

Accounting for the volume of individual catch and fish consumption is completely absent. It should be noted that according to unofficial data, the consumption of fish obtained as a result of an individual catch in the Volga River accounts for between 18% and 80% of official statistics. In sum, this is a fairly large part of the fish and fish products consumed in the region. Therefore, it is very important to assess the level of accumulation of mercury in the tissues of fish that are most common in the Volga basin.

The purpose of the research was to determine the level of accumulation of mercury in the tissues of fish caught in the river Volga and the study of the features of this accumulation of certain species of fish.

II. METHODS

The main commercial fish species in the Volga basin are roach, ruff, chub, crucian carp, rudd, bream, tench, roach, perch, sturgeon, carp, catfish, sturgeon, pike perch, pike and ide [11]. Fishing was carried out during the spring–summer–autumn seasons of 2016–2018. Basically, the capture was carried out directly by the participants of this project, partly the lack of fish was filled by buying from local fishermen. Fish catch areas are shown in Figure 1.

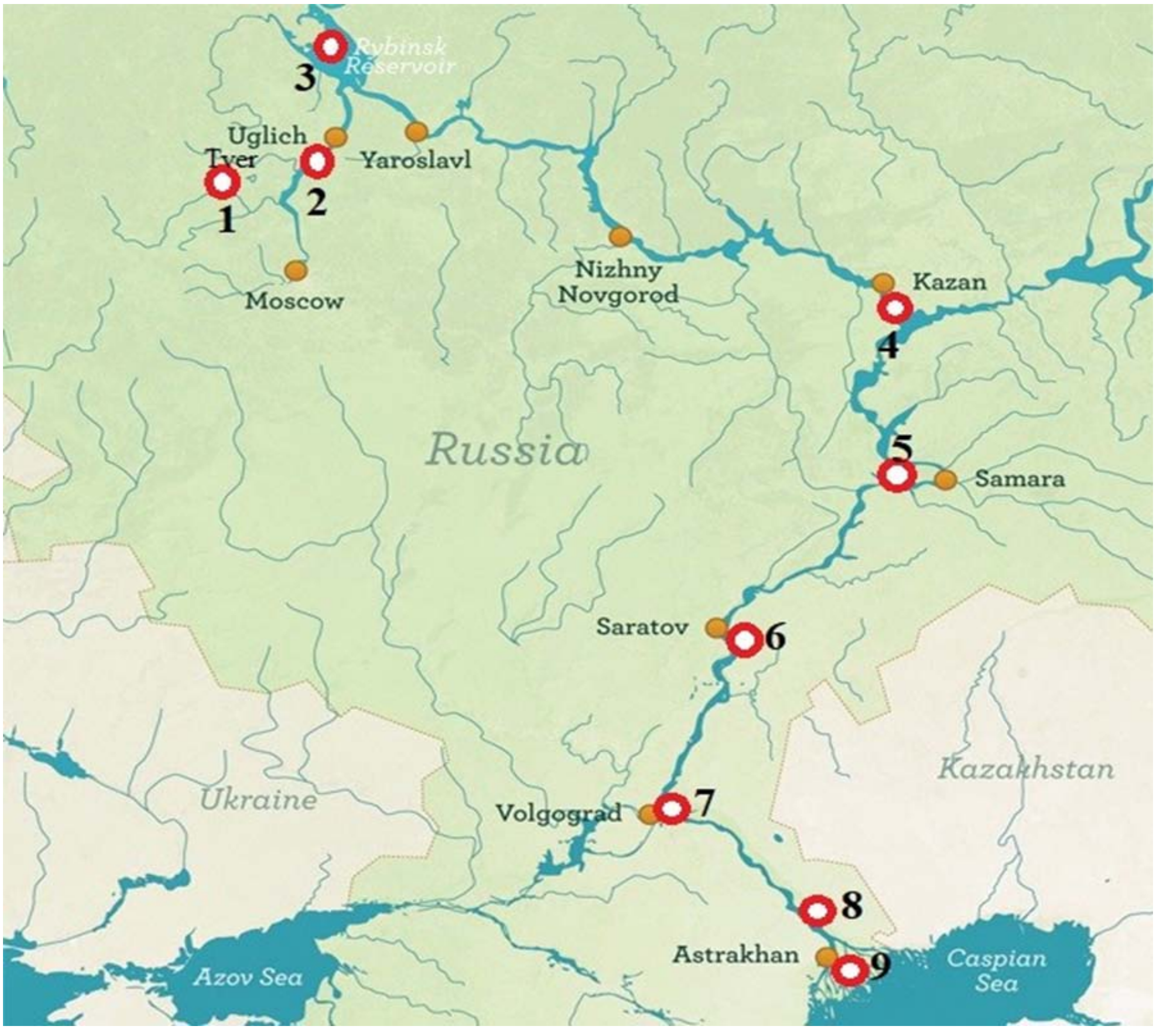


Figure 1: Sampling areas

1 –Upper Volga, the area of the city of Rzhev:Staritsa; 2 – Upper Volga, the region of the town of Kimry: the town of Bely Gorodok; 3 –Rybinsk Reservoir; 4 – District of Kazan; 5 –District of Samara; 6 – District of Saratov; 7 – District of Volgograd; 8 –Volga River delta, district of Tsagan:Aman; 9 –Volga River delta, district Ikryanoye:Beketovka

A general list of selected samples with fish sizes is shown in Table 1. To assess the features of mercury accumulation by various species of fish, we experimented on catching fish in a semi-closed Bay of the Volga river in the area of point 2 (figure 1). The current In the Bay is only along the Central fairway, the water acidity was pH= 6.5-7.0. The most common types of fish were caught-perch, bream, and pike. In total, 42 samples of perch weighing from 12 to 589 grams, 27 samples of bream weighing from 21 to 560grams, 31 samples of pike weighing from 43 to 2700grams were selected.

Table 1: The general list of selected samples
(n is the number of samples)

#	Objects, n is number of samples	Massag	
		Min-мах	**Mean**
1	Ruff. n = 9	15-35	25.4
2	Crucian carp (*Carassiuscarassius*), n = 19	100-220	171
3	Rutiluscaspicus, n = 21	82-141	100
4	Ballerusballerus, n = 5	105-540	215
5	Pelecuscultratus, n = 27	300-690	410
6	Bream, n = 30	100-560	340
7	Aspiusaspius, n = 16	520-3100	890
8	Goby, n = 15	155-420	215
9	Whitefish, n = 7	273-725	405
10	Roach, n = 28	49-96	75
11	Carp, n = 11	450-1100	743
12	Perch, n = 36	12-145	66.5
13	Common carp (*Cyprinuscarpio*) , n = 16	510-2320	1330
14	Zander, n = 25	156-533	331
15	Sturgeon, n = 4	5100-8300	6200
16	Pike, n = 21	90-2700	909
17	Silurusglanis, n = 5	1000-2600	1750

Samples were taken in zip-lock plastic bags, cleaned of external contaminants, and washed with distilled water. For long-term transportation, samples were frozen at -20 °C. In total, about 300 samples were taken. In preparation for the analysis, the fish were thawed and placed in enameled cuvettes, then cut from the left side, starting from the dorsal fin to the beginning of the ribs along the body, 2–4 g of skeletal muscles. The entire instrument and glassware were washed with 5–10 percent nitric acid and rinsed with distilled water. Samples were taken for analysis with natural moisture content.

III. RESULTS

The main criterion for the quality of fish and fish products is the value of the maximum permissible concentration (MPC) of mercury in fish meat. The value of the maximum permissible concentrations (MPC) accepted in the Russian Federation of mercury for various types of fish and fish products are given in Table 2.

Table 2: MPL of mercury in fish and fish products [12]

Products		MPL, mg/kg
Live, chilled, frozen fish, minced meat, fillet	Freshwaternon-predatory	0.3
	Freshwaterpredatory	0.6
Caviar and milk of fish and products from them		0.2
Liver fish and products from it		0.5
Shell fish crustaceans		0.2

Table 2 provides general data on the concentration of mercury in the muscles of fish caught in the Volga River basin. These data are arranged as the average arithmetic concentration increases and shows that the maximum permissible concentration of mercury for all fish species is not exceeded.

The highest concentration of mercury is characteristic of carp, carp, pike, perch, sturgeon,and catfish; the lowest concentration of mercury is for ruff and crayfish. From literary sources, it is known that up to 80-90% of mercury accumulated in fish falls into methylated forms [7, 13,14]. As noted above, methylmercury is highly soluble in fats and easily penetrates cell barriers. Given the fact that each egg is a drop of fat, it was possible to assume that the concentration of mercury in the eggs and muscles of the fish will be the same or at least close in magnitude between these biomaterials.

However, the data presented in Table 3 show that in the eggs of the ruff, roach, pike, and perch, the concentration of mercury is minimal. This concentration averages 8.6 μg/kg, and the concentration of mercury in roach roe is eight times less than the concentration in the muscles, and the concentration of mercury in the eggs of pike, and perch is 20 times lower than the same concentration in the muscles of these fish.

These data show that with an increase in mercury concentration in the muscles of fish, no increase in the concentration in the eggs is observed, a correlation between the concentration of mercury in the eggs and muscles is not found.

Table 3: Hg content in the muscles of the fish Volga basin
(n is the number of samples)

#	Object	C Hg, mkg/kg (ppb)	
		Min-Max	C_{av}
1	Ruff, n = 9	6-16	11
2	Crucian carp (*Carassiuscarassius*), n = 19	18-42	31
3	Vobla*(Rutiluscaspicus)*, n = 21	16-46	31
4	Cyanets(*Ballerusballerus)*, n = 5	13-51	32
5	Chehon*(Pelecuscultratus)*, n = 27	21-60	42
6	Bream, n = 30	29-93	45
7	Zhereh*(Aspiusaspius)*, n = 16	29-71	51
8	Goby, n = 15	22-92	57
9	Whitefish, n = 7	31-125	73
10	Roach, n = 28	38-105	83
11	Carp, n = 11	35-151	98
12	Perch, n = 36	35-241	126
13	Common carp (*Cyprinuscarpio*), n = 16	43-260	150
14	Zander, n = 25	98-380	152
15	Sturgeon, n = 4	102-276	189
16	Pike, n = 21	65-301	213
17	Som, n = 5	173-342	260
18	*Crayfish, n = 9*	3.5-16.5	11
19	*Calfruff, n = 3*	5.0-9.3	7.1
20	*Roeroach, n = 4*	8.7-13.5	11
21	*Caviarpike, n = 4*	7.5-14	11
22	*Redfishroe, n = 9*	4.4-8.5	5.2

Figure 2 shows the change in the concentration of mercury in the muscles of bream, roach, perch, pike, and pike-perch caught in the areas of Rzhev–Staritsa, Rybinsk Reservoir, Samara and the Volga River delta. Volga. The lowest concentration of mercury is typical for the Upper Volga region – the region of the city of Rzhev–Staritsa, the maximum concentration is characteristic of the Rybinsk reservoir, which is consistent with the data from literary sources [3, 4]. Most mercury accumulates in the muscles of pikeperch and pike, then perch, roach and bream follow in the direction of reduction. In general, the ratio in the accumulation of mercury represented by fish species persists throughout the Volga River.

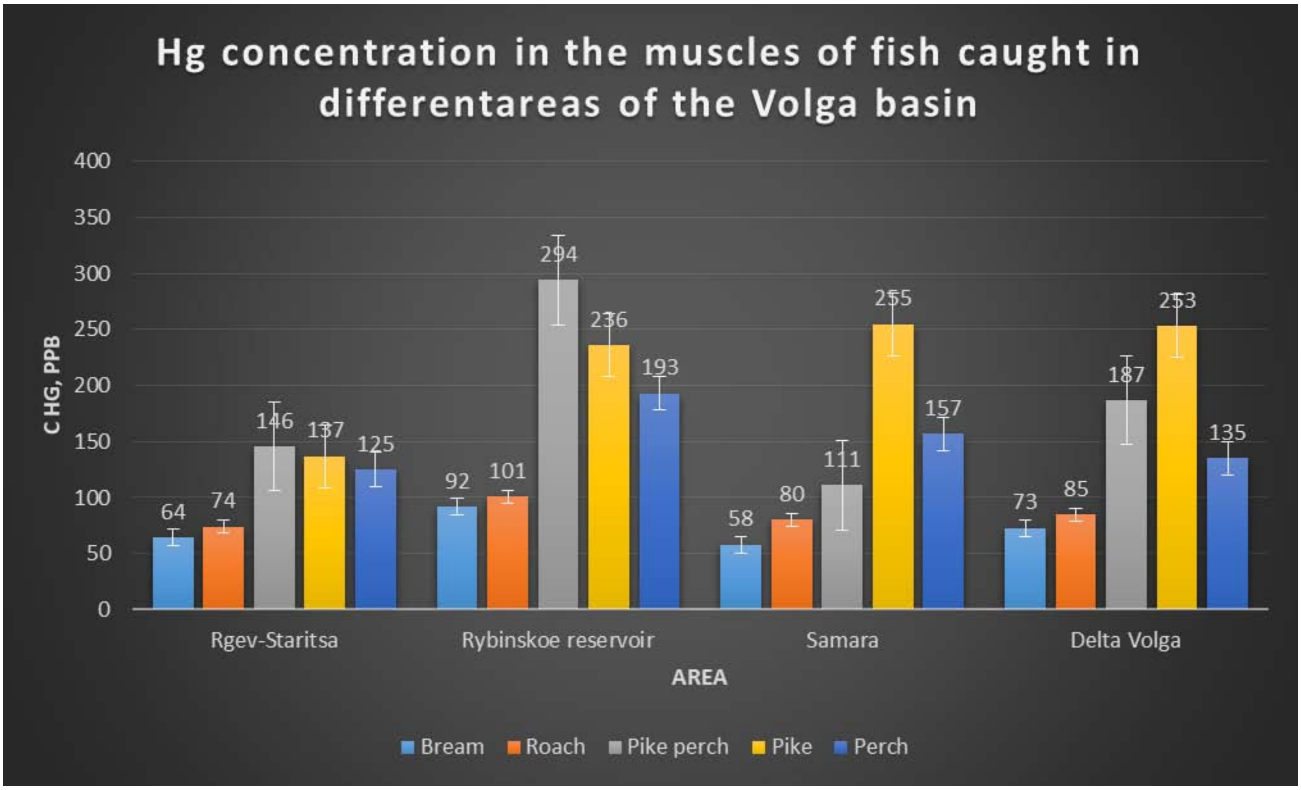


Figure 2: The concentration of mercury in fish caught in the upper (Rzhev – Starica, Rybinskoe Reservoir), middle (Samara) and lower (Delta Volga) areas of the Volga river

IV. Discussion

From literature sources, it is known that under certain conditions, the accumulation of mercury in the muscles of the fish is natural. In particular, cases have been described where the concentration of mercury in the muscles of the lake perch was directly proportional to the weight of the fish [15, 6, 7]. In the same works, it was reported that no such dependence for pike was observed. To assess the characteristics of mercury accumulation in the muscles of perch, pike, and bream, we conducted an experiment to catch these species of fish in the bay Chechera at the confluence of the Volga River.

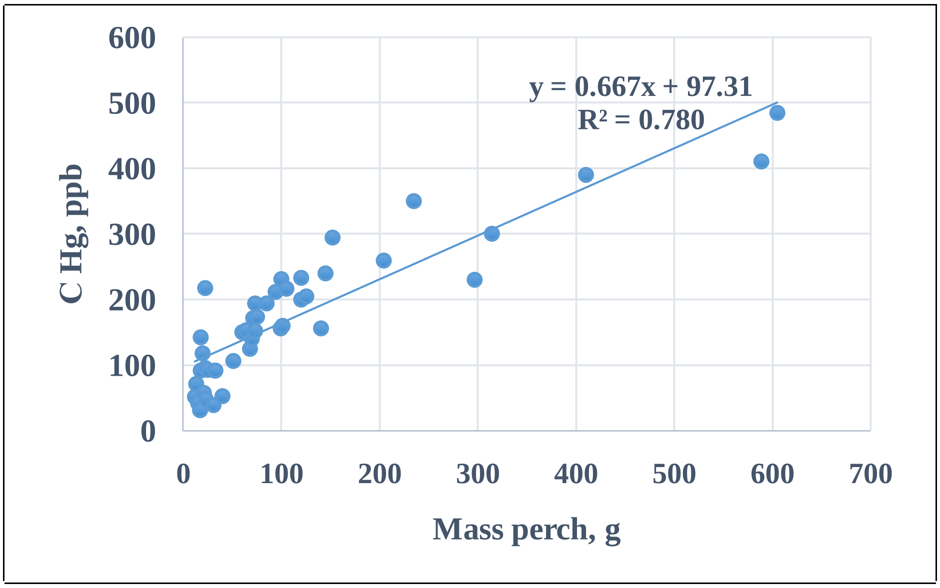
The characteristic features of these fish are listed below:

Perch: This is one of the most common predator fish in the Russian freshwater. Zooplankton, insect larvae, worms, mollusks, the caviar of other fish, small fish,and juveniles are included in the perch diet. In general, it is one of the most voracious and omnivorous carnivorous fish. It feeds on everything in the pond. Perch grows very slowly. For the first year, its size is about 5 cm. A two years, the average perch is 11 cm long and weighs 23 g; by nine years old it is 29cm and 580 g, respectively.

Pike: The main food of the pike is all kinds of fish that live in a particular body of water, and preference is given to narrow-bodied breeds. Along with the narrow-bodied fish, which she prefers, large frogs, tadpoles, mice, etc. were repeatedly encountered in the stomachs of pikes. Pike grows very fast. During the first year of life, it reaches a length of 25–30 cm with a weight of up to 300 grams, in the second year 25–45 cm weighing up to 1.5 kg. For the third year, it grows to 60 cm and can reach a weight of just over 2 kg. A ten-year-old pike can weigh 10 kg with a length of 1 meter.

Bream: The physiological characteristics of the bream imply a purely bottom way of life. Bream feeds mainly on larvae, small crustaceans, mollusks, earthworms, land larvae and insects, and all sorts of vegetable food (young shoots of aquatic plants, etc.). Bream grows somewhat faster than perch but significantly slower than pike: by the end of the second year of life, it has an average length of about 15–17cm and a weight of about 150–170g.

As shown above, these fish are fundamentally different in growth rate and food base. Therefore, a large contrast of the experimental results was expected. Figure 3 shows graphs of mercury accumulation in the muscles of perch, pike, and bream. As can be seen from these graphs, there is a directly proportional relationship between the concentration of mercury in perch muscles and the mass of fish ($r = 0.881$, $p = 0.018$).



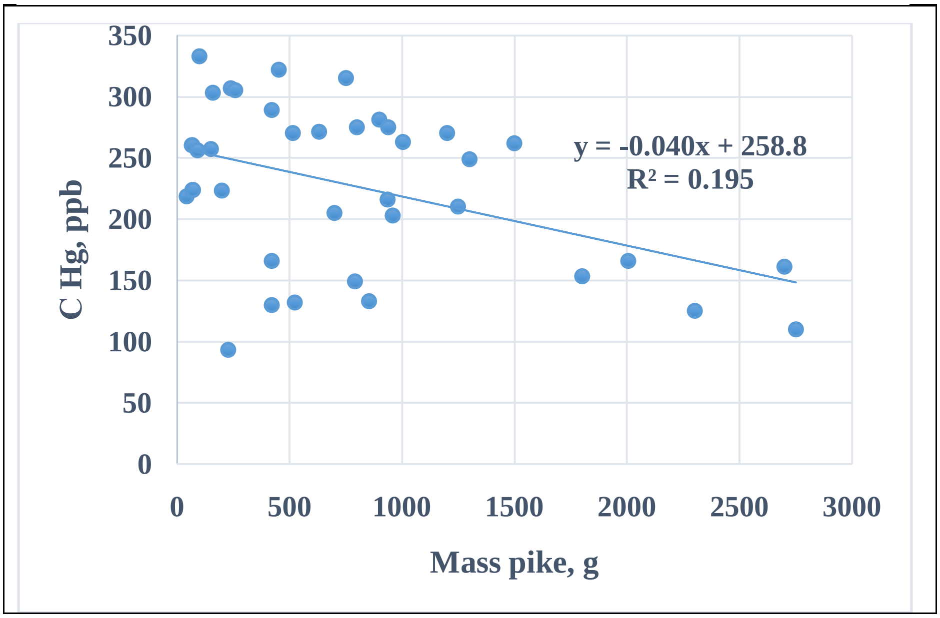


Figure 3: Character of mercury accumulation in perch and pike muscles

For a pike, on the contrary, the maximum mercury concentration is typical for fish weighing up to 1 kg, then a decrease in mercury concentration is observed (one should emphasize that we are talking about concentration and not abut total mercury in fish), the correlation coefficient was r = - 0.653, p = 0.029 (the calculation was carried out using the Minitab 17 program).

In the first case, we can state a high degree of dependence, in the second - a moderate degree of dependence of mercury concentration on the mass of fish. In the first case, it is a dependency with a sign (+), in the second case - with a sign (-). These facts raise some questions: in our case, the habitat of both pike and perch is the same. The habitat conditions of both types of fish are the same; the food base and the catch time are also the same. The concentration of mercury in the water did not change during capture and was 0.025-0.033 mcg/l (ppb). Nevertheless, a fundamental difference was found in the regularity of mercury accumulation in the muscles of perch and pike. The explanation of this phenomenon must be sought in fundamentally different growth rates of perch and pike. As mentioned above, the perch grows very slowly, it gains a mass of 500g and more by 8-9 years of life, while pike can gain a mass of 9-10kg over the same period. Consequently, the distribution of mercury coming from food occurs in a significantly larger mass, which leads to a peculiar decrease in the value of mercury concentration in the pike muscles. For bream, the dependence of mercury concentration in muscles on body mass was not found.

V. Conclusions

1. The concentration of mercury in the muscles of all fish species represented in work does not exceed the accepted standards (MPL). The highest concentration of mercury is characteristic of carp, carp, pike perch, pike, perch, sturgeon, and catfish;the lowest concentration of mercury is for ruff and crayfish. It has been found that mercury concentration in eggs is minimal and does not depend on the concentration of mercury in the muscles of the fish;
2. In the study of the spatial distribution of mercury in fish throughout the Volga river, it was found that in general the maximum concentration of mercury in the muscles of fish is characteristic of the Rybinsk reservoir, the minimum is for the Upper Volga;
3. The features of mercury distribution in the muscles of perch, pike, and bream were evaluated. It was found that the accumulation of mercury in the muscles of perch in the absence of human-made impact and the level of acidity of water 6.5-7.0 is directly proportional, in the muscles of pike-inversely proportional. For bream, the dependence of the concentration of mercury in the muscles on body weight was not found.

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Fuel Wood Systems: Reduction of Greenhouse Gas Emissions

By Benjamin Ternenge Abur, Amodu Ahiaba Haruna & Bawa M. A.
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Abstract- Fuel wood systems offer significant possibilities for reducing greenhouse gas emissions when bio-energy replaces fossil fuel in energy production. This research paper provide analysis of calorific value, wood density, moisture content and ash content of commonly used fuel woods in Girei local government area of Adamawa state-Nigeria to determine the fuel-woods which are suitable as energy source. Nine (9) commonly used wood species of interest were selected for test evaluation. Test result show that Tamarindus Indica, Dalbergia Melanoxylon and Prosopis African have relatively high wood density, high calorific value and low percentage ash content when combusted. Their low ash content is also desirable as fuel since only non-significant part of the volume cannot be converted into useful energy. These wood species should be planted as a source of fuel-wood while efficient wood burning stoves should be develop and adopted in local communities. It is recommended that thermal test performance and emission characteristics of these wood species should be conducted.

Keywords: *calorific value, wood density, ash content, moisture content, greenhouse gas emissions.*

GJSFR-H Classification: *FOR Code: 829802*

FUELWOODSYSTEMSREDUCTIONOFGREENHOUSEGASEMISSIONS

Strictly as per the compliance and regulations of:

Fuel Wood Systems: Reduction of Greenhouse Gas Emissions

Benjamin Ternenge Abur [α], Amodu Ahiaba Haruna [σ] & Bawa M. A. [ρ]

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I. Introduction

Biomass has been a major source of energy throughout the world. It refers to the energy of biological systems obtain from animals and plants. It is an indirect form of solar energy because it arises due to photosynthesis of plants. It is the primary source of energy for nearly 50% of the world's population (Kithyoma et al, 2006). Wood biomass is a major renewable energy source in the developing world representing a significant proportion of the rural energy supply (Hashiramoto, 2007). The resources that make up biomass can be classified into wood biomass, forge, grasses and shrubs; residues and waste (forestry, agricultural, municipal and industrial) as well as aquatic biomass. Organic materials, including cultivated products, solid agricultural waste, urban and rural material waste are abundant in most developing countries of the tropics. The biomass which is considered most significant in terms of energy source is wood and wood waste. Wood is a traditional fuel and about 50% of the wood harvested in the world is used as fuel (Doglas, 1994). The reasonable energy from wood compares favorably with other classes of energy sources such as solar, wind, tidal and geothermal. Wood is cheap, abundant and renewable as it could be grown consistently for energy utilization as long as there is land, water and sunshine. Wood energy provides an alternative to fossil fuels, a means to combat a changing global climate, and an environmentally sound sustainable energy future. Wood provides about 2.4% of Australia's total primary energy needs while developing countries such as Nepal, Ethiopia and Kenya obtain majority of their energy needs from the burning of wood, animal dung and other biomass (Badcock *et al*., 1978). Nigeria uses 80 million cubic metres of fuel wood annually for cooking and other domestic purposes (Sambo, 2005). Most woods burn readily but some species are fire retardant and will not burn except in the mixture of more flammable woods. While some woods burn readily, they may not be suitable for fuel woods because of excessive spark production, toxic or irritating smoke. The wood of Sesbania grandiflora for example is not highly regarded as fuel because of the excessive smoke it produces when burning (Hegde, 1990). Fuel wood properties include calorific value, wood density and wood moisture content. The importance of these factors for domestic fuel wood use depends on the type of stove used, cooking methods and the adequacy of ventilation. Local preferences may also be important depending on the effects of the fuel wood on the flavour of the cooked food. Gross calorific value is not an important property since there is little variation among species (Harker *et al*., 1982). However, the total energy contained in wood is not converted completely to available heating energy since this includes heat generated by the combustion of hydrogen (about 6% of wood mass). Heat is also lost in vapourising moisture contained in the wood. The result obtained from the research is to used to recommend the fuel wood species with better energy value and characteristics value for plantation so as curtail indiscriminate the felling of trees in Girei local government area of Adamawa state.

II. Materials and Equipments

The commonly used wood species in Girei local government of Adamawa state, Nigeria were used for the study. Young fresh branches of the trees species were obtained from the sudan savannah forest. Table 1 gives the botanical, English and Hausa names of the

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woods species. The equipments used for the tests were Cusson's bomb calorimeter set consisting of Bomb Calorimeter vessel of double walled outer vessel, Beckman thermometer, thermocouple, Galvanometer Crucibles porcelain, low wide form 3ml, covers numbered with furnace-proof ink. Other equipments were Muffle furnace with pyrometric controller, Analytical balance of sensitive 0.1mg, desiccators, drying oven, wood cutting machine, a digital weigh scale, and Venier caliper and oxygen cylinder.

Table 1: Names of commonly used wood species

S/No.	Botanical	English	Hausa
1	Ficus Thonningii	Strangler	Chediya
2	Vitex Doniana	Black Plum	Dinya
3	Prosopis African	Iron wood	Kiriya
4	Balanites Aegyptiaca	Soap Berry	Aduwa
5	Piliostigma Reticulatum	Camel's foot	Kargo
6	Danlella Oliver	Copaila Balsam	Maje
7	Dalbergia Melanoxylon	African Black wood	Karye Gatari
8	Parki Biglobosa	African locust bean	Dorowa
9	Tamarindus indica	Tamarin	Tsamiya

III. METHODOLOGY

a) *Sample preparation*

The wet branches of the woods species were split into medium size mostly used for fuel wood and air-dried for 90 days to reduce the moisture content. The dried wood samples were then sawed using the wood cutting machine and the dust collected for the test.

b) *Determination of Calorific Value*

The calorific values of the wood species were determined using Cusson's bomb calorimeter. One kilogram of the sawdust of each sample was loaded into the bomb calorimeter crucible. To initiate the burning process of the saw dust wood, a 50mm long cotton thread was inserted between the Nichrome firing wire coils and the center of the test sample specimen in the crucible. The sealing of the bomb calorimeter was positioned in its groove avoiding surface flows of the seal ring. The knurled locking of the ring of the calorimeter was raised and bomb body lowered into the ring and the body rotated until its threads fully engage the thread of the ring. The sealing ring was then tightly screwed on the thermocouple plugged into position through the top of the bomb calorimeter. Oxygen was then passed into the interior of the bomb calorimeter from a cylinder through the top valve on the calorimeter to a pressure of about 25bars. The indicator on the galvanometer was adjusted to zero and left to stabilize for about 30 seconds to check the stability of the ambient temperature within the bomb calorimeter. The bomb calorimeter content was then ignited for the combustion process. The maximum temperature for the combustion process was then noted through the thermometer inserted on the bomb calorimeter.

The calorific value of each wood species was calculated using equation 1

$$\text{Calorific Value}\left(\frac{Q}{M}\right) = C\Delta t$$

Where;

Q=Quantity of heat released during combustion (KJ)

M=Mass of wood burnt (kg)

C=heat capacity of bomb calorimeter 1238KJ/°C

Δt=temperature rise

c) *Determination of percentage Ash content*

The air-dried wood samples were weighed to 5g each. The crucible with covers were dried for 2-hours at 100°C in an oven and removed from the oven to the desiccators. They were cooled and weighed with their covers to the nearest 0.1mg and the result recorded as M_1 while the 5g earlier weighed was recorded as M_o. The crucibles and the samples were weight together and the result recorded as M_2 .The sample was then Ash in furnace at 600°C for 2-hours. The crucibles with covers were allowed to cool in furnace to a temperature of less than 200°C and placed in desiccators with vented top. The crucibles were then weighed with covers and the ash content to the nearest 0.1mg and recorded as M_3. The percentage ash content of the wood species was calculated using equation 2

$$\text{Percentage Ash content} = \frac{M_3 - M_1}{M_O} \times 100$$

Where:

M_O=weight of the sample

M_1=weight of the crucible

M_2=weight of crucible and dry wood sample

M_3=weight of the crucible and ash

d) *Determination of Density*

The wood species were cut into cuboids and the mass of each pellet was obtained using a digital weighing scale. The mass was recorded as M. The dimensions of the cuboids shaped pellet were obtained by measurement using a vernier caliper. The dimensions were recorded as length (l), breadth (b) and width (w) and the volumes of the wood species obtained through calculation. The density of the wood species were calculated using equation 3

$$\text{Density, } \rho = \frac{M}{V}$$

Where:
ρ is the density of wood species
M is the mass of wood species
V is the volume of wood species

e) Determination of Moisture Content

The wood species were cut into pellet and the mass of the wet pellet measured and recorded as M_{wet}. The wet wood specimens were placed in an oven at a temperature of 103°C for 24 hours. Then the mass of the oven dried woods specimen were measured and recorded as M_{od}. The moisture content of the wood species were calculated in percentages using equation 4.

$$\text{Moisture content (M)} = \frac{M_{wet} - M_{od}}{M_{od}} \times 100\%.....$$

Where
M_{wet} is the mass of wet wood species
M_{od} is the mass of oven dried wood species

IV. RESULTS AND DISCUSSION

Table 2 shows the calorific value, density, ash content and moisture content of the nine most commonly used fuel woods species in Girei local government area of Adamawa state.

Table 2: Calorific value, Density, Ash content and Moisture content of the nine tested woods species

S/No.	Wood species	Calorific Value (KJ/Kg)	Density (Kg/m^3)	Ash Content (%)	Moisture Content (%)
1	Ficus Thonningii	19.30	440.0	5.20	9.10
2	Vitex Doniana	21.22	606.1	7.40	13.35
3	Prosopis African	21.47	1034.4	3.00	11.35
4	Balanites Aegyptiaca	21.47	894.3	5.60	12.01
5	Piliostigma Reticulalum	22.18	636.4	8.20	14.35
6	Danlella Oliver	20.76	746.2	15.00	11.60
7	Dalbergia Melanoxylon	22.50	1420.4	7.20	11.20
8	Parki Biglobosa	22.14	782.1	5.00	12.06
9	Tamarindus Indica	23.12	1061.9	4.20	10.05

a) Percentage of Ash Content

High ash content of wood is less desirable for fuel wood as it is characterized as non combustible products and reduces heat of combustion (Klasnja *et al*., 2002). Higher ash content signifies that higher percentage of the wood is not combusted. This shows that Danlella Oliver and Piliostigma Reticulalum are less desirable wood species for combustion process due to their high percentage ash content while Prosopis African and Parki Biglobosa have low ash content and could yield high level of useful energy when combusted.

b) Density of wood species

The density of wood determines its duration in fire when combusted. A higher wood density will sustains combustion for a long duration of time and produces long-lasting coals and thus more desirable. It can also be used as a parameter in determining the softness or hardness of wood species. Dalbergia Melanoxylon, Tamarindus Indica and Prosopis African have high densities of more than 1000kg/m^3 and are most likely to be hard woods. Since hard woods are known for sustaining long lasting combustion process as well as long lasting coals, they are more economical where heating requires steady concentrated long heat production.

c) Calorific value

When choosing wood for burning there are three factors which have an effect on the calorific value (CV) or the amount of available heat per unit of fuel (type of species, wood density and the moisture content). Hard woods give higher net kilo-Watt hour (kWh) of heat from a cubic-metre, m^3 of wood than soft woods. Thus, Dalbergia Melanoxylon, Tamarindus Indica and Prosopis African will give a higher calorific value than Ficus Thonningii, Piliostigma Reticulalum and Vitex Doniana. As show in the table of results, the moisture content and wood density has considerable effect on the calorific value of the wood when combusted as higher moisture content and low wood density tend to gives a lower calorific value.

d) Moisture content

There is variation in calorific value between wood species due to the amount of water naturally present in the wood when felled. Thus, fresh woods have lowered calorific as part of the useful heat is used in vapourising moisture contained in the wood. Similar wood species dried to the same moisture content will have similar calorific value. From the table of results, it can be inferred that less heat would be lost to vaporizing the moisture in Ficus Thonningii and Tamarindus Indica than the other wood species. In practical term, if the combustion process of these woods species takes place in an open air where the heat of combustion will not be completely capture, then the heating value of these woods would be less than the value shown in result table. From literature it was recorded that if the moisture content of wood is less than 20% it will burn without smoking. It can also be inferred from Figure 4 that the woods under study will burn without smoking and are considered as good candidate for usage without polluting the environment.

V. CONCLUSION AND RECOMMENDATION

The use of fuel wood is not an ideal intervention method when addressing energy crises due to poor indoor air quality associated with biomass combustion and negative effect of deforestation on the environment. However, when choosing wood for burning, three factors are of paramount interest; wood species, wood density and moisture content are to be establish. Hardwoods (deciduous, broadleaved tree species) tend to be denser and hence making a tonne of hardwood logs to burn for a longer period of time than softwood softwoods (evergreen, coniferous species) which contain more resins. From literature, the moisture content of wood has the greatest effect on calorific value than any of the variables. Water moisture left in the timber has to be evaporated away before the wood will burn. This reduces the net energy released as useful heat. Generally, density of wood biomass, calorific value and percentage ash content are important wood fuel variables that affect the burning characteristics (combustion) and energy released of the fuel including the type of combustion equipment used. The choice of fuel wood in the local government area is not governed by factors like the burning duration, the maximum obtainable temperature and ash content of the wood species and thereby using whatever fuel wood is available. Indiscriminate clearing of land and exploitation of trees for fuel wood without replacement is a major problem today most especially in developing countries. If deforestation and its associated environmental degradation effects are to be curtailed, then only efficient wood burning species should be used as fuel wood. Improve efficient wood burning stoves should be develop and the thermal performance and emissions characteristics of the stove using the wood species should be carryout to select the most efficient wood species while at the same time government should embark on afforestation programmmes.

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Adsorption of Cyanide Contained in Aqueous Solution using Activated Carbon Obtained from Coffee Residue: Adsorption Efficiency; Equilibrium and Kinetic Models

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Abstract- This research aimed to evaluate the adsorption process of cyanide ion (CN^-) contained in synthetic aqueous solution, using activated carbon obtained from coffee residue, studying its efficiency and equilibrium and kinetic models. Activated carbon was characterized by Fourier Transform infrared analysis (FTIR), X-ray diffraction (DRX), and iodine number determination. A central composite design (CCD) with three factors adapted to three levels each and six central points was applied to study the effect of pH (A), contact time (B) and adsorbent dosage (C); According to the analysis of variance, the factors A, B, C, and the square AA were significant in the adsorption efficiency of cyanide onto activated carbon, whose maximum value reached was 54.68% and 67.65% for the predictive level. According to the coefficient of determination (R^2), Freundlich's isothermal model (0.954) and the three kinetic equations of pseudo-second order (0.991, 0.993, 0.993) fit the experimental process. From the results obtained, the active carbon prepared from coffee residue can be used as a potential adsorbent of CN^-, contained in aqueous solutions of low concentrations.

Keywords: adsorption; active carbon; cyanide; isotherm; coffee waste.

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Adsorption of Cyanide Contained in Aqueous Solution using Activated Carbon Obtained from Coffee Residue: Adsorption Efficiency; Equilibrium and Kinetic Models

Gonzalo Aranguri-LLerena α & Wilson Reyes-Lázaro σ

Abstract- This research aimed to evaluate the adsorption process of cyanide ion (CN^-) contained in synthetic aqueous solution, using activated carbon obtained from coffee residue, studying its efficiency and equilibrium and kinetic models. Activated carbon was characterized by Fourier Transform infrared analysis (FTIR), X-ray diffraction (DRX), and iodine number determination. A central composite design (CCD) with three factors adapted to three levels each and six central points was applied to study the effect of pH (A), contact time (B) and adsorbent dosage (C); According to the analysis of variance, the factors A, B, C, and the square AA were significant in the adsorption efficiency of cyanide onto activated carbon, whose maximum value reached was 54.68% and 67.65% for the predictive level. According to the coefficient of determination (R^2), Freundlich's isothermal model (0.954) and the three kinetic equations of pseudo-second order (0.991, 0.993, 0.993) fit the experimental process. From the results obtained, the active carbon prepared from coffee residue can be used as a potential adsorbent of CN^-, contained in aqueous solutions of low concentrations.

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I. INTRODUCTION

The CN^- is one of the toxic chemicals found in sewage discharges from electroplating, metal finishing, steel hardening, mining (Processing of metals such as gold and silver), manufacturing of auto parts, photography, pharmaceuticals and coal processing units (Dwivedi et al., 2014), food and chemical synthesis (nylon, fibers, resins, fertilizers, pesticides, and herbicides) (Halet et al., 2015). It is estimated that the release of cyanide from industries is more than 14 million kg/year in the world (Gupta et al., 2012) and can exist in three forms: total cyanide (CNT), WAD cyanide (Weak acid dissociable) and free cyanide (CNL). The CNT includes strong metal-cyanide complexes, such as iron ($[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$), gold ($[Au(CN)_2]^-$, cobalt ($[Co(CN)_6]^{4-}$), and Cyanide WAD (CN WAD); which includes both: CNL and metal complexes of weak and moderately strong cyanide; such as cadmium ($[Cd(CN)_4]^{2-}$), zinc ($[Zn(CN)_4]^{3-}$, copper cyanides ($[Cu(CN)_2]^-$, $[Cu(CN)_3]^{2-}$, $[Cu(CN)_4]^{3-}$), nickel ($[Ni(CN)_4]^{2-}$) and silver ($[Ag(CN)_2]^-$); the CNL includes CN^- and hydrogen cyanide (HCN) (Aranguri and Reyes-López, 2018).

Cyanide when emitted in concentrations that exceed environmental regulations, constitutes a dangerous compound for humans, aquatic organisms and the environment in general, because it exerts an inhibitory action on certain metabolic enzymes; the main compound affected is the enzyme cytochrome c oxidase; its inhibition causes the blocking of the electron transport chain at the mitochondrial level, avoiding the absorption of oxygen (Luque-Almagro et al., 2016). According to Azamat and Khataee (2017); Between 0.5 and 3.5 mg of cyanide per kilogram of body mass in people can cause death.

The United States Environmental Protection Agency (USEPA) has proposed a regulation for drinking water regarding the CNT in 0.2 mg/L and in terms of CNL for protection of aquatic life in freshwater, it is set at 0.022 and 0.0052 mg/L (Botz et al., 2016). Peruvian regulations for water quality standards (DS N ° 002 - 2008 -MINAM), established the CN WAD at 0.1 mg/L (category 3: irrigation of vegetables and animal drinks) and for CNL at 0.022 mg/L (category 4: conservation of the aquatic environment).

Liquid emissions containing cyanide over the permissible limits are processed by conventional chemical methods such as alkaline chlorination, the INCO process (SO_2/air) (International Nickel Company`s), hydrogen peroxide, the Caro´s acid method (H_2SO_4/H_2O_2), ozonation, among others (Aranguri and Reyes-López, 2018; Botz et al., 2016); however, for Dwivedi et al. (2014) chemical processes to degrade cyanide are not appropriate for environmental and economic perspectives; due to its high demand for chemical products and the formation of secondary pollutants, they need additional treatment before disposal and argues that adsorption is a simple and attractive method for the elimination of toxic effluent compounds due to their high efficiency, handling, and economic feasibility.

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According to bibliographic references, there are several reports of adsorbents; with and without treatment to adsorb CN^-; namely: olive stone and coffee ground (Halet et al., 2015), shea butter seed husk (Tsunatu et al., 2015), coconut shell (Singh and Balomajumder, 2016), rice husk (Naeem et al., 2011), almond shells and leaves of teak (Dwivedi et al., 2016), active carbon (D 45/2 - Carbo Tech) (Stavropoulos et al., 2015) and in the present study, active carbon is used, prepared from the coffee residue, and a method little studied in the carbonization and activation of the precursor is explored; Nitrogen gas was not used to generate an inert atmosphere.

According to the International Coffee Organization (ICO), in 2018, the world coffee production was 168.093 million bags of 60 kg. Its processing generates significant amounts of agricultural waste, ranging from 30% to 50% of the total coffee weight produced, depending on the type of processing (Oliveira and Franca, 2015). According to Mussatto et al. (2011), approximately 50% of the world's coffee production is used to prepare soluble, and the ground coffee residues are in the order of 6 million tons per year, worldwide. The intention is to give added value to these wastes.

Thus, the purpose of the present work was to evaluate the adsorption process of cyanide, contained in aqueous solution, on activated carbon, obtained from coffee residue, studying its efficiency as well as the equilibrium and kinetic models.

II. MATERIALS AND METHODS

a) *Preparation of activated carbon from coffee residue (CARC)*

Cofee residue (after roasting, grinding and extracting its flavorings), from the *Coffea arabica* variety, produced in the province of Chanchamayo (Perú), was collected from the “Valentino” cafeteria (Trujillo Central Market); washed with spout water to remove dust, impurities, and soluble substances; then it was rinsed with boiled distilled water until the black dye disappears and dried at 110°C for eight horas in a Universal Oven UF55- Memmert. Subsequently, carbonization and chemical activation is experienced at 500 and 450 °C, respectively; in refractory clay crucible, provided with a lid (Guang-zhen et al., 2016); contained in a Barnstead Thermolyne 6000 electric muffle, for one hour for each stage. Nitrogen gas was not used to generate inert conditions; each crucible was supplied from its respective lid to avoid oxidizing atmosphere.

Before chemical activation; chemical impregnation was applied to carbon, with a solution of phosphoric acid (H_3PO_4) (Halet et al., 2015; Shamsuddin et al., 2016) at 40%; 3 mL of phosphoric acid is added for each gram of carbon (3 v/p) (Reffas et al., 2010) were stirred for 15 hours at 80°C.

The yield and burn off in the carbonized process were measured according to (Reffas et al., 2010). The carbonization yield or degree of conversion to coal (Equation 1), is the percentage of the product obtained after carbonization concerning the dry weight of the precursor used and the burn-off or lost by combustion (Equation 2), is the percentage of precursor eliminated during the carbonization process ((Fombuena and Valentín, 2010).

The CARC was reduced and classified to a particle size between +74 and -500 microns, washed with distilled water to a neutral pH, and dried at 150 °C for six hours.

$$\text{Yield (\%)} = m_2 \,.100/m_1 \qquad (1)$$

$$\text{Burn off (\%)} = (m_1\text{-}m_2)\,.\,100/m_1 \qquad (2)$$

Where: m_1 = initial precursor mass and m_2 = mass of carbon obtained.

b) *Characterization of the adsorbent*

The functional groups present on the surfaces of the coffee residue were determined; to its respective CARC and CARC after adsorbing CN^-, applying a solid phase FTIR analysis, using a Thermo Nicolet IS50 FT-IR ATR spectrometer. To identify the amorphous nature and the metal oxides present in the CARC; A DRX analysis was performed using the Rigaku brand Diffractometer, model Miniflex 600. Likewise, its iodine number was determined, according to NMX-F-296-SCFI, 2011, and ASTM-D4607, 2006. For the three analyzes, the samples were reduced to a size of -75 microns.

c) *Optimization of the adsorption process*

The CCD was applied; their independent variables, and their respective levels, which determined the adsorption percentage (Y) responses, are shown in Table 2. The adsorption tests of the CN^- (mg/L), were performed randomly; Their results were evaluated using the Minitab 18 statistical software, with an “α” level of 5% and adsorption efficiency was calculated according to equation 3.

$$\text{\% Adsorption} = (C_i\text{-}C_f)\,.100/C_i \qquad (3)$$

Where C_i and C_f, represent the initial and final concentration of CN^- (mg/L), for each test, respectively.

d) *Study of equilibrium and kinetic models*

To study the interaction of CN^- molecules and the surfaces of the CARC particles, as well as identify a model equation to predict the equilibrium adsorption of the CN^- by the CARC, the experimental equilibrium data were tested, with the isothermal models of Freundlich, Langmuir, and Temkin.

The separation factor or equilibrium parameter "R_L" (constant without dimensions) is used to express the essential characteristics of the Langmuir isotherm (Equation 4).

$$R_L = 1/(1+bC_0) \qquad (4)$$

Where: b is the Langmuir constant and C_0 is the initial concentration of CN^- (mg/L). R_L indicates the conditions of the isotherm. If, $R_L > 1$ (unfavorable), $R_L = 1$ (linear adsorption), $R_L = 0$ (irreversible) and if $0 < R_L < 1$ (favorable) (Eletta et al., 2016; Gupta et al., 2013).

The mass transfer efficiency of the CN^- to CARC was evaluated, applying the first and second-order pseudo models, and to determine whether intraparticle diffusion was the limiting stage for cyanide adsorption on CARC, the experimental data were analyzed by the Weber-Morris model.

For the equilibrium and kinetic study, the concentrations of CN^- solutions were measured and the adsorption capacity in the equilibrium (qe, mg/g), was calculated; as well as the adsorption capacity of CN^- at time t (qt, mg/g) for predetermined time intervals; according to equation 5 and equation 6.

$$qe=(C_0-C_e)\ .\ V/W \qquad (5)$$

$$qt=(C_0-C_t)\ .\ V/W \qquad (6)$$

Where C_0 (mg/L) is the initial concentration of CN^-; C_e (mg/L) is the concentration of CN^- in the equilibrium; C_t (mg/L) is the CN^- concentration of the cyanide solution at time t (min); V (L) the volume of the cyanide solution and W (g) the amount of activated carbon (Halet et al., 2015).

Table 1 shows the linear forms for the equilibrium and kinetic equations adapted from (Dwivedi et al., 2014) and from (Tsunatu et al., 2015).

Table 1: Equilibrium and kinetic models used to explain adsorption processes

Models	Linear equation	Parameters
Equilibrium models		
Freundlich model	$\log q_e = \log K_f + 1/n \log C_e$	K_f (mg/g)/(mg/L), 1/n and n, are constants
Langmuir model	$C_e/q_e = 1/Q_{max}\, b + C_e/Q_{max}$	Q_{max} (mg/g) is the maximum adsorption capacity in the monolayer and b (L/mg) is the constant related to the capacity and energy of adsorption, representing the affinity between adsorbate and adsorbent.
Temkin model	$q_e = B \ln A + B \ln C_e$	A and B are the constants of Temkin
Kinetic models		
Pseudo first order	$\log(q_e - q_t) = \log(q_e) - K_1 t/2{,}303$	q_e y q_t are the adsorption capacities (mg/g) of adsorbent, at equilibrium and at a time "t," K_1 is the pseudo first order adsorption rate constant (s^{-1})
Pseudo second order	$t/q_t = 1/K_2 q_e^2 + t/q_e$	K_2 is the pseudo second order adsorption rate constant (g/mg s)
Intra particle diffusion	$q_t = K_{di}\ t^{1/2} + C$ (Weber-Morris (1963)	q_t is sorption concentration at time "t". K_{di} is the rate constant of intra particle transport (mg/g/time $^{1/2}$). C (mg/g) it is a constant related to the thickness of the adsorbent boundary layer

The tests for the isothermal and kinetic model will be carried out at ambient conditions (30 °C), using 50 ml of pH 8 synthetic solution with 1.5 g of adsorbent contained in 250 ml flasks. The known concentrations for each test were diluted from a cyanide stock solution of 1000 mg/L of CN^- and filtered after each test for analysis. An IKA WORKS KS orbital shaker is used for all agitation tests.

e) Analytical measurements and of pH

Depending on the concentration of the solution, the CN^- was determined, either by the cyanide ion-selective electrode method or by titration; For the latter, Vogel's "method A" (Vogel, 1989) and Standard Methods 4500-CN-D (Greenberg et al., 1992) are considered with the adaptation of a concentration of silver nitrate ($AgNO_3$) of 2 g/L (0.01 M) and as an indicator rhodamine (p-Dimethylamino benzalrhodamine) at 0.1 g/100 mL of acetone. For the cyanide selective electrode method, a Thermo Scientific, Orion Versa Star Pro multiparameter, and a cyanide specific ion electrode, Thermo Scientific model, Orion 9606 BNWP are used. Potentiometric readings performed on a magnetic stirrer IKA WORKS, model C-MAG-HS7. The pH of all solutions was regulated by the addition of *HCl* or *NaOH* solutions (10 and 1 N for both) and was measured using a Thermo Scientific Orion electrode.

III. RESULTS AND DISCUSSION

a) Preparation of CARC

The yield and burn off, for carbonization (14.73% and 85.27%) and chemical activation (72.86% and 27.14%) of the coffee residue at 500 and 450 °C respectively were evaluated. Molina-Sabio and Rodríguez-Reinoso (2004) report that in the carbonization of lignocellulosic materials, the degradation of the precursor takes place between 200 and 350 °C; for the present experiment studied, it occurred at an average temperature of 310°C.

The carbonization yield (14.73%); It is relatively superior to what was experienced by Reffas et al. (2010), who gives a value of 9.7% for simple carbonizations of the same material; This could be by the difference in the temperature of carbonization.

The yield obtained in the chemical activation stage is high (72.86%); compared to the 50% yield found by Al Bahri et al. (2012) in the activation of seeds of grapes impregnated with H_3PO_4 (3 p/v), in a single-phase and at 38 and 32% of Reffas et al. (2010) for chemical activation with single-step H_3PO_4 at 450 °C, for ground coffee residues at different impregnation rates; This notable difference is because in the first phase of carbonization of the coffee residue, were expelled the most volatile material.

b) Characterization of the adsorbent

According to the FTIR analyzes of the precursor (Fig. 1a) it reveals that it has a broad adsorption band due to the formation of hydrogen bridges, with a peak around 3335 cm^{-1} and is related stretching vibration of the hydroxyl groups *OH*, overlapping with *N-H* junctions: alcohols-phenols, carboxyl and amino (Reffas et al., 2010), which is corroborated by the formation of signals at 1154 and 1032 cm^{-1} for phenols and alcohols, as well as the two acute bands at 2922 and 2853 cm^{-1} show the presence of the stretching vibrations *C-H* (alkanes) (Ma and Ouyang, 2013). The peaks at 1743 and 1647 cm^{-1} are assigned to the stretching vibrations *C=O* in the carboxylic acids, anhydrides, and lactones (Imessaoudene et al., 2016), and the acetyl group in the hemicellulose (Shamsuddin et al., 2016). The bands at 1455 and 1377-1240 cm^{-1} ascribed to the symmetrical and asymmetric bending of the CH_3 group; also the 1240 cm^{-1} band is associated with the *C-O* stretching of the aryl group in lignin (Shamsuddin et al., 2016). The signals between 666 and 871 cm^{-1} correspond to out of plane bending vibrations (Rattanapan et al., 2017) and the *N-H* and *C-H* aromatic groups (Reffas et al., 2010). Similar bands have been reported by Ballesteros et al. (2014) and Liu et al. (2015), who agree in their FTIR analysis, that the coffee bean has adsorption bands of lignocellulosic materials.

Fig. 1b shows the FTIR spectrum of CARC; it is appreciated that the precursor has undergone significant changes in its structure that suggests the complete carbonization of the precursor when subjected to the activation process. Volatile and organic compounds have decomposed or removed, resulting in an efficient modification of the surface of the carbon (Ma and Ouyang, 2013; Rattanapan et al., 2017). The band of the precursor between 3600 and 3050 cm^{-1}, as well as the peaks at 2922, 2853, 1743, and 1032 cm^{-1}, have virtually disappeared. Only a small peak of weak intensity remained around 2980 and 2900 cm^{-1} products of the *C-H* aliphatic stretching in an aromatic methoxy group (Reffas et al., 2010; Xu et al., 2014) and the peaks observed around 1560 and 1150-1060 cm^{-1} are due to stretching vibrations type *C=C* and *C-C* respectively. The peak band to 1560 cm^{-1} is overlap with the bending vibration of the *N-H* group (amines and amides); similarly the peaks at 1150-1060 cm^{-1} with the stretching vibrations *C-O* of ethers, esters (Rattanapan et al., 2017) with shoulder at 1190 cm^{-1}; they are characteristic signals of phosphocarbonaceous compounds present in carbons activated with phosphoric acid (Reffas et al., 2010). The band at 870 cm^{-1} is related to out of plane bending vibrations *C = C-H* (Rattanapan et al., 2017).

The spectrum of Fig. 1c has not undergone significant changes in the position of its peaks concerning Fig. 1b, however it has suffered a slight displacement at lower values of the transmittance percentage. It may be due to the adsorption of CN^- onto active carbon.

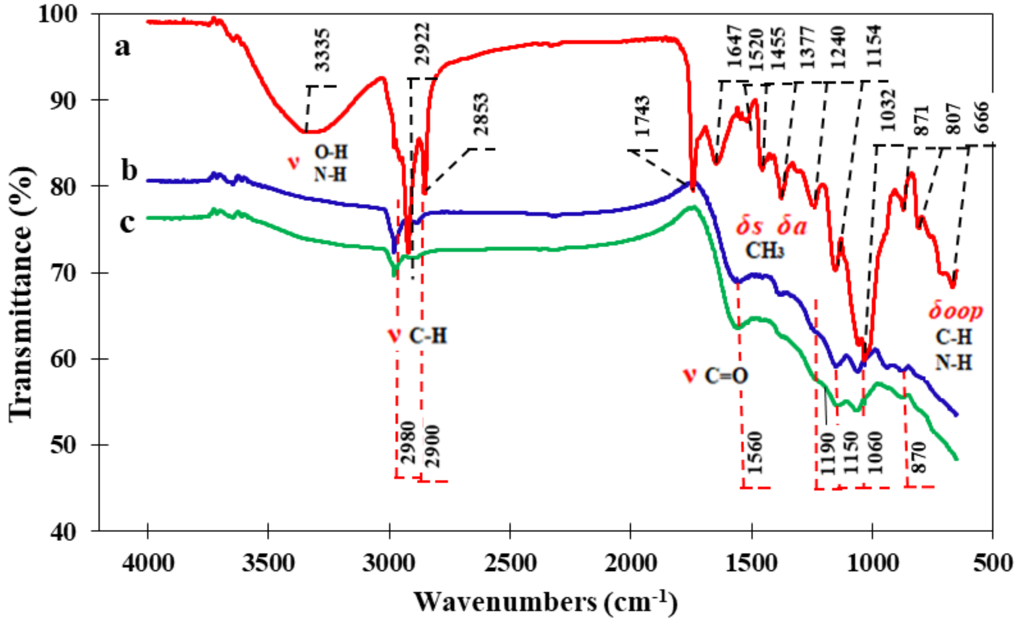

Fig. 1: Comparison of FTIR spectra. a) Coffee residue; b) CARC; c) CARC after adsorption test. The numbers indicated on the bands in the figure correspond to wavenumber (cm^{-1}). ν: stretching vibrations; δa: asymmetric bending vibrations, δs: symmetrical bending vibrations; δoop: out-of-plane bending vibrations.

According to the DRX (Fig. 2), two strong and wide diffraction peaks are observed at 23.58 °C and 43.6 °C on the 2-theta scale, which corresponds to the planes (002) and (101) of the graphite carbon (Rawal et al., 2018), which are dominant characteristics of amorphous coals (Awasthi et al., 2018; Herrera et al., 2018;). According to Gupta et al. (2013), X-ray diffraction patterns in the broad peak of 15 ° to 35° indicate the presence of amorphous silica and alumina wairakite ($CaAl_2(SiO_3)_4.2H_2O$), mordenite ($(Ca,Na_2,K_2)Al_2Si_{10}O_{24}.7H_2O$), ferro-axinite ($Ca_2Al_2BSi_4O_{15}OH$), latiumite ($(Ca,\ K_2)_8Al_8\ (Si,\ Al)_7O_{25}\ (SO_3)$) and several other calcium and aluminum oxides.

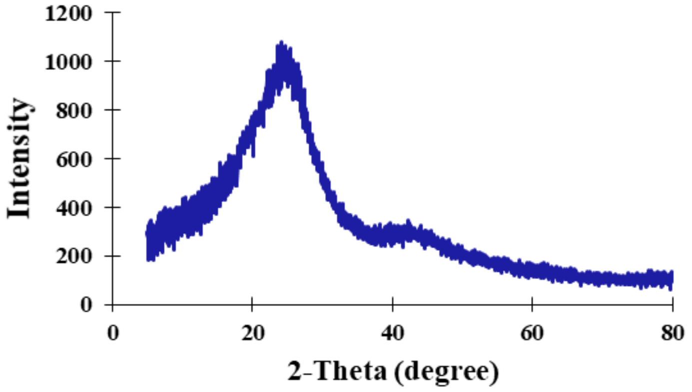

Fig. 2: Experimental diffraction pattern for activated carbon from coffee residue

The iodine number of the CARC is determined at 215.15 mg I_2/g; as an index of the surface area; It is relatively low; it is presumed that H_3PO_4 molecules occupied active carbon sites after impregnation. However, the coal studied does have acceptable adsorption capacity of CN^- at a pH of 8. In contrast to similar support Halet et al., (2015), found the iodine number at 460 mg I_2/g, the difference it could be, when using a higher activation temperature (700 °C); according to Ghanizadeh and Asgari (2010), they determined it at 134.44 mg I_2/g for bone carbon without any impregnation.

c) *Optimization of the adsorption process*

The DCC was applied with three factors adapted to three levels each and six central points; The effect of pH, contact time, and dosage of CARC on the adsorption efficiency of CN^- was studied. The adsorption percentages obtained from the experiments were entered in response to the matrix generated from the DOE (Minitab 18), according to Table 2. The data were analyzed using the response surface methodology (RSM) from the which derived the analysis of adjusted variance, where the factors A, B, C, and the AA interaction, as well as the coefficients of Equation 5, were significant (p-value $<\alpha = 0.05$). Significant F values indicated the suitability of the model, and the square of the regression coefficient (98.60%) suggests that the model studied was consistent.

Table 2: Matrix for the central composite design, with the response variable based on process variables and coded

Run order	Process variable			Coded variable			Adsorption %
	pH	Time (min)	Dosage (g/L)	A	B	C	
1	9	90	20	-1	-1	-1	38,77
2	12	90	20	1	-1	-1	9,36
3	9	180	20	-1	1	-1	43,74
4	12	180	20	1	1	-1	12,49
5	9	90	40	-1	-1	1	48,74
6	12	90	40	1	-1	1	18,74
7	9	180	40	-1	1	1	53,12
8	12	180	40	1	1	1	24,99
9	7,977	135	30	-1,682	0	0	54,68
10	13,023	135	30	1,682	0	0	8,11
11	10,5	59,32	30	0	-1,682	0	31,22
12	10,5	210,68	30	0	1,682	0	42,49
13	10,5	135	13,182	0	0	-1,682	24,99
14	10,5	135	46,818	0	0	1,682	44,99
15	10,5	135	30	0	0	0	34,60
16	10,5	135	30	0	0	0	34,60
17	10,5	135	30	0	0	0	33,90
18	10,5	135	30	0	0	0	34,20
19	10,5	135	30	0	0	0	34,60
20	10,5	135	30	0	0	0	33,80

$$Y = 34{,}25 - 14{,}43\,A + 2{,}76\,B + 5{,}48\,C - 1{,}68\,AA \tag{5}$$

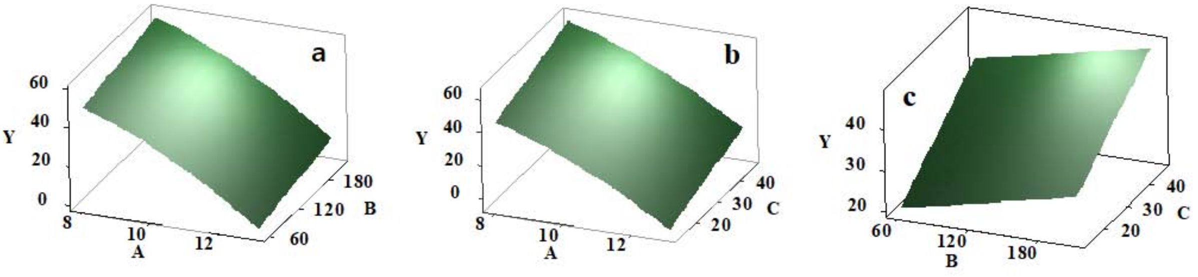

Fig. 3: Effects of the combination of factors on the percentage of adsorption of the CN^- (Y). a) pH (A) vs contact time (B); b) pH (A) vs adsorbent dosage (C); c) contact time (B) vs adsorbent dosage (C).

Fig. 3 shows the 3D graphs of the response surface, which estimates the optimal values for the three factors under study. Thus, Figure 3a shows the combined effect of pH and contact time; the adsorption increased to 55% when the pH dropped to 8 and the contact time increased to 220 minutes. Fig. 3b shows the combined effect of pH and the dosage of CARC; It is noted that when the pH dropped to 8, and the dosage increased to 50 g/L, an adsorption percentage of approximately 55% is achieved. Fig. 3c represented the combined effect of contact time and reagent dosage; the lowest adsorption percentage of 45% is obtained when the contact time and the dose of adsorbent increased to about 220 minutes and 50 g/L respectively. Similar trends experiment Eletta et al. (2016) for the effects of the combination of its factors when using calcined eggshell for adsorption of cyanide.

According to the MSR; the maximum adjustment for the adsorption of the *CN^-* of 67.65%, was achieved with a pH of 7.98, contact time of 210.68 minutes and dosage of 46.82 g/L of the CARC; similar trend for a pH of 8, Gebresemati et al. (2017) in the improvement of cyanide adsorption by coffee husk.

d) Study of Equilibrium and kinetic models

Table 3 shows the experimental values of the equilibrium isotherms studied: Freundlich model (Fig. 4a), Langmuir (Fig. 4b), and Temkin (Fig. 4c). Experimental data were obtained at room temperature (30 °C), pH of 8, using 50 mL of solution with initial concentrations of 50, 60, 70, 80, 90, 100, 110, 120, 130, 140 mg of *CN^-*/L and 1.5 g of adsorbent; stirred at 200 rpm for 140 min.

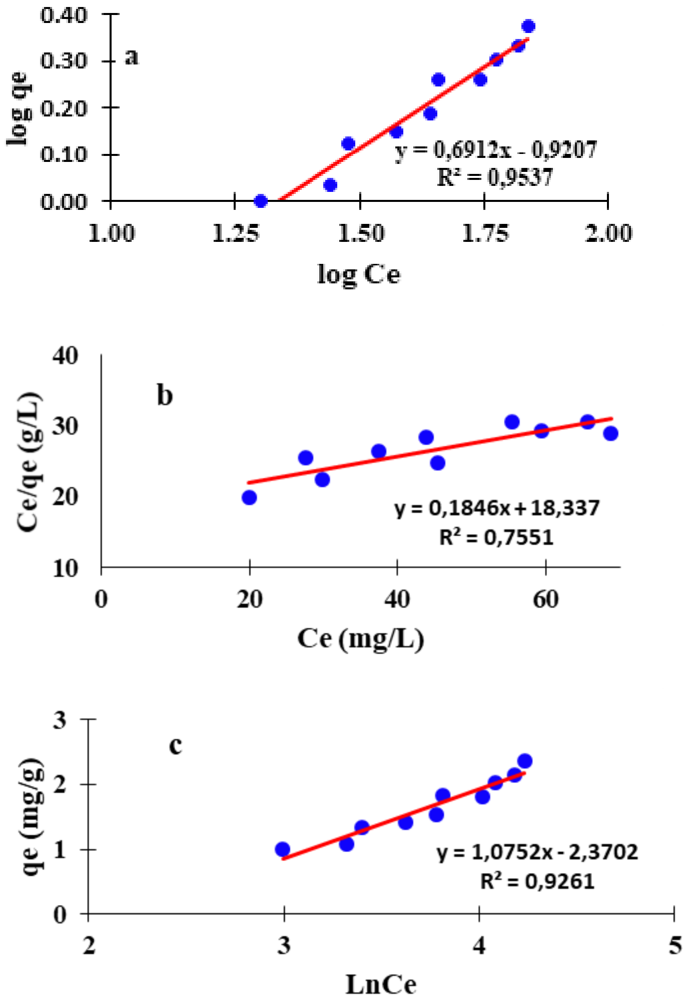

Fig. 4: Equilibrium models; a) Freundlich; b) Langmuir; c) Temkin. For the adsorption of *CN^-* onto activated carbon from coffee residue. Process conditions: pH: 8; room temperature: 30°C; contact time: 140 min; adsorbent dose: 30 g/L and stirred at 200 rpm.

R^2 values are in the following order: Freundlich (0.954)> Temkin (0.9261)> Langmuir (0.7551); suggests that the experimental values of the adsorption of *CN^-* onto the CARC, fitted to the Freundlich model; its value of n> 1, supports that the adsorption of the *CN^-* is favorable and occurred in multilayers (physisorption); this according to Tsunatu et al. (2015) and Halet et al. (2015); both find that their data fitted to the Temkin and Freundlich model, they report that the adsorption of *CN^-* did not occur in monolayer.

For the Langmuir isotherm, the maximum monolayer adsorption capacity is found to be 5.42 mg *CN^-*/g CARC; its value 0 <RL (0.67) <1 indicates that adsorption is favorable, according to Mondal et al. (2019) and Tsunatu et al. (2015) that they found, experimental values of 0 <RL <1 when removing cyanide with coke charcoal and shea seed husk respectively. However, the maximum adsorption capacity obtained in the equilibrium; It is relatively low, compared to the results obtained by Halet et al. (2015) and Stavropoulos et al. (2015); the first when using active carbon of similar support obtains 20.04 mg CN^-/g at 20 °C; it should, which applied higher temperature (700 °C) and activation time (2 h); the second, by using active carbon D45/2 - Carbo Tech obtains maximum adsorption capacities of 28.3 and 21.25 mg CN^-/g, for 20 °C and 30 °C respectively and indicates that at low adsorption capacity there is a weak adsorption mechanism between cyanide and coal.

Table 3: Parameters and their values for the adsorption isotherms of the CN^- onto the CARC

Models	Parameters	Coefficients
Freundlich		
	R^2	0,954
	n	1,447
	1/n	0,691
	K_f (L/mg)	0,12
Langmuir		
	R^2	0,7551
	Q_{max} (mg/g)	5,42
	b (L/mg)	0,01
	R_L	0,67-0,42
Temkin		
	R^2	0,9261
	B (mg/g)	1,08
	A	0,11

The effect of contact time was studied (Fig. 5). The experimental results of equilibrium concentrations (*Ce*) were carried out at room temperature (30 °C), with different times (20 - 200 min) and initial concentrations of 80, 100, and 120 mg/L at pH 8. Adsorption of cyanide onto CARC was very gradual, and the percentage of adsorbed cyanide increased for the initial low concentrations. That is, the adsorption efficiency depended of the initial cyanide concentration (Asgari et al., 2012), this is explained by the saturation of the active sites of the CARC as the concentration of CN^- is higher in the solution (Eletta et al., 2016; Dwivedi et al., 2016).

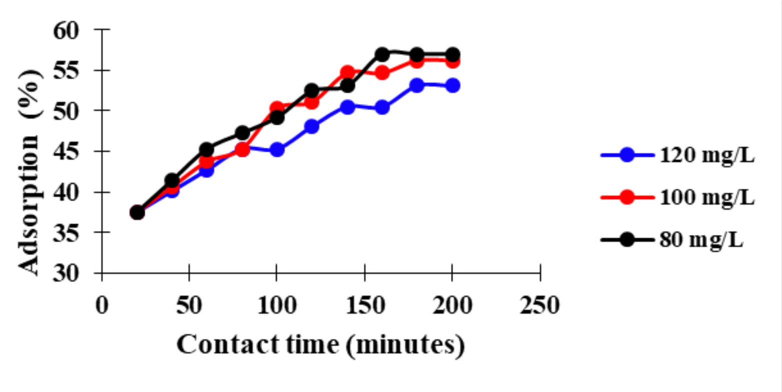

Fig. 5: Effect of contact time (20-200 min.) of the adsorption of the CN^- onto the CARC. Process conditions: pH: 8; temperature: 30 °C; adsorbent dose: 30 g/L; initial cyanide concentration: 80, 100 and 120 mg/L; rpm: 200

The adsorption kinetics of the CN^- onto the CARC was studied according to the graphs for the kinetic models of the first pseudo (Fig. 6a) and second-order (Fig. 6b), as well as the intraparticle diffusion model (Fig. 6c). The kinetic parameters with their results (Table 4) suggest that the adsorption kinetics of the CN^- onto the CARC, fitted to the pseudo second-order model. For the three initial concentrations under study (80, 100, and 120 mg / L), their R^2 values of the three equations: 0.991, 0.993, 0.993, are greater than the R^2 of the intraparticle diffusion model (0.999, 0.981, 0.983) and that of pseudo-first order (0.974, 0.881, 0.905). Eletta et al., (2016) and Tsunatu et al., (2015) in their studies found that the kinetic models of pseudo-second order explained the adsorption of cyanide onto the calcined egg shell and Shea Butter Seed Husk carbon, respectively.

Fig. 6c represents the correlation of the experimental data to three different initial concentrations and shows multilinearity; the first linear portion of 0 to 4.47 $min^{0.5}$, is the steepest part, explains the immediate use of the active sites of the CARC by the CN^-; It is generally attributed to the diffusion of the boundary layer (Dwivedi et al., 2016). The section from 4.47 to 6.32 min$^{0.5}$ suggests that the internal diffusion process is a very gradual stage and illustrates the diffusion of macropores. The third portion represents the final stage of equilibrium or adsorption process itself, suggests the diffusion of micro and mesopores (Gupta et al., 2012); gradual for the adsorption of the CN^- onto the CARC. According to R^2 values> 0.98, (for all three equations), the intraparticle diffusion model responds to the adsorption kinetics of the CN^- onto the CARC and suggests the diffusion of CN^- directly into the pores (Halet et al., 2015), so that intraparticle diffusion was not the limiting stage, during the adsorption process of the CN^- onto CARC.

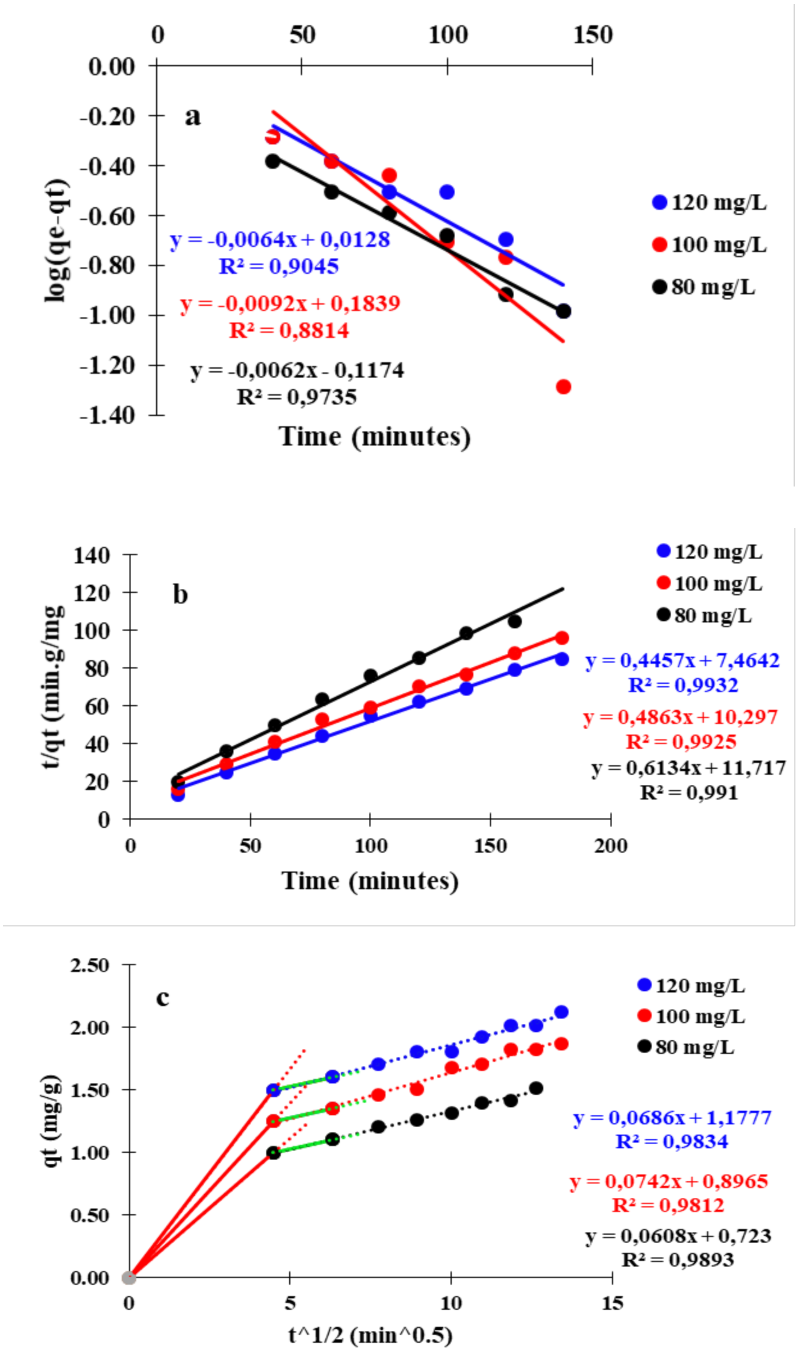

Fig. 6: Kinetic models: a) Pseudo-first order; b) Pseudo-second order; c) intraparticle diffusion, for the adsorption of CN^- onto CARC. Process conditions: pH: 8; temperature: 30 °C; adsorbent dose: 30 g/L; initial cyanide concentration: 80, 100 and 120 mg/L; rpm: 200

Tabla 4: Details of the parameters with their kinetic values for the adsorption of the *CN^-* onto the CARC

Co (mg/L)	Pseudo-first order model			Pseudo-second order model			Intra particle diffusion model		
	K_1 (1/s)	q_e (mg/g)	R^2	K_2 (g/(mg s))	q_e (mg/g)	R^2	Kdi (mg/g $min^{0.5}$)	C(mg/g)	R^2
80	0,014	0,76	0,97	0,032	1,63	0,99	0,061	0,72	0,99
100	0,021	1,53	0,88	0,023	2,06	0,99	0,074	0,90	0,98
120	0,015	1,03	0,91	0,027	2,24	0,99	0,069	1,18	0,98

IV. CONCLUSIONS

The optimization study was carried out and the equilibrium models of Freundlich, Langmuir and Temkin were evaluated, as well as the kinetic models of pseudo-first order, the pseudo-second order and intraparticle diffusion of the *CN^-* adsorption process onto the CARC obtained from coffee residue. The FTIR, XRD analyzes confirmed the structural change of the precursor to activated carbon. The optimization study suggests that the adsorption process of *CN^-* by CARC is sensitive to pH; With its value of 8, it reached 54.68% adsorption percentage and 67.65% for the predictive level. The factorial regression coefficient of 98.59% of its analysis of variance showed that the study was consistent. The larger R^2, for the equilibrium and kinetic studies, showed that the experimental data for cyanide adsorption onto the CARC, fitted to the Freundlich model (0.954) and pseudo-second order (> 0.99) respectively and intraparticle diffusion (> 0.98) responds to the adsorption kinetics of the *CN^-* on the CARC. The values of 0 <RL (0.67) <1 and n (1.45)> 1, for the Langmuir and Freundlich isotherms, respectively suggest that the adsorption of *CN^-* on the CARC is favorable and according to the equlibrium model of Langmuir, maximum adsorption of 5.42 mg of *CN^-*/g of CARC is obtained. The feasibility of preparing activated charcoal using the spent coffee residue as support and could be used as adsorbent potential in the decontamination of wastewater containing low concentrations of *CN^-* is demonstrated; however, new procedures for activating coffee residue, at different impregnation rates of *H_3PO_4* and temperatures for chemical activation, could be studied to modify its surface and improve its adsorption capacity of *CN^-*.

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Determination of the Amplitude - Frequency Characteristics of the Well Pressure Preventing the Destruction of Wellbore Rocks

By R. A. Hasanov, I. Y. Shirali & M. I. Kazimov
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Keywords: borehole, mountain rocks, face-plastic model, deformation processes, dynamic instability, frequency and amplitude characteristics, volume deformation.

GJSFR-H Classification: FOR Code: 030703

DETERMINATIONOFTHEAMPLITUDEFREQUENCYCHARACTERISTICSOFTHEWELLPRESSUREPREVENTINGTHEDESTRUCTIONOFWELLBOREROCKS

Strictly as per the compliance and regulations of:

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I. INTRODUCTION

It is well-known that the need for maintaining hydrocarbon coefficient (> 35%) in the development of fields is below the world standards (> 35%), which is closely related to the maintenance and enhancement of the existing well stock. The drilling of additional wells, especially in the aquatic area and the increase in the UVA, requires additional costs for the efficient use of the existing well stock. This problem exacerbates the problem of long-term exploitation of bedding resources, which have been modified as a result of geomechanical processes, and the development of hard-to-extract and large-scale deposits. Since the solution of these problems is not possible with the use of relatively low cost vertical drilling practices, over the past few decades, the use of horizontal wells with large and divergent direction has been widely used in world practice.

II. PROBLEM SETTING

About 80% of investments in the commissioning of new fields, development and delivery of products to the consumer falls on drilling. The funding will also be eliminated as a result of uncertainty in the management of complex and hazardous technological operations related to the increase of the drainage rate and the increase in oil supply through the proper design of the pipeline route. However, there are still many unresolved problems related to drilling wells (geological substantiation, selection of pipeline route and calculation of well structures), designing of technology and related technical equipment (constructive justification of wells), completion and mastering (development of filter nodes). [1-3].

Theoretical and experimental studies of the tensile state of mountain rocks [4-5] show that these problems are mainly deformation processes of laminated mountain rocks, which are considered as the most suitable model by the self-plastic model.

III. SOLUTION OF THE PROBLEM

The loading and discharge stages of the volcanic self-plastic mountain rocks can be written according to the following differential equations:

- for the recovery process

$$m_H \frac{d^2\theta_H}{dt^2} + \eta \frac{d\theta_H}{dt} + k_H\theta_H \le P_H - P_b - \sigma_b \qquad (1)$$

- for the exemption process

$$m_p \frac{d^2\theta_p}{dt^2} + \eta_p \frac{d\theta_p}{dt} + k_p\theta_p \le P_p - P_b - \sigma_{dm} \qquad (2)$$

here and ther θ_H and $\theta_p -$ respectively, relative dimensional deformations for loading and unloading processes; $P_H, P_p -$ pressures arising from appropriate processes; $k_H, k_p -$ volume in these processes are compression modules; $P_\delta -$ side pressure of mountain rocks; $\sigma_{rp} -$ resistance to hydraulic fracturing of mountain rocks; $\sigma_{dm} -$ resistance of mountain rocks to tension ; $m_H = \frac{\pi D}{g} P_H, m_p = \frac{\pi D}{g} P_p -$ are the masses brought into the unit length of the tuber; $D -$ Diameter of well; $g -$ acceleration of gravity; $\eta, k -$ respectively, the coefficients that characterize the viscosity and elasticity of mountain rocks. In general, the relative deformation of the volume is defined as the best function of the pressure in the pipe:

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$$\theta_H = aP^b \qquad (3)$$

If the loading process is with residual deformation, then

$$\theta_p = \theta_0 + a_1 P_p^{b_1} \qquad (4)$$

Thus, the equilibrium equation of self-elastic mountain rocks (including some sands, mergers, shale etc.) in well conditions can be expressed in the following equation:

$$m\theta''(t) + \eta\theta'(t) + k\theta(t) + P_b - P_{hy} - \Delta P = 0 \qquad (5)$$

(5) represent a unique self-elastic environment model of mountain rocks and their direct contact with neutral drilling mud. The physical and mechanical interaction of mountain rocks with drilling mud is different and has not been studied until now.

It is well known that the pressure drop in the borehole

$$\Delta P = \gamma H - P_{lay} + P_{ялавя} \qquad (6)$$

is designated as.

Here is:

$\gamma -$the specific gravity of the drilling mud;

$H -$depth of well;

P_{rop}-- lay pressure;

$P_{ялавя}$ – an additional pressure that occurs in a single space.

Usually this pressure is assumed to be constant [4], in fact, the pressure of the drilling mud changes in a small space while performing various technological processes in the drilling process. Therefore, the following approximate dependencies can be assumed to change this pressure:

$$\Delta P = \gamma H - P_{lay} + P_{ялавя} \qquad (7)$$

$$P_{ялавя} = c\cos\omega t \text{ , where}$$

C and $\omega -$the amplitude and frequency of additional pressure changes, respectively.

In general, the pressure changes in a single space can be represented as the Furye sequence:

$$P_{ялавя}(l,t) = \sum_{-\infty}^{+\infty} A_H \exp(in\omega t), \qquad (8)$$

$$A_H = \frac{\omega}{2\pi}\int_{-\frac{\pi}{\omega}}^{\frac{\pi}{\omega}} f(t)\exp(in\omega t)dt, \qquad (n = 0;\pm1;\pm2\ldots) \qquad (9)$$

For simplifications, we accept that these variables are subject to the expression (7).

(6) and (7) if we take into account (5)

$$(A + B\cos\omega t)\theta''(t) + \eta\theta'(t) + k\theta(t) = F(t) \qquad (10)$$

(10) in the equation

$$A = \frac{\pi D}{g}(\gamma H - P_{lay}),$$

$$B = \frac{\pi Dc}{g}, \qquad (11)$$

$$F(t) = P_{hy} + \gamma H - P_b - P_{lay} - c\cos\omega t.$$

Thus, it is clear that the dynamic stability of the boulders around the well is represented by a nonlinear linear differential equation with variable and periodic coefficients.

The periodic solution of 2T periodic equations (10) is sought in the following equation:

$$\theta(t) = a_1 \sin\frac{\omega t}{2} + b_1 \cos\frac{\omega t}{2} + \ldots \qquad (12)$$

Given the equation (12) and zeroing the coefficients $\sin k\omega t$ və $\cos k\omega t$ of the same set, we construct the system of algebraic equations below:

$$a_1\left(k - A\frac{\omega^2}{4} + \frac{1}{2}B\frac{\omega^2}{4}\right) - b_1\eta\frac{\omega}{2} = 0,$$

$$b_1\left(k - A\frac{\omega^2}{4} - \frac{1}{2}B\frac{\omega^2}{4}\right) - a_1\eta\frac{\omega}{2} = 0. \qquad (13)$$

The existence of periodic solutions of the equation Birzins different from zero is conditioned by the fact that the determinant of the conditional (13) system is zero. Using this condition, we obtain the following critical frequency equations:

$$\begin{vmatrix} k - A\frac{\omega^2}{4} + \frac{1}{2}B\frac{\omega^2}{4} & -\eta\frac{\omega^2}{4} \\ \eta\frac{\omega^2}{4} & k - A\frac{\omega^2}{4} - \frac{1}{2}B\frac{\omega^2}{4} \end{vmatrix} = 0 \qquad (14)$$

From the Determinant

$$\omega_{1,2} = \sqrt{\frac{4kA - 2\eta \pm 2\sqrt{\eta^4 + 4k^2B^2 - 4kA\eta^2}}{A^2 - 0{,}25B^2}} \qquad (15)$$

For all of the values within the range defined by the formula (15), the amplitudes obtained from the uniform equation solutions are infinitely increasing. (15) The formulas allow for the amplitude and frequency of the additional pressure changes in the low-pressure space, which causes the volatile state of the wells, that is, in these pressure changes the inlet tubes are inevitable. For absolute elastics, that is, for the case $\eta = 1$

$$\omega_{1,2} = 2\sqrt{\frac{k(A \pm B)}{A^2 - 0{,}25B^2}} \tag{16}$$

that is, for absolute elastics, there is also an amplitude and frequency of extra pressure in the low-pressure space, which causes instability.

The following linear algebraic equations system as a result of the solution of periodic T-waves

$$\begin{aligned} &k \cdot b_0 - 0 \cdot a_2 - 0{,}5 \cdot B \cdot \omega^2 \cdot b_2 = 0,\\ &0 \cdot b_0 + \left(k - A\omega^2\right) \cdot a_2 - \eta\omega b_2 = 0,\\ &0 \cdot b_0 + \eta\omega a_2 + \left(k - A\omega^2\right) \cdot b_2 = 0. \end{aligned} \tag{17}$$

and the solution of its determinant

$$\begin{vmatrix} k & 0 & -0{,}5B\omega^2 \\ 0 & k - A\omega^2 & -\eta\omega \\ 0 & \eta\omega & k - A\omega^2 \end{vmatrix} = 0 \tag{18}$$

The following expression is used to change the frequency that determines the boundaries of the first instability region:

$$\omega_{3,4} = \frac{1}{A}\sqrt{kA - 0{,}5\eta^2 \pm \eta\sqrt{0{,}25\eta^2 - kA}} \tag{19}$$

The analysis conducted was based on models that assumed linear variation of parameters. If the models include $\xi -$nonlinear viscosity coefficients and $\gamma -$nonlinear elasticity coefficients, the first equation is to use the equation where the nonlinear coefficients are:

$$(A + B\cos\omega t)\theta'' + \eta\theta' + \xi\theta^1\theta^2 + k\theta + \gamma\theta^3 = 0 \tag{20}$$

The solution of equation (20) can be searched as 2T or T periodic (12) sequences. For this purpose, non-linear assemblies are divided into Furye ranks.

For periodic solutions with 2T periodicity

$$\xi\theta^1\theta^2 + \gamma\theta^3 = \Phi(a_1 b_1)\sin\frac{\omega t}{2} + \psi(a_1 b_1)\cos\frac{\omega t}{2} + \ldots, \tag{21}$$

$$\left.\begin{aligned} \Phi(a_1 b_1) &= \frac{\omega}{2\pi}\int_0^{4\pi\omega-1}\left(\xi\theta^1\theta^2 + \gamma\theta^3\right)\sin\frac{\omega t}{2}\,dt,\\ \psi(a_1 b_1) &= \frac{\omega}{2\pi}\int_0^{4\pi\omega-1}\left(\xi\theta^1\theta^2 + \eta\theta^3\right)\cos\frac{\omega t}{2}\,dt. \end{aligned}\right\} \tag{22}$$

(21) and (22) based on the reports

$$\begin{aligned} &\xi\theta^1\theta^2 + \gamma\theta^3 = \frac{a^2}{4}(3\gamma a_1 + \xi\omega b_1)\sin\frac{\omega t}{2} + \frac{a^2}{4}(3\gamma b_1 + \xi\omega a_1)\cos\frac{\omega t}{2} + \ldots,\\ &a^2 = a_1^2 + b_1^2. \end{aligned} \tag{23}$$

Given (22) and (23) (20), and if we accept the coefficients $\sin k\omega t$ və $\cos k\omega t$ of expression coefficients, then

$$\begin{aligned} &a_1\left(k - A\frac{\omega^2}{4} + \frac{1}{2}B\frac{\omega^2}{4}\right) - b_1\eta\frac{\omega}{4} + \frac{a^2}{4}(\gamma a_1 3 - \xi\omega b_1) = 0,\\ &b_1\left(k - A\frac{\omega^2}{4} - \frac{1}{2}B\frac{\omega^2}{4}\right) + a_1\eta\frac{\omega}{2} + \frac{a^2}{4}(3\gamma b_1 - \xi\omega a_1) = 0. \end{aligned} \tag{24}$$

The condition of the existence of solutions of the system (24) that is different from zero is that its determinant is zero;

$$\begin{vmatrix} k - A\frac{\omega^2}{4} + \frac{a^2}{4}3\gamma + \frac{1}{2}B\frac{\omega^2}{4} & -\eta\frac{\omega}{2} - \frac{a^2}{4}\xi\omega \\ \eta\frac{\omega}{2} + \frac{a^2}{4}\xi\omega & k - A\frac{\omega^2}{4} + \frac{a^2}{4}3\gamma - \frac{1}{2}B\frac{\omega^2}{4} \end{vmatrix} = 0 \tag{25}$$

From the opening of the determinant, we determine that

$$a = \sqrt{4\sqrt{\frac{g}{4P^2} - \frac{l}{P} - \frac{2g}{P}}}, \tag{26}$$

where

$$\begin{aligned} &g = 6\gamma k + \eta\xi\omega^2 - 1{,}5\gamma\omega^2 A,\\ &P = 9\gamma^2 + \gamma^2\omega^2,\\ &l = k^2 - \frac{1}{2}k\omega^2 A + \frac{1}{4}\eta^2\omega^2 + \frac{1}{16}A^2\omega^4 - \frac{1}{64}B^2\omega^4 \end{aligned} \tag{27}$$

Equations (25) and (26) determine the amplitude-frequency dependence of the main variables of equation (20).

(20) Unstable solutions of the equation are characterized by a lower curve of the resonance curve.

(25) Shows that if nonlinear constants are eliminated, then unsteady solutions are defined by the boundaries of linear theory, i.e., equations (15) and (16).

Let's investigate the coordinated mode of changes near the main resonance. (20) Solving equation

$$\theta(t) = a(t)\sin\frac{\omega t}{2} + b(t)\cos\frac{\omega t}{2} + \ldots, \tag{28}$$

Let's look for it.

Here are $a(t), b(t) -$"authentic changing functions".

Considering equation (20) in equation (20), and following intervals, we construct the following equation system:

$$\begin{aligned} &(A - 0{,}5B)\left(a'' - \omega b' - 0{,}25\omega^2 a\right) + \eta\left(a' - 0{,}5\omega b\right) + ka + \Phi(a,b) = 0,\\ &(A + 0{,}5B)\left(b'' + \omega a' - 0{,}25\omega^2 b\right) + \eta\left(b' + 0{,}5\omega a\right) + kb + \Phi(a,b) = 0. \end{aligned} \tag{29}$$

(29) The system of equations can be simplified according to the requirements of the method of "real variable functions". For this reason, if we do not take into account small collections in Schedule 2, then

$$(A-0{,}5B)(0{,}25\omega^2 a+\omega b')=\Phi(a,b)+ka-0{,}5\eta\omega b,$$
$$(A+0{,}5B)(0{,}25\omega^2 b-\omega a')=\psi(a,b)+kb+0{,}5\eta\omega a. \quad (30)$$

(30) shows that the relationships used for the set regimes are

$$a'(t)=b'(t)=0. \quad (31)$$

condition.

By excluding non-linear assemblies in the pre-decision system (30).

$$a(t)=\alpha\exp(ht),$$
$$b(t)=\beta\exp(ht). \quad (32)$$

can be used, where $\alpha,\beta,h-$are constant coefficients.

Given the expression (32) in (30), we have the following system of equations

$$\left[(A-0{,}5B)0{,}25\omega^2-k\right]\alpha+(\omega h+0{,}5\eta\omega)\beta=0,$$
$$\left[(A+0{,}5B)0{,}25\omega^2-k\right]\beta-(\omega h+0{,}5\eta\omega)\alpha=0. \quad (33)$$

We can set an index of increase (decrease) given the existence of solutions other than zero (32):

$$h=\pm\sqrt{0{,}015625B^2\omega^2-\left(0{,}25A-\frac{k}{\omega}\right)^2}-0{,}5\eta \quad (34)$$

$h-$positive prices correspond to an increase in the amplitude of the unresolved variables and a decrease in the negative value.

As a result, it is worth noting that based on studies [6] to clarify the effect of reflection changes on the deformation of mountain rocks, it has been found that there are three characteristic parts of the deformation change curves:

Unresolved deformation area, field of deformation and intensity of self-plastic deformation. Obviously, the deformations identified will be typical of a number of mountain rocks in general. Thus, using the results of the above analysis to determine the coefficients k and η and to determine the deformation profiles that can occur with the rocks, and to prepare proposals for their elimination.

In order to continue the study of mountain rock instability (10) let us determine the relative changes in volume relative deformation based on the solution of equation. Write this equation explicitly [3,6]:

$$(A+B\cos\omega t)\theta''(t)+\eta\theta'(t)+k\theta(t)=d+c\cos\omega t \quad (35)$$

$$d=\sigma_{qr}+\gamma H-P_B-P_{lay} \quad (36)$$

and seek its solution as follows:

- "2T" periodic solutions

$$\theta(t)=\sum_{n=1}^{\infty}\left(x_n\cos\frac{\omega t}{n}+y_n\sin\frac{\omega t}{n}\right), \quad (37)$$

- "T" periodic solutions

$$\theta(t)=\sum_{n=1}^{\infty}(x_n\cos n\omega t+y_n\sin n\omega t), \quad (38)$$

$x_n, y_n-$are the coefficients determined by the joint solution of equations(35), (37) and (38).

Let us investigate the characteristic case with periodic variations of "T". (38) We find that

$$\theta'(t)=\sum_{n=1}^{\infty}n\omega(y_n\cos n\omega t-x_n\sin n\omega t), \quad (39)$$

$$\theta''(t)=\sum_{n=1}^{\infty}n\omega^2(x_n\cos n\omega t+y_n\sin n\omega t), \quad (40)$$

Considering (38) - (40) in (35), we create an infinite linear algebraic equation system for x_n, y_n to sum the coefficients $\cos k\omega t$ və $\sin k\omega t$ to zero:

$$x_n, y_n;$$

$$(k-\omega^2A)x_1-\eta\omega y_1-\omega^2B\left(4\cdot\frac{1}{2}x_2\right)=c,$$

$$\left[k-\omega^2A(4)\right]x_2-\eta\omega 2y_2-\omega^2B\left(1\cdot\frac{1}{2}x_1+9\cdot\frac{1}{2}x_3\right)=0,$$

$$\left[k-\omega^2A(9)\right]x_3-\eta\omega 3y_3-\omega^2B\left(4\cdot\frac{1}{2}x_2+16\cdot\frac{1}{2}x_4\right)=0,$$

……………………………………………………

$$\left[k-\omega^2 A(n)\right]x_n-\eta\omega(n)y_n-\omega^2 B\left[(n-1)^2\cdot\frac{1}{2}x_{n-1}+(n+1)^2\cdot\frac{1}{2}x_{n+1}\right]=0,$$

$$\left(k-\omega^2 A\right)y_1-\eta\omega x_1-\omega^2 B\left(4\cdot\frac{1}{2}y_2\right)=0,$$

$$\left[k-\omega^2 A(4)\right]y_2-\eta\omega x_2-\omega^2 B\left(1\cdot\frac{1}{2}y_1+9\cdot\frac{1}{2}y_3\right)=0,$$

$$\left[k-\omega^2 A(9)\right]y_3-\eta\omega x_3-\omega^2 B\left(4\cdot\frac{1}{2}y_2+16\cdot\frac{1}{2}y_4\right)=0,$$

……………………………………………………

$$\left[k-\omega^2 A(n)^2\right]y_n-\eta\omega(n)x_n-\omega^2 B\left[(n-1)^2\cdot\frac{1}{2}y_{n-1}+(n+1)^2\cdot\frac{1}{2}y_{n+1}\right]=0. \qquad (41)$$

There is a simple solution of the system of equations (41) for absolute elastics(status $\eta = 0$) mountain rocks:

$$x_1=-\frac{2d}{B\omega^2},$$
$$x_2=\frac{\left(k-A\omega^2\right)x_1-c}{2B\omega^2},$$
$$x_3=\frac{2\left(k-4A\omega^2\right)}{9B\omega^2}x_2-\frac{1}{2}x_1, \qquad (42)$$
$$x_4=\frac{2\left(k-9A\omega^2\right)}{16B\omega^2}x_3-\frac{4}{16}x_2,$$
$$x_n=\frac{2\left[k-(n-1)^2A\omega^2\right]}{n^2B\omega^2}x_{n-1}-\left(\frac{n-2}{n}\right)x_{n-2},$$
$$n=5,6...$$

In the end result (41) defines a reactive approach to solving the system.

It is also necessary that the deformation changes $n\to\infty$ – da $x_n\to\infty$ are stable. From the last (42) formula to paying for this condition

$$\left|\frac{2\left[k-(n-1)^2A\omega^2\right]}{n^2B\omega^2}\right|<1 \qquad (43)$$

anticipation of inequality is necessary and sufficient.

The latter is conditional, and this result can be used to solve technological issues.

Let's test the appropriateness of the mathematical dependence obtained on the following data. Assuming that mountain rocks are also composed of clay slag, the density of clay mortar is 190mm; pressure difference

We set the parameters at these prices.

(42) from the system of equations

$x_1=-0{,}365;$ $x_2=-4{,}330;$ $x_3=-20{,}403;$ $x_4=-48{,}000;$

$x_5=-55{,}819;$ $x_6...x_{15}=4{,}064;$ $x_{25}=0{,}883;$ $x_{35}=-0{,}319.$

(38) can be written for stationary displacement changes (ie condition) by the expression of relative deformation.

$$\theta(t)=\sum_{n=1}^{\infty}x_n\cos n\omega t \qquad (44)$$

based on the formula. Table 1 presents the changes in relative relative deformation under the above conditions:

Table 1: Relative volume deformation

ωt	0	$\frac{\pi}{30}$	$\frac{2\pi}{30}$	$\frac{3\pi}{30}$	$\frac{4\pi}{30}$	$\frac{5\pi}{30}$	$\frac{6\pi}{30}$	$\frac{7\pi}{30}$	$\frac{8\pi}{30}$	$\frac{9\pi}{30}$	$\frac{\pi}{3}$
$\theta(t)$	-124,997	-102,447	-83,893	11,214	-0,032	0,000	-0,032	11,214	-83,893	-102,447	-124,997

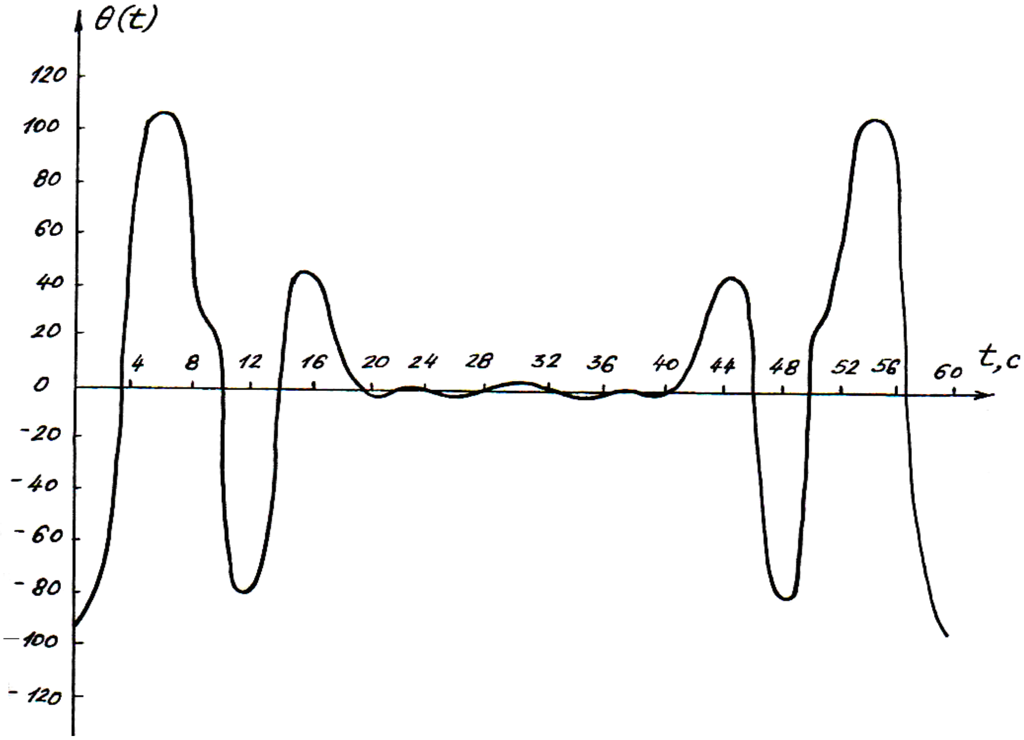

Figure 1: Relative deformation of anisotropic mountain rockregularity of amplitude change

The obtained results allow estimation of the velocity and amplitude characteristics of the well pressure change, which prevents the process of rock erosion (ie preventing the well wall from collapsing and collapsing on the wall itself).

IV. OUTCOME AND SUGGESTIONS

1. Thus, for the first time, the problem of dynamic instability of self-elastic rock rocks has been modeled and solved;
2. The conditions for the presence of stationary and non-stationary changes in the relative deformation of the self-elastic mountain rocks at periodic changes in the additional pressure in the population space;
3. A formula is proposed that allows the determination of the frequency and amplitude characteristics of the increase or decrease of deformation (for elastic rocks).

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Remediation of Spent Engine Oil Polluted Soil using *Glycine Max* (L.) (Soybean) and *Vigna Unguiculata* (L.) (Cowpea)

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Abstract- Spent engine oil is synthetic oil that contains impurities or loss of major properties thus affecting its unique purpose. In this study, an experiment was carried out at the contaminated site of Federal College of Forestry; Ibadan to investigate the remediation of spent engine oil polluted soil using soybean and cowpea. The treatments are soybean planted on polluted soil (T1), cowpea planted on nonpolluted soil (T2), cowpea planted on polluted soil (T3), soybean planted on nonpolluted soil (T4). The treatments were arranged in a complete randomized design (CRD) and replicated four times. The soil analysis before and after harvesting was carried out. The growth parameters measured for the legumes were plant height (cm), stem girth (cm), number of leaves, and number of branches. The result of this study shows that the overall growth performance of the two legumes reduced significantly ($p<0.05$) due to the presence of spent engine oil in the soil, which introduced heavy metals above critical level into the soil.

Keywords: *remediation; soil nutrient; soybean; cowpea.*

GJSFR-H Classification: *FOR Code: 070599*

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Abstract- Spent engine oil is synthetic oil that contains impurities or loss of major properties thus affecting its unique purpose. In this study, an experiment was carried out at the contaminated site of Federal College of Forestry; Ibadan to investigate the remediation of spent engine oil polluted soil using soybean and cowpea. The treatments are soybean planted on polluted soil (T1), cowpea planted on nonpolluted soil (T2), cowpea planted on polluted soil (T3), soybean planted on nonpolluted soil (T4). The treatments were arranged in a complete randomized design (CRD) and replicated four times. The soil analysis before and after harvesting was carried out. The growth parameters measured for the legumes were plant height (cm), stem girth (cm), number of leaves, and number of branches. The result of this study shows that the overall growth performance of the two legumes reduced significantly ($p < 0.05$) due to the presence of spent engine oil in the soil, which introduced heavy metals above critical level into the soil. At six weeks after planting (6 WAP), the number of leaves and number of branches was significantly reduced in soybean and cowpea polluted soil when compared with the control. The stem girth of soybean (1.37 cm) was significantly reduced ($p < 0.05$) more than cowpea (1.94 cm) in polluted soil while the plant height of cowpea (14.86 cm) was significantly reduced more than soybean (18.59 cm). For both pre-planting and post-planting chemical properties analysis, it was observed that the level of Cd, Cr, Pb, and Ni in the pre-planting analysis reduced significantly in the post-planting chemical properties. This shows that both soybean and cowpea exhibited significant remediating ability. However, the level of Cr, Pb, and Ni in the soil cropped by soybean was higher than cowpea and level of Cr, Cd, Pb in soybean plant was higher than that of cowpea, respectively. It can be concluded that soybean is a good crop legume to remediate spent engine oil polluted soil due to its high remediating ability and is recommended that farmers should take considerable measures of cleaning up their polluted farmland with the use of leguminous crops such as soybean.

Keywords: remediation; soil nutrient; soybean; cowpea.

I. INTRODUCTION

Soil pollution is the presence of xenobiotic (human-made) chemicals or other alteration in the natural soil environment. It is typically caused by industrial activity, agricultural chemicals, or improper disposal of waste, and the most common chemicals involved are petroleum hydrocarbons, polynuclear aromatic hydrocarbons (such as naphthalene and benzopyrene), solvent, pesticides, lead and other heavy metals (Alloway, 1990). The degree of soil pollution correlates with the degree of industrialization and intensity of chemical usage in that environment. The danger of toxic metals is aggravated by their almost indefinite persistence in the environment (Garbisu *et al*. 2001). Pollution of the biosphere with toxic metals has accelerated dramatically since the beginning of the industrial revolution (Memon *et al*. 2000). Spent motor oil, also called used lubricating oil, is obtained after servicing. The disposal of spent oil into gutters, water drains, open vacant plots, and farms in Nigeria is a common occurrence, and this is mostly done by automatics and allied artisans with workshops on roadsides and open places. (Agbogidi, 2011) reported that spent oil is the commonest soil contaminant in the rural areas of Nigeria where agriculture/farming forms the mainstay of the rural inhabitants. The used oil may contain some toxic materials, including heavy metals that could affect growth, yield, and general performance of plants (Agbogidi and Egbuchua, 2010). The contamination of the natural environment by petroleum-derived substances contributes to the degradation of land (Shcwab, 1999). The most important and common symptoms observed in the plants contaminated with oil and its by-products include the degradation of chlorophyll, alterations in the stomata mechanisms and reduction in photosynthesis and respiration, increase in the production of stress-related phytohormone, accumulation of toxic substances or their by-products in vegetal tissue (Baker, 1970), decrease in size and less production of biomass (Ayotamuno *et al.* 2004). In response to a growing need to address environmental and soil contamination which would affect the growth of the plant, phytoremediation has been developed to treat contaminated soil (Riser-Robert, 1998).

Phytoremediation is the use of plants and their associated rhizosphere microorganisms to remove degrade or immobilize various contaminants from polluted soil (Singh *et al.* 2003). Phytoremediation is, on average, ten-fold cheaper than engineering-based remediation methods such as soil excavation, soil washing, or burning or pump and treat systems (Glass, 1999). Plants have a range of potential mechanisms at

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the cellular level that might be involved in the detoxification and tolerance to heavy metal stress. These all appear to be involved primarily in avoiding the buildup of toxic concentration at sensitive sites within the cell, thus preventing the damaging effects (Hall, 2002).

Legume is a plant in the family Fabaceae or the fruit or seed of such a plant. Legumes are notable in that most of them have symbiotic nitrogen-fixing bacteria in a structure called root nodules (Smil, 2000). Legumes are important for nitrogen cycling in the environment and agriculture due to the ability of nitrogen-fixation by rhizobia. Legume species can form a symbiosis with various beneficial micro-organisms, arbuscular mycorrhizal fungi, and plant growth-promoting bacteria. These plant microbe associations implications imply plant growth, nutrition, and disease. The symbiosis of the legume and micro-organisms provides nutrient for the plant, stimulates plant growth, exerts an anti-stress effect on the plant, improves soil fertility, and restore ecosystem biodiversity and function (Postgate, 1998). Legumes species vary significantly in the ability to accumulate metals from contaminated soils, as a balance between the uptake of essential metals ions to maintain growth and development and the ability to protect sensitive cellular activity and structure from excessive levels of essential and non-essential metals is required (Garbisu and Alkorta, 2001). Even though legumes are grown in Nigeria, little has been known about the phytoremediation of polluted soil using different legumes. The objective of the study was to evaluate the phytoremediation potentials of two legumes (*Glycine max and Vigna unguiculata*) by comparing their growth response on soils polluted by the spent engine oil.

II. MATERIALS AND METHODS

The experiment was conducted at the Federal College of Forestry Jericho Hill, (latitude 7^{0}26^{1}N and longitude 8^{0}36^{1}E) Ibadan, Oyo State, Nigeria. The annual rainfall 1500 mm with a bimodal pattern and has a minimum temperature of 21.9^{o}C and a maximum temperature of 35.5^{o}C with an average relative humidity of about 74.55%. Spent engine oil was collected from a mechanic shop and used to pollute the soil at the rate of 0.25L of oil to 4kg soil. The polluted soil were potted. Two leguminous crops, *Glycine max* (soybean) and V*igna unguiculata* (cowpea), were planted at a depth of 4cm. The experimental design was complete randomized design (CRD) replicated four times.

a) *Data collection*

Three plants from mid-row of the experimental units were randomly selected and used for the data collection on plant height (cm), number of leaves, number of branches, stem girth (cm) at 2, 3, 4, 5, 6, 7 weeks after planting (WAP).

b) *Data analysis*

Data collected was analyzed statistically using Genstat Statistical Software package and was subjected to Analysis of variance. Means were separated using Least significantly difference (LSD) at 5% level of significance.

III. RESULTS AND DISCUSSION

The analysis in Table 1 further confirms this assertion and also reveals that the soils are moderate in zinc, high in potassium, and phosphorous. Organic carbon and total nitrogen content of the soil were 69.77 and 5.87g kg,$^{-1}$ respectively, which is above the critical range (Adeoye and Agboola, 1985), nearly neutral pH. The extractable Mn and Fe contents of the soil are high, with 141.00 mg kg^{-1} and 151 mg kg^{-1}, respectively. The soil bulk density was 1.2 g cm^{-3}, with sandy loam texture. Saturated hydraulic conductivity value of 12.64cm hr^{-1} indicated a well-drained soil suitable for the production of the legumes. These physical properties were adequate for crop production (Agbede *et al.,* 2011). The heavy metals in the polluted soil were; lead (Pb) (13.40 mg kg^{-1}), chromium (Cr) (59.85 mg kg^{-1}), cadmium (Cd) (0.70 mg kg^{-1}) and nickel (Ni) (9.30 mg kg^{-1}). According to the (WHO, /2005) moderate level recommendation, Ni (1.5 mg kg^{-1}), Pb (10 mg kg^{-1}), Cr (1.5 mg kg^{-1}), and Cd (0.3 mg kg^{-1}), this shows that the level of heavy metals in the soil was high. High level of heavy metals causes deficiency of available nutrients needed to maintain growth at apical regions of the crops: there is negative effect which could be due to impermeability effect of petroleum hydrocarbons or immobilization of nutrients mainly nitrogen or inhibitory effect of some polycyclic aromatic compounds as a result of high level of heavy metals (Ogbuehi and Ezeibekwe, 2010).

The post-planting soil and plant chemical analysis were presented in table 2. it shows that the level of Cr (18.0 mg kg^{-1}), Pb (10.4 mg kg^{-1}) and Ni (0.38 mg kg^{-1}) in the soil cropped to soybean was higher than that of the soil cropped to cowpea respectively of Cr (13.50 mg kg^{-1}), Pb (8.3 mg kg^{-1}) and Ni (0.32 mg kg^{-1}) while the level of Cd (0.17 mg kg^{-1}) in cowpea was higher than that of soybean Cd (0.13 mg kg^{-1}). These agree with the finding of Adenipekun *et al*. (2008), which says that crops differ in their response to the pollutant. It was observed that the low level of Cd, Cr, Pb, Ni in soil cropped to cowpea was due to the ability of cowpea to extract the heavy metals than soybean. This agrees with the finding of Fitter and Stickland (1991), which says that the root morphological traits such as the pattern of root density, maximum depth, and specific root length help in the extraction of heavy metals in soil.

It was also observed that the level of Cr (1.10 mg kg^{-1}), Pb (1.25 mg kg^{-1}) and Ni (0.28 mg kg^{-1}) in soybean plant was higher than that of cowpea plant Cr (0.98 mg kg^{-1}), Pb (1.00 mg kg^{-1}) and Ni (0.25 mg kg^{-1}) respectively while the range of Cadmium (Cd) in both plants is the same. The level of Cr, Cd, Pb and Ni of both legumes was observed to be above critical level for human consumption when compared to World Health Organization recommendation Cd (0.1 - 0.3 mg kg^{-1}), Pb (0.5 - 0.8 mg kg^{-1}), Ni (0.1 - 0.2 mg kg^{-1}) and Cr (0.2 - 0.5 mg kg^{-1}) respectively (W.H.O, 2005).

a) *Effect of Remediation of Spent Oil Polluted Soil on Number of Branches using Soybean and Cowpea*

The effect of remediation of spent oil-polluted soil on a number of branches using soybean and cowpea was presented in table 3. The data shows that significant differences ($p<0.05$) exist between polluted and nonpolluted soil in the number of branches of the plant. At six weeks after planting, the number of branches reduced by spent engine oil pollution. This reduction in number of branches may be due to the limitation of nutrients uptake necessary for the production of branches occasioned by a high level of pollutants. This agrees with findings of (Agbogidi *et al*. 2010) who reported that oil contamination also reduces the soil fertility by causing immobilization of nutrients by microbes such immobilization of nutrients leads to difficulty in the uptake of nutrients in oil-contaminated soil which will be difficult despite the presence of such nutrients in the soil.

b) *Effect of Remediation of Spent Oil Polluted Soil on Plant Height using Soybean and Cowpea*

The effect of remediation of spent oil-polluted soil on plant height using soybean and cowpea result were presented in table 4. The data shows that significant differences ($p<0.05$) exist between polluted and nonpolluted soil in the plant height of the plant. The plant height was significantly reduced by a high level of pollution, and it was observed that the plant height of cowpea was adversely affected compared to soybean. This could be attributed to a deficiency in the availability of nutrients needed to maintain physiological processes involved in plant growth occasioned by nutrient stress due to influence of spent engine oil. This observation was in line with (Ogbuehi and Ezeibekwe, 2010), who reported that crude oil causes a deficiency of the availability of nutrients needed to maintain growth at apical regions of the crops.

c) *Effect of Remediation of Spent Oil Polluted Soil on Number of Leaves using Soybean and Cowpea*

The effect of remediation of spent oil-polluted soil on a number of leaves using soybean and cowpea was presented in table 5. It shows that significant differences ($p<0.05$) exist between polluted and nonpolluted soil in the number of leaves of the plant. Also, it was observed that the number of leaves of soybean was more adversely affected compared to cowpea. This could be inferred as having caused by a reduction in available macro elements needed for the production of leaves. This agrees with the findings of (Jung, 2008); it could be due to the presence of heavy metals and polycyclic aromatic compounds found in spent engine oil, which could cause distort within the plant tissues.

d) *Effect of Remediation of Spent Oil Polluted Soil on Stem Girth using Soybean and Cowpea*

The effect of remediation of spent oil-polluted soil on stem girth using soybean and cowpea was presented in table 6. It shows that a significant differences ($p<0.05$) exist between polluted and nonpolluted soil in the stem girth of the plant. There is a significant difference ($p<0.05$) exist between polluted and nonpolluted soils in the stem girth of the plants. It was also observed that the stem girth of soybean was significantly reduced when compared to that of cowpea. According to (Edem *et al*., 2009) the poor growth was due to metals which were present in high toxic levels and partially to the inability of the plants in the polluted medium to absorb the nutrient from the soil possibly due to poor insulation and poor functioning of vascular (phloem and xylem tissues) bundles.

IV. CONCLUSION

The result showed that the spent engine oil hurts the growth of cowpea (*Vigna unguiculata*) and soybean (*Glycine max*). It was be observed from the result that the plant height, stem girth, number of leaves and number of branches were significantly ($p<0.05$) reduced due to the presence of spent engine oil which contains some heavy metals (Cd, Cr, Ni, Pb) which can cause a significant reduction in the growth performance of plant in the spent engine oil soil when compared to control. For both pre-planting and post-planting chemical properties analysis, it was observed that the level of Cd, Cr, Pb, and Ni in the pre-planting analysis reduced significantly in the post-planting chemical properties. This shows that both soybean and cowpea exhibited significant remediating ability. However, the level of Cr, Pb, and Ni in the soil cropped by soybean was higher than cowpea and level of Cr, Cd, Pb in soybean plant was higher than that of cowpea respectively, but the level Cd, Cr, Pb, and Ni in both plant is above the World Health Organization critical level recommendation.

Therefore, it can be concluded that cowpea is a good crop legume to remediate spent engine oil polluted soil due to its high remediating ability and easy availability of the crop seed in the market. It is recommended that there is a need for the government to enact a strict law and educate the citizenry on indiscriminate disposal of this pollutant (spent engine oil) on farmlands to ensure optimal growth of plant and crop safe for human consumption.

Farmers should also take considerable measures of cleaning up of their farmland with the use of leguminous crops such as cowpea to remediate their spent engine oil-polluted soil.

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Table 1: Soil Physical and Chemical Properties

Parameters	Polluted Soil	Non Polluted Soil	W.H.O Moderate Level Recommendation
pH (H_2O)	5.7	6.1	
Organic carbon (g kg^{-1})	69.77	27.4	
Total Nitrogen (g kg^{-1})	5.86	1.74	
Available Phosphorous (mg kg^{-1})	16.38	6.04	
Exchangeable cation (cmol kg^{-1})			
Ca	9.08	10.11	
Mg	2.32	1.70	
K	0.32	0.28	
Na	0.61	0.39	
Extractable micro nutrients (mg kg^{-1})			
Mn	141.00	109.70	
Fe	151.00	122.20	
Cu	27.20	3.92	
Zn	27.20	12.18	
Exchangeable Acidity (cmol kg^{-1})	1.5	1.5	
Heavy metals (mg kg^{-1})			
Pb	13.4		10
Cd	0.70		0.3
Cr	59.85		1.5
Ni	9.30		1.5
Particle size distribution (g kg^{-1})			
Sand	660.0		
Silt	174.0		
Clay	166.0		
Textural class	Sandy loam		
Bulk density (g cm^{-3})	1.2		
Saturated Hydraulic Conductivity (cm hr^{-1})	12.64		

Table 2: Post-Planting Soil and Plant Chemical Properties

Samples	Cadmium(Cd)	Chromium(Cr)	Lead (Pb)	Nickel (Ni)
	←	(mg kg^{-1})	←	
Soil cropped to soybean	0.13	18.00	10.4	0.38
Soil cropped to cowpea	0.12	13.50	8.3	0.32
Soybean plant	0.02	1.10	1.25	0.28
Cowpea plant	0.02	0.98	1.00	0.25
W.H.O moderate level for plant	0.1- 0.3	0.2- 0.5	0.5- 0.8	0.1-0.2

Table 3: Effect of Remediation of Spent Oil Polluted Soil on Number of Branches using Soybean and Cowpea

Treatment	Weeks After Planting					
	1	2	3	4	5	6
Soybean + pollution	0.00	0.92	2.25	3.08	4.33	5.58
Cowpea	0.25	2.1	4.83	9.17	15.83	24.58
Cowpea + pollution	0.00	0.92	1.50	2.92	4.42	5.42
Soybean	0.00	1.75	3.50	5.25	8.25	10.92
LSD	0.19*	0.35**	0.58**	1.31**	2.09**	3.18**

ns = not significantly different *=$P \leq 0.05$ **= $P \leq 0.01$

Table 4: Effect of Remediation of Spent Oil Polluted Soil on Plant Height using Soybean and Cowpea

Treatment	Weeks After Planting (Cm)					
	1	2	3	4	5	6
Soybean + pollution	5.94	9.04	11.44	12.47	16.01	18.59
Cowpea	10.46	12.54	14.75	15.18	23.14	26.02
Cowpea + pollution	7.35	8.38	9.46	10.58	12.52	14.86
Soybean	7.49	11.57	14.80	16.94	24.70	30.26
LSD	1.23**	1.47**	1.79**	2.04**	2.34**	3.19**

*ns = not significantly different *=P≤ 0.05 **= P ≤ 0.01*

Table 5: Effect of Remediation of Spent Oil Polluted Soil on Number of Leaves using Soybean and Cowpea

Treatment	Weeks After Planting (Cm)					
	1	2	3	4	5	6
Soybean + pollution	5.94	9.04	11.44	12.47	16.01	18.59
Cowpea	10.46	12.54	14.75	15.18	23.14	26.02
Cowpea + pollution	7.35	8.38	9.46	10.58	12.52	14.86
Soybean	7.49	11.57	14.80	16.94	24.70	30.26
LSD	1.23**	1.47**	1.79**	2.04**	2.34**	3.19**

*ns = not significantly different *=P≤ 0.05 **= P ≤ 0.01*

Table 6: Effect of Remediation of Spent Oil Polluted Soil on Stem Girth using Soybean and Cowpea

	Weeks After Planting (Cm)					
Treatment	1	2	3	4	5	6
Soybean + pollution	0.78	0.90	1.05	1.14	1.19	1.37
Cowpea	1.27	1.43	2.06	2.56	3.72	3.21
Cowpea + pollution	1.056	1.11	1.28	1.41	1.73	1.94
Soybean	0.97	1.10	1.26	1.44	1.68	1.84
LSD	0.12**	0.10**	0.17**	0.21**	0.31**	0.24**

*ns = not significantly different *=P ≤ 0.05 **= P ≤ 0.01*

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1. Substantial contributions to the conception and acquisition of data, analysis, and interpretation of findings.
2. Drafting the paper and revising it critically regarding important academic content.
3. Final approval of the version of the paper to be published.

Changes in Authorship

The corresponding author should mention the name and complete details of all co-authors during submission and in manuscript. We support addition, rearrangement, manipulation, and deletions in authors list till the early view publication of the journal. We expect that corresponding author will notify all co-authors of submission. We follow COPE guidelines for changes in authorship.

Copyright

During submission of the manuscript, the author is confirming an exclusive license agreement with Global Journals which gives Global Journals the authority to reproduce, reuse, and republish authors' research. We also believe in flexible copyright terms where copyright may remain with authors/employers/institutions as well. Contact your editor after acceptance to choose your copyright policy. You may follow this form for copyright transfers.

Appealing Decisions

Unless specified in the notification, the Editorial Board's decision on publication of the paper is final and cannot be appealed before making the major change in the manuscript.

Acknowledgments

Contributors to the research other than authors credited should be mentioned in Acknowledgments. The source of funding for the research can be included. Suppliers of resources may be mentioned along with their addresses.

Declaration of funding sources

Global Journals is in partnership with various universities, laboratories, and other institutions worldwide in the research domain. Authors are requested to disclose their source of funding during every stage of their research, such as making analysis, performing laboratory operations, computing data, and using institutional resources, from writing an article to its submission. This will also help authors to get reimbursements by requesting an open access publication letter from Global Journals and submitting to the respective funding source.

PREPARING YOUR MANUSCRIPT

Authors can submit papers and articles in an acceptable file format: MS Word (doc, docx), LaTeX (.tex, .zip or .rar including all of your files), Adobe PDF (.pdf), rich text format (.rtf), simple text document (.txt), Open Document Text (.odt), and Apple Pages (.pages). Our professional layout editors will format the entire paper according to our official guidelines. This is one of the highlights of publishing with Global Journals—authors should not be concerned about the formatting of their paper. Global Journals accepts articles and manuscripts in every major language, be it Spanish, Chinese, Japanese, Portuguese, Russian, French, German, Dutch, Italian, Greek, or any other national language, but the title, subtitle, and abstract should be in English. This will facilitate indexing and the pre-peer review process.

The following is the official style and template developed for publication of a research paper. Authors are not required to follow this style during the submission of the paper. It is just for reference purposes.

Manuscript Style Instruction (Optional)

- Microsoft Word Document Setting Instructions.
- Font type of all text should be Swis721 Lt BT.
- Page size: 8.27" x 11'", left margin: 0.65, right margin: 0.65, bottom margin: 0.75.
- Paper title should be in one column of font size 24.
- Author name in font size of 11 in one column.
- Abstract: font size 9 with the word “Abstract” in bold italics.
- Main text: font size 10 with two justified columns.
- Two columns with equal column width of 3.38 and spacing of 0.2.
- First character must be three lines drop-capped.
- The paragraph before spacing of 1 pt and after of 0 pt.
- Line spacing of 1 pt.
- Large images must be in one column.
- The names of first main headings (Heading 1) must be in Roman font, capital letters, and font size of 10.
- The names of second main headings (Heading 2) must not include numbers and must be in italics with a font size of 10.

Structure and Format of Manuscript

The recommended size of an original research paper is under 15,000 words and review papers under 7,000 words. Research articles should be less than 10,000 words. Research papers are usually longer than review papers. Review papers are reports of significant research (typically less than 7,000 words, including tables, figures, and references)

A research paper must include:

a) A title which should be relevant to the theme of the paper.
b) A summary, known as an abstract (less than 150 words), containing the major results and conclusions.
c) Up to 10 keywords that precisely identify the paper’s subject, purpose, and focus.
d) An introduction, giving fundamental background objectives.
e) Resources and techniques with sufficient complete experimental details (wherever possible by reference) to permit repetition, sources of information must be given, and numerical methods must be specified by reference.
f) Results which should be presented concisely by well-designed tables and figures.
g) Suitable statistical data should also be given.
h) All data must have been gathered with attention to numerical detail in the planning stage.

Design has been recognized to be essential to experiments for a considerable time, and the editor has decided that any paper that appears not to have adequate numerical treatments of the data will be returned unrefereed.

i) Discussion should cover implications and consequences and not just recapitulate the results; conclusions should also be summarized.
j) There should be brief acknowledgments.
k) There ought to be references in the conventional format. Global Journals recommends APA format.

Authors should carefully consider the preparation of papers to ensure that they communicate effectively. Papers are much more likely to be accepted if they are carefully designed and laid out, contain few or no errors, are summarizing, and follow instructions. They will also be published with much fewer delays than those that require much technical and editorial correction.

The Editorial Board reserves the right to make literary corrections and suggestions to improve brevity.

FORMAT STRUCTURE

It is necessary that authors take care in submitting a manuscript that is written in simple language and adheres to published guidelines.

All manuscripts submitted to Global Journals should include:

Title

The title page must carry an informative title that reflects the content, a running title (less than 45 characters together with spaces), names of the authors and co-authors, and the place(s) where the work was carried out.

Author details

The full postal address of any related author(s) must be specified.

Abstract

The abstract is the foundation of the research paper. It should be clear and concise and must contain the objective of the paper and inferences drawn. It is advised to not include big mathematical equations or complicated jargon.

Many researchers searching for information online will use search engines such as Google, Yahoo or others. By optimizing your paper for search engines, you will amplify the chance of someone finding it. In turn, this will make it more likely to be viewed and cited in further works. Global Journals has compiled these guidelines to facilitate you to maximize the web-friendliness of the most public part of your paper.

Keywords

A major lynchpin of research work for the writing of research papers is the keyword search, which one will employ to find both library and internet resources. Up to eleven keywords or very brief phrases have to be given to help data retrieval, mining, and indexing.

One must be persistent and creative in using keywords. An effective keyword search requires a strategy: planning of a list of possible keywords and phrases to try.

Choice of the main keywords is the first tool of writing a research paper. Research paper writing is an art. Keyword search should be as strategic as possible.

One should start brainstorming lists of potential keywords before even beginning searching. Think about the most important concepts related to research work. Ask, “What words would a source have to include to be truly valuable in a research paper?” Then consider synonyms for the important words.

It may take the discovery of only one important paper to steer in the right keyword direction because, in most databases, the keywords under which a research paper is abstracted are listed with the paper.

Numerical Methods

Numerical methods used should be transparent and, where appropriate, supported by references.

Abbreviations

Authors must list all the abbreviations used in the paper at the end of the paper or in a separate table before using them.

Formulas and equations

Authors are advised to submit any mathematical equation using either MathJax, KaTeX, or LaTeX, or in a very high-quality image.

Tables, Figures, and Figure Legends

Tables: Tables should be cautiously designed, uncrowned, and include only essential data. Each must have an Arabic number, e.g., Table 4, a self-explanatory caption, and be on a separate sheet. Authors must submit tables in an editable format and not as images. References to these tables (if any) must be mentioned accurately.

Figures

Figures are supposed to be submitted as separate files. Always include a citation in the text for each figure using Arabic numbers, e.g., Fig. 4. Artwork must be submitted online in vector electronic form or by emailing it.

PREPARATION OF ELETRONIC FIGURES FOR PUBLICATION

Although low-quality images are sufficient for review purposes, print publication requires high-quality images to prevent the final product being blurred or fuzzy. Submit (possibly by e-mail) EPS (line art) or TIFF (halftone/ photographs) files only. MS PowerPoint and Word Graphics are unsuitable for printed pictures. Avoid using pixel-oriented software. Scans (TIFF only) should have a resolution of at least 350 dpi (halftone) or 700 to 1100 dpi (line drawings). Please give the data for figures in black and white or submit a Color Work Agreement form. EPS files must be saved with fonts embedded (and with a TIFF preview, if possible).

For scanned images, the scanning resolution at final image size ought to be as follows to ensure good reproduction: line art: >650 dpi; halftones (including gel photographs): >350 dpi; figures containing both halftone and line images: >650 dpi.

Color charges: Authors are advised to pay the full cost for the reproduction of their color artwork. Hence, please note that if there is color artwork in your manuscript when it is accepted for publication, we would require you to complete and return a Color Work Agreement form before your paper can be published. Also, you can email your editor to remove the color fee after acceptance of the paper.

TIPS FOR WRITING A GOOD QUALITY SCIENCE FRONTIER RESEARCH PAPER

Techniques for writing a good quality Science Frontier Research paper:

1. Choosing the topic: In most cases, the topic is selected by the interests of the author, but it can also be suggested by the guides. You can have several topics, and then judge which you are most comfortable with. This may be done by asking several questions of yourself, like "Will I be able to carry out a search in this area? Will I find all necessary resources to accomplish the search? Will I be able to find all information in this field area?" If the answer to this type of question is "yes," then you ought to choose that topic. In most cases, you may have to conduct surveys and visit several places. Also, you might have to do a lot of work to find all the rises and falls of the various data on that subject. Sometimes, detailed information plays a vital role, instead of short information. Evaluators are human: The first thing to remember is that evaluators are also human beings. They are not only meant for rejecting a paper. They are here to evaluate your paper. So present your best aspect.

2. Think like evaluators: If you are in confusion or getting demotivated because your paper may not be accepted by the evaluators, then think, and try to evaluate your paper like an evaluator. Try to understand what an evaluator wants in your research paper, and you will automatically have your answer. Make blueprints of paper: The outline is the plan or framework that will help you to arrange your thoughts. It will make your paper logical. But remember that all points of your outline must be related to the topic you have chosen.

3. Ask your guides: If you are having any difficulty with your research, then do not hesitate to share your difficulty with your guide (if you have one). They will surely help you out and resolve your doubts. If you can't clarify what exactly you require for your work, then ask your supervisor to help you with an alternative. He or she might also provide you with a list of essential readings.

4. Use of computer is recommended: As you are doing research in the field of science frontier then this point is quite obvious. Use right software: Always use good quality software packages. If you are not capable of judging good software, then you can lose the quality of your paper unknowingly. There are various programs available to help you which you can get through the internet.

5. Use the internet for help: An excellent start for your paper is using Google. It is a wondrous search engine, where you can have your doubts resolved. You may also read some answers for the frequent question of how to write your research paper or find a model research paper. You can download books from the internet. If you have all the required books, place importance on reading, selecting, and analyzing the specified information. Then sketch out your research paper. Use big pictures: You may use encyclopedias like Wikipedia to get pictures with the best resolution. At Global Journals, you should strictly follow here.

6. Bookmarks are useful: When you read any book or magazine, you generally use bookmarks, right? It is a good habit which helps to not lose your continuity. You should always use bookmarks while searching on the internet also, which will make your search easier.

7. Revise what you wrote: When you write anything, always read it, summarize it, and then finalize it.

8. Make every effort: Make every effort to mention what you are going to write in your paper. That means always have a good start. Try to mention everything in the introduction—what is the need for a particular research paper. Polish your work with good writing skills and always give an evaluator what he wants. Make backups: When you are going to do any important thing like making a research paper, you should always have backup copies of it either on your computer or on paper. This protects you from losing any portion of your important data.

9. Produce good diagrams of your own: Always try to include good charts or diagrams in your paper to improve quality. Using several unnecessary diagrams will degrade the quality of your paper by creating a hodgepodge. So always try to include diagrams which were made by you to improve the readability of your paper. Use of direct quotes: When you do research relevant to literature, history, or current affairs, then use of quotes becomes essential, but if the study is relevant to science, use of quotes is not preferable.

10. Use proper verb tense: Use proper verb tenses in your paper. Use past tense to present those events that have happened. Use present tense to indicate events that are going on. Use future tense to indicate events that will happen in the future. Use of wrong tenses will confuse the evaluator. Avoid sentences that are incomplete.

11. Pick a good study spot: Always try to pick a spot for your research which is quiet. Not every spot is good for studying.

12. Know what you know: Always try to know what you know by making objectives, otherwise you will be confused and unable to achieve your target.

13. Use good grammar: Always use good grammar and words that will have a positive impact on the evaluator; use of good vocabulary does not mean using tough words which the evaluator has to find in a dictionary. Do not fragment sentences. Eliminate one-word sentences. Do not ever use a big word when a smaller one would suffice.

Verbs have to be in agreement with their subjects. In a research paper, do not start sentences with conjunctions or finish them with prepositions. When writing formally, it is advisable to never split an infinitive because someone will (wrongly) complain. Avoid clichés like a disease. Always shun irritating alliteration. Use language which is simple and straightforward. Put together a neat summary.

14. Arrangement of information: Each section of the main body should start with an opening sentence, and there should be a changeover at the end of the section. Give only valid and powerful arguments for your topic. You may also maintain your arguments with records.

15. Never start at the last minute: Always allow enough time for research work. Leaving everything to the last minute will degrade your paper and spoil your work.

16. Multitasking in research is not good: Doing several things at the same time is a bad habit in the case of research activity. Research is an area where everything has a particular time slot. Divide your research work into parts, and do a particular part in a particular time slot.

17. Never copy others' work: Never copy others' work and give it your name because if the evaluator has seen it anywhere, you will be in trouble. Take proper rest and food: No matter how many hours you spend on your research activity, if you are not taking care of your health, then all your efforts will have been in vain. For quality research, take proper rest and food.

18. Go to seminars: Attend seminars if the topic is relevant to your research area. Utilize all your resources.

19. Refresh your mind after intervals: Try to give your mind a rest by listening to soft music or sleeping in intervals. This will also improve your memory. Acquire colleagues: Always try to acquire colleagues. No matter how sharp you are, if you acquire colleagues, they can give you ideas which will be helpful to your research.

20. Think technically: Always think technically. If anything happens, search for its reasons, benefits, and demerits. Think and then print: When you go to print your paper, check that tables are not split, headings are not detached from their descriptions, and page sequence is maintained.

21. Adding unnecessary information: Do not add unnecessary information like "I have used MS Excel to draw graphs." Irrelevant and inappropriate material is superfluous. Foreign terminology and phrases are not apropos. One should never take a broad view. Analogy is like feathers on a snake. Use words properly, regardless of how others use them. Remove quotations. Puns are for kids, not grunt readers. Never oversimplify: When adding material to your research paper, never go for oversimplification; this will definitely irritate the evaluator. Be specific. Never use rhythmic redundancies. Contractions shouldn't be used in a research paper. Comparisons are as terrible as clichés. Give up ampersands, abbreviations, and so on. Remove commas that are not necessary. Parenthetical words should be between brackets or commas. Understatement is always the best way to put forward earth-shaking thoughts. Give a detailed literary review.

22. Report concluded results: Use concluded results. From raw data, filter the results, and then conclude your studies based on measurements and observations taken. An appropriate number of decimal places should be used. Parenthetical remarks are prohibited here. Proofread carefully at the final stage. At the end, give an outline to your arguments. Spot perspectives of further study of the subject. Justify your conclusion at the bottom sufficiently, which will probably include examples.

23. Upon conclusion: Once you have concluded your research, the next most important step is to present your findings. Presentation is extremely important as it is the definite medium though which your research is going to be in print for the rest of the crowd. Care should be taken to categorize your thoughts well and present them in a logical and neat manner. A good quality research paper format is essential because it serves to highlight your research paper and bring to light all necessary aspects of your research.

Informal Guidelines of Research Paper Writing

Key points to remember:

- Submit all work in its final form.
- Write your paper in the form which is presented in the guidelines using the template.
- Please note the criteria peer reviewers will use for grading the final paper.

Final points:

One purpose of organizing a research paper is to let people interpret your efforts selectively. The journal requires the following sections, submitted in the order listed, with each section starting on a new page:

The introduction: This will be compiled from reference matter and reflect the design processes or outline of basis that directed you to make a study. As you carry out the process of study, the method and process section will be constructed like that. The results segment will show related statistics in nearly sequential order and direct reviewers to similar intellectual paths throughout the data that you gathered to carry out your study.

The discussion section:

This will provide understanding of the data and projections as to the implications of the results. The use of good quality references throughout the paper will give the effort trustworthiness by representing an alertness to prior workings.

Writing a research paper is not an easy job, no matter how trouble-free the actual research or concept. Practice, excellent preparation, and controlled record-keeping are the only means to make straightforward progression.

General style:

Specific editorial column necessities for compliance of a manuscript will always take over from directions in these general guidelines.

To make a paper clear: Adhere to recommended page limits.

Mistakes to avoid:

- Insertion of a title at the foot of a page with subsequent text on the next page.
- Separating a table, chart, or figure—confine each to a single page.
- Submitting a manuscript with pages out of sequence.
- In every section of your document, use standard writing style, including articles ("a" and "the").
- Keep paying attention to the topic of the paper.
- Use paragraphs to split each significant point (excluding the abstract).
- Align the primary line of each section.
- Present your points in sound order.
- Use present tense to report well-accepted matters.
- Use past tense to describe specific results.
- Do not use familiar wording; don't address the reviewer directly. Don't use slang or superlatives.
- Avoid use of extra pictures—include only those figures essential to presenting results.

Title page:

Choose a revealing title. It should be short and include the name(s) and address(es) of all authors. It should not have acronyms or abbreviations or exceed two printed lines.

Abstract: This summary should be two hundred words or less. It should clearly and briefly explain the key findings reported in the manuscript and must have precise statistics. It should not have acronyms or abbreviations. It should be logical in itself. Do not cite references at this point.

An abstract is a brief, distinct paragraph summary of finished work or work in development. In a minute or less, a reviewer can be taught the foundation behind the study, common approaches to the problem, relevant results, and significant conclusions or new questions.

Write your summary when your paper is completed because how can you write the summary of anything which is not yet written? Wealth of terminology is very essential in abstract. Use comprehensive sentences, and do not sacrifice readability for brevity; you can maintain it succinctly by phrasing sentences so that they provide more than a lone rationale. The author can at this moment go straight to shortening the outcome. Sum up the study with the subsequent elements in any summary. Try to limit the initial two items to no more than one line each.

Reason for writing the article—theory, overall issue, purpose.

- Fundamental goal.
- To-the-point depiction of the research.
- Consequences, including definite statistics—if the consequences are quantitative in nature, account for this; results of any numerical analysis should be reported. Significant conclusions or questions that emerge from the research.

Approach:

  - Single section and succinct.
  - An outline of the job done is always written in past tense.
  - Concentrate on shortening results—limit background information to a verdict or two.
  - Exact spelling, clarity of sentences and phrases, and appropriate reporting of quantities (proper units, important statistics) are just as significant in an abstract as they are anywhere else.

Introduction:

The introduction should "introduce" the manuscript. The reviewer should be presented with sufficient background information to be capable of comprehending and calculating the purpose of your study without having to refer to other works. The basis for the study should be offered. Give the most important references, but avoid making a comprehensive appraisal of the topic. Describe the problem visibly. If the problem is not acknowledged in a logical, reasonable way, the reviewer will give no attention to your results. Speak in common terms about techniques used to explain the problem, if needed, but do not present any particulars about the protocols here.

The following approach can create a valuable beginning:

- Explain the value (significance) of the study.
- Defend the model—why did you employ this particular system or method? What is its compensation? Remark upon its appropriateness from an abstract point of view as well as pointing out sensible reasons for using it.
- Present a justification. State your particular theory(-ies) or aim(s), and describe the logic that led you to choose them.
- Briefly explain the study's tentative purpose and how it meets the declared objectives.

Approach:

Use past tense except for when referring to recognized facts. After all, the manuscript will be submitted after the entire job is done. Sort out your thoughts; manufacture one key point for every section. If you make the four points listed above, you will need at least four paragraphs. Present surrounding information only when it is necessary to support a situation. The reviewer does not desire to read everything you know about a topic. Shape the theory specifically—do not take a broad view.

As always, give awareness to spelling, simplicity, and correctness of sentences and phrases.

Procedures (methods and materials):

This part is supposed to be the easiest to carve if you have good skills. A soundly written procedures segment allows a capable scientist to replicate your results. Present precise information about your supplies. The suppliers and clarity of reagents can be helpful bits of information. Present methods in sequential order, but linked methodologies can be grouped as a segment. Be concise when relating the protocols. Attempt to give the least amount of information that would permit another capable scientist to replicate your outcome, but be cautious that vital information is integrated. The use of subheadings is suggested and ought to be synchronized with the results section.

When a technique is used that has been well-described in another section, mention the specific item describing the way, but draw the basic principle while stating the situation. The purpose is to show all particular resources and broad procedures so that another person may use some or all of the methods in one more study or referee the scientific value of your work. It is not to be a step-by-step report of the whole thing you did, nor is a methods section a set of orders.

Materials:

Materials may be reported in part of a section or else they may be recognized along with your measures.

Methods:

- Report the method and not the particulars of each process that engaged the same methodology.
- Describe the method entirely.
- To be succinct, present methods under headings dedicated to specific dealings or groups of measures.
- Simplify—detail how procedures were completed, not how they were performed on a particular day.
- If well-known procedures were used, account for the procedure by name, possibly with a reference, and that's all.

Approach:

It is embarrassing to use vigorous voice when documenting methods without using first person, which would focus the reviewer's interest on the researcher rather than the job. As a result, when writing up the methods, most authors use third person passive voice.

Use standard style in this and every other part of the paper—avoid familiar lists, and use full sentences.

What to keep away from:

- Resources and methods are not a set of information.
- Skip all descriptive information and surroundings—save it for the argument.
- Leave out information that is immaterial to a third party.

Results:

The principle of a results segment is to present and demonstrate your conclusion. Create this part as entirely objective details of the outcome, and save all understanding for the discussion.

The page length of this segment is set by the sum and types of data to be reported. Use statistics and tables, if suitable, to present consequences most efficiently.

You must clearly differentiate material which would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matters should not be submitted at all except if requested by the instructor.

Content:

- Sum up your conclusions in text and demonstrate them, if suitable, with figures and tables.
- In the manuscript, explain each of your consequences, and point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation of an exacting study.
- Explain results of control experiments and give remarks that are not accessible in a prescribed figure or table, if appropriate.
- Examine your data, then prepare the analyzed (transformed) data in the form of a figure (graph), table, or manuscript.

What to stay away from:

- Do not discuss or infer your outcome, report surrounding information, or try to explain anything.
- Do not include raw data or intermediate calculations in a research manuscript.
- Do not present similar data more than once.
- A manuscript should complement any figures or tables, not duplicate information.
- Never confuse figures with tables—there is a difference.

Approach:

As always, use past tense when you submit your results, and put the whole thing in a reasonable order.

Put figures and tables, appropriately numbered, in order at the end of the report.

If you desire, you may place your figures and tables properly within the text of your results section.

Figures and tables:

If you put figures and tables at the end of some details, make certain that they are visibly distinguished from any attached appendix materials, such as raw facts. Whatever the position, each table must be titled, numbered one after the other, and include a heading. All figures and tables must be divided from the text.

Discussion:

The discussion is expected to be the trickiest segment to write. A lot of papers submitted to the journal are discarded based on problems with the discussion. There is no rule for how long an argument should be.

Position your understanding of the outcome visibly to lead the reviewer through your conclusions, and then finish the paper with a summing up of the implications of the study. The purpose here is to offer an understanding of your results and support all of your conclusions, using facts from your research and generally accepted information, if suitable. The implication of results should be fully described.

Infer your data in the conversation in suitable depth. This means that when you clarify an observable fact, you must explain mechanisms that may account for the observation. If your results vary from your prospect, make clear why that may have happened. If your results agree, then explain the theory that the proof supported. It is never suitable to just state that the data approved the prospect, and let it drop at that. Make a decision as to whether each premise is supported or discarded or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."

Research papers are not acknowledged if the work is imperfect. Draw what conclusions you can based upon the results that you have, and take care of the study as a finished work.

- You may propose future guidelines, such as how an experiment might be personalized to accomplish a new idea.
- Give details of all of your remarks as much as possible, focusing on mechanisms.
- Make a decision as to whether the tentative design sufficiently addressed the theory and whether or not it was correctly restricted. Try to present substitute explanations if they are sensible alternatives.
- One piece of research will not counter an overall question, so maintain the large picture in mind. Where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

Approach:

When you refer to information, differentiate data generated by your own studies from other available information. Present work done by specific persons (including you) in past tense.

Describe generally acknowledged facts and main beliefs in present tense.

The Administration Rules

Administration Rules to Be Strictly Followed before Submitting Your Research Paper to Global Journals Inc.

Please read the following rules and regulations carefully before submitting your research paper to Global Journals Inc. to avoid rejection.

Segment draft and final research paper: You have to strictly follow the template of a research paper, failing which your paper may get rejected. You are expected to write each part of the paper wholly on your own. The peer reviewers need to identify your own perspective of the concepts in your own terms. Please do not extract straight from any other source, and do not rephrase someone else's analysis. Do not allow anyone else to proofread your manuscript.

Written material: You may discuss this with your guides and key sources. Do not copy anyone else's paper, even if this is only imitation, otherwise it will be rejected on the grounds of plagiarism, which is illegal. Various methods to avoid plagiarism are strictly applied by us to every paper, and, if found guilty, you may be blacklisted, which could affect your career adversely. To guard yourself and others from possible illegal use, please do not permit anyone to use or even read your paper and file.

Criterion for Grading a Research Paper (Compilation) by Global Journals

Please note that following table is only a Grading of "Paper Compilation" and not on "Performed/Stated Research" whose grading solely depends on Individual Assigned Peer Reviewer and Editorial Board Member. These can be available only on request and after decision of Paper. This report will be the property of Global Journals.

Topics	Grades		
	A-B	**C-D**	**E-F**
Abstract	Clear and concise with appropriate content, Correct format. 200 words or below	Unclear summary and no specific data, Incorrect form Above 200 words	No specific data with ambiguous information Above 250 words
Introduction	Containing all background details with clear goal and appropriate details, flow specification, no grammar and spelling mistake, well organized sentence and paragraph, reference cited	Unclear and confusing data, appropriate format, grammar and spelling errors with unorganized matter	Out of place depth and content, hazy format
Methods and Procedures	Clear and to the point with well arranged paragraph, precision and accuracy of facts and figures, well organized subheads	Difficult to comprehend with embarrassed text, too much explanation but completed	Incorrect and unorganized structure with hazy meaning
Result	Well organized, Clear and specific, Correct units with precision, correct data, well structuring of paragraph, no grammar and spelling mistake	Complete and embarrassed text, difficult to comprehend	Irregular format with wrong facts and figures
Discussion	Well organized, meaningful specification, sound conclusion, logical and concise explanation, highly structured paragraph reference cited	Wordy, unclear conclusion, spurious	Conclusion is not cited, unorganized, difficult to comprehend
References	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

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