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Research Article

EFFECTS OF pH, IONIC STRENGTH AND TEMPERATURE ON THE RATE OF OXIDATION OF ARSENIC (III) BY DISSOLVED ORGANIC MATTER, DOM OBTAINED FROM SAWDUST, GROUNDNUT HUSK, AND RICE HUSK

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ABSTRACT

Objective: Industrial and many other processes produce waste streams that end in the environment and may contain toxic metals at concentrations above the permissible limits. Arsenic(III) is one of the most toxic 'metal' contaminants found in water and is well known to have adverse effects, such as skin cancer, etc. Thus, oxidation of arsenic(III) to the less toxic and less mobile arsenic(V) by dissolved organic matter (DOM) will help in controlling the environmental pollution by As(III).

Methods: Oxidation of Arsenic(III) ions by DOM obtained from Sawdust, DOM(SD), Groundnut Husk, DOM(GH) and Rice Husk, DOM(RH) was done at varying pH, ionic strength and temperature. These reactions rate were monitored using UV-visible spectrophotometry. DOM samples were confirmed by their UV-visible and infrared spectrophotometry.

Results; The reaction products were identified as As^{5+}, as it forms molybdenum blue salt {a product of ammonium molybdate(VI) with As(V) ions (in the environment of hydrazine sulphate)}, DOM samples were confirmed by their UV-visible absorption maxima having λ_{max} of 256 nm, 250 nm and 260 nm for DOM(GH), DOM(SD) and DOM(RH) respectively, and their infrared spectra with major absorption bands in the regions of 2500–3500 cm^{-1} and 650-770 cm^{-1} (O-H stretching and out of plane bending groups), 2500–3500 cm^{-1}, 1350–1470 $cm^{-1}$and 690–900 cm^{-1} (C–H stretching, deformation, and bending and ring puckering respectively), 1650–1800 cm^{-1} (C=O stretching of COOH), 1620–1680 cm^{-1} (alkene/aromatic C=C stretching), 970–1250 cm^{-1} (C–O stretching of alcohols/phenols) 880–995 cm^{-1} and 1395–1440 cm^{-1} (=C–H out of plane bending/C-O-H bending). The rate of oxidation of As(III) to As(V) by DOM increased with an increase in mass/volume percent of DOM {the increment was highest with DOM(SD)}, increased with an increase in pH and independent of the ionic strength. The reaction rate {oxidation of As(III) to As(V) by DOM} also increased with temperature but having a rate at 273 K comparable to that at 303-308 K.

Conclusion: It can be seen that DOM obtained from these wastes oxidised As(III) to As(V) as confirmed from the formation of molybdenum blue salt, and the spectroscopic analysis of the DOM.

Keywords: Dissolved organic matter, Arsenic(III), Oxidation, Molybdenum blue salt, Temperature, Ionic strength

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INTRODUCTION

Environmental contamination by heavy metals can occur through metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and groundwater. The contamination can also come from natural phenomena such as weathering and volcanic eruptions [1], as well as industrial sources [2]. Arsenic is a toxic element for animals and the majority of plants in spite of there being some evidence that it is also an essential element. The toxicity of different As species vary in the order arsenite>arsenate>monomethylarsonate>dimethylarsinate. As(III) is about 60 times more toxic than As(V), and inorganic As compounds are about 100 times more toxic than organic As compounds [3]. The major environmental concern about As is not related to its presence in soils and sediments in anomalous amounts, but to its anomalous concentration in surface waters and its availability to living beings.

Water is essential for living beings and is the dominant As exposure pathway. Humans are the main concern of the As environmental problem and As-contaminated waters are used by populations of some parts of the world, with large-scale disasters occurring in particular regions of Asia, Africa, and Central and South America involving some millions of inhabitants [4]. Several techniques effectively lower As concentrations in aqueous solutions; coagulation/precipitation, reverse osmosis, ion exchange, and adsorption to mention a few. Coagulation and softening with metal ions such as aluminium and ferric salts require the use of large-scale facilities for implementing water treatment. Reverse osmosis requires the use of membranes, which are expensive to maintain and replace, and ion exchange uses costly resins. Again, coagulation, reverse osmosis, and ion exchange require the treatment of reject stream for the ultimate disposal of As contaminants [5]. Unlike the adsorption technique that is aimed at removing toxic metals from the aqueous solutions, oxidation technology leaves them in the medium but minimize their toxicity and mobility. Oxidation of As converts As(III) to the less toxic or more useful As(V) [6]. Also, various agricultural and industrial wastes are found to be lethal to the environment especially within the areas in which such wastes are produced. Groundnut husks, for instance, is non-decomposable (at least within a year or two) if disposed of as such. Other such wastes include rice husks and sawdusts which are produced at one point or the other and are of little or no use. The oxidation of arsenic(III) to arsenic(V) by organic matter obtained from these wastes may turn out to be a greener approach to the remediation of arsenic

MATERIALS AND METHODS

Chemicals, reagents and apparatus

$NaAsO_2$, (LOBA^{AR} CHEMIE PVT Ltd), HNO_3 (BDH^{AR}), $NaNO_3$ (Fenxichun^{AR}), ammonium molybdate $\{(NH_4)_6Mo_7O_{24}\,.\,4H_2O\}$, (Guangdong Guanghua Sci-Tech. Co. Ltd^{AR}), hydrazine sulphate $\{(N_2H_5)HSO_4\}$, groundnut husk, sawdust, rice husk H_2SO_4 (97–99 % assay, JHD^{AR}), O-phosphoric acid, H_3PO_4 (Fenxichun^{AR}), o-phenanthroline (Qualikems^{AR}), $FeSO_4.7H_2O$ (JHD^{AR}), $Fe(NH_4)_2(SO_4)_2\,.\,6H_2O$ (LOBA^{AR} CHEMIE PVT Ltd), distilled and deionised water, muffle furnace (NEY M-525), mechanical shaker (HY-2 Speed adjusting multipurpose vibrator), thermostatic water bath (Clifton unstirred bath model 92498), UV-visible spectrophotometer (Unico^{R} 2800P), pH meter (Hanna Instrument H19024), analytical balance (aeADAM PW 184, AE 437531), freeze dryer (Lyodry, Grande freeze dryer model), FTIR spectrophotometer (Agilant Technolologies, Cary 630 FTIR), Sieve (Cole Parmer-typed sieve of 0.80 mm mesh) and normal laboratory glassware.

Determination of UV-visible spectrum of the molybdenum blue

Absorbances were taken from a solution of the molybdenum blue salt {a product of ammonium molybdate(VI) with As(V) ions (in the environment of hydrazine sulphate)} [7, 8]. The wavelengths of maximum absorption were obtained by plotting absorbances versus wavelengths.

Preparation and characterisation of DOM from sawdust (SD), groundnut husk (GH) and rice husk (RH)

The waste materials were collected locally; sawdust from a local sawmill (along George Akume Road, International Market, Makurdi, Benue State-Nigeria), rice husk from Makurdi Rice Mill (Lafia Road, Wurukum, Makurdi, Benue State-Nigeria) and groundnut husk from a groundnut farm (at Jauro Yinu, Wukari Road, Jalingo, Taraba State-Nigeria). The sawdust was sieved with a Cole Parmer-typed sieve of about 0.80 mm mesh to obtain the desired size fraction. Then, the sieved sawdust was washed with distilled water to remove any residues or impurities such as ash and dust. The same process was applied to the rice husk. Groundnut husk on the other hand, was first washed with distilled water, dried in an oven and grounded through the sieve to lower the surface area, followed by the procedure described above [9, 10].

Subsequently, these were dried in an oven and pyrolysed (at<350 °C for 20 min) in a furnace to obtain the biochar [9].

10 g of the biochar obtained from rice husk, sawdust and groundnut husk each were suspended in a reaction vessel with 1 L deionised water and agitated on a shaker at an average speed at room temperature for 24 h (to reach an apparent equilibrium). The suspensions were then passed through a filter paper and then a 0.2 µm membrane filter to obtain dissolved organic matter (DOM) [11]. The percentage mass/volume of DOM was analysed by the Walkley-Black titrimetric method [10, 12, 13].

To determine the chemical structure and functional groups involved in As(III) oxidation reaction, DOM samples (DOM(GH), DOM(RH) and DOM(SD) containing a percentage mass/volume of carbon were analyzed. To achieve this, 300 ml of DOM samples each containing varying percentage mass/volume DOM were freeze-dried and analyzed. The functional groups were analyzed after freeze-drying the DOM samples using FTIR and UV-visible spectrophotometers [11, 14].

Optimisation of concentration of reagents in the kinetics of oxidation of arsenic(III) with organic matter

Optimisation of concentration of hydrazine sulphate

The intensity of the colour of the molybdenum blue complex is significantly affected by the concentration of hydrazine sulphate in the solution [14]. To achieve maximum absorbance, the effect of concentration of hydrazine sulphate on the intensity of the colour of the molybdenum blue complex was investigated by taking various volumes (0.1-1.0 ml) of the hydrazine sulphate solution (0.5 $molL^{-1}$), 2 ml of ammonium molybdate (of 2.5 %), 2 ml of $NaAsO_2$, (0.08 $molL^{-1}$) and 20 ml of DOM in a 50 ml volumetric flask. Then the mixtures were diluted and made up to the mark with distilled water and left for maximum colour development. After this the absorbance of each mixture was measured at the wavelength of maximum absorbance to get the most sensitive concentration.

Optimisation of concentration of ammonium molybdate

The molybdenum blue complex so obtained in the reaction of ammonium molybdate(VI) with As(V) ions depends on the concentration of ammonium molybdate [14]. The effect of concentration of ammonium molybdate on the formation of molybdenum blue complex was investigated by varying the volumes (1–8) ml of ammonium molybdate (of 2.5 %), with the addition of 1 ml (0.5 $molL^{-1}$) hydrazine sulphate, 2 ml of $NaAsO_2$, (0.08 $molL^{-1}$) and 20 ml of DOM in a 50 ml volumetric flask and then made up to mark with deionized water. After the maximum colour has been developed, the absorbance of these solutions was measured at the wavelength of maximum absorbance to get the most sensitive concentration.

Kinetic studies

All rate measurements were made using Unico^{R} 2800P UV-visible spectrophotometer at the wavelength of maximum absorption. The reaction rates were monitored at the wavelength by noting the increase in absorbances of the reaction mixtures with time.

All kinetic measurements were made under pseudo-first-order conditions with concentrations of AsO_2^- ions at least 60 times greater than that of the DOM [14].

The pseudo-first-order rate constants, k_{obs}, were obtained from the plots of $\ln(A_t\text{-}A_\infty/A_o\text{-}A_\infty)$ against time (where A_t, A_o and A_∞ are the absorbances of the reaction mixtures at time t, zero time and infinite time, respectively). The temperature was kept constant at ambient (297–300 K), pH = 6 and I = 0.1 $molL^{-1}$.

pH dependence studies

The pseudo-first-order rate constants, k_{pH} for the oxidation of As(III) by DOM were determined at pH in the range of 2–10 (using HNO_3 and NaOH) while keeping other conditions constant.

Temperature dependence studies

The temperature dependence rate study for the oxidation of As(III) by DOM was carried out over the temperature range of 288 K-305 K while keeping other conditions constant. Kinetic activation parameters (activation energy, E_a, entropy changeΔS, and enthalpy change, ΔH) were obtained from Arrhenius and Eyring plots, Equations 1 and 2 [15-17].

$$k = Ae^{-Ea/RT} \ldots\ldots (1)$$

$$\ln(\frac{k}{T}) = \ln(\frac{k_B}{h}) + (\frac{\Delta S^*}{R}) - (\frac{\Delta H^*}{RT}) \ldots. (2)$$

Ionic strength effect

The effect of ionic strength changes on the rate of oxidation of As(III) by DOM was being studied over a range of (0.001-0.021) $molL^{-1}$ concentrations of $NaNO_3$ salt while keeping other conditions constant.

RESULTS AND DISCUSSION

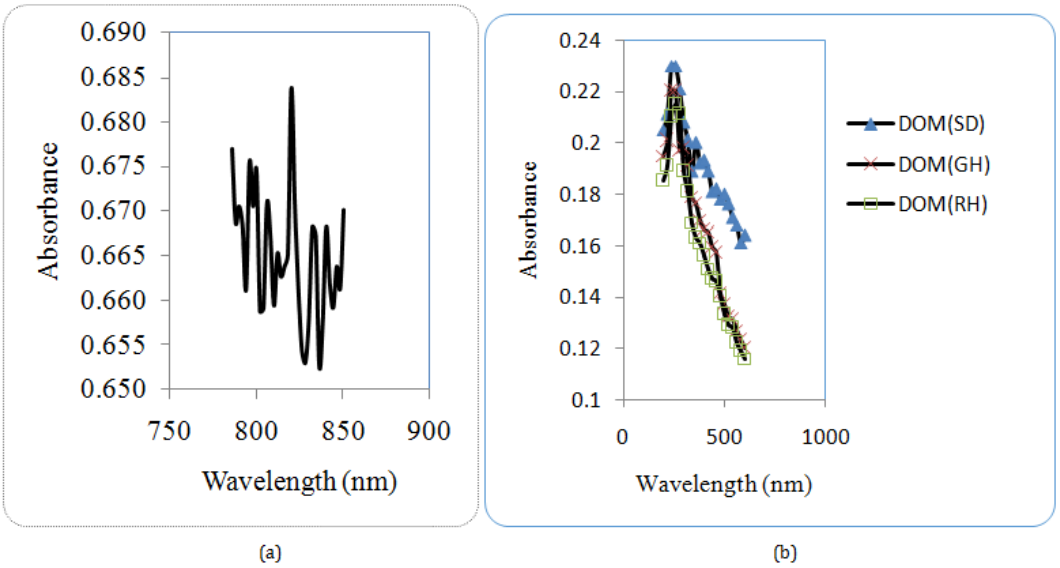


Fig. 1: Determination of λ_{max} for (a) molybdenum blue solution and (b) dissolved organic matter, DOM obtained from sawdust, SD, groundnut husk, GH and rice husk, RH

UV-Visible spectra consideration of the solutions used

The absorption of electromagnetic radiations in the UV region of the spectrum results in transitions between electronic energy levels; that is, metal ions can absorb visible light because electrons in the metal atoms can be excited from one electronic state to another [14]. In fig. 1(a) above, the bands correspond to the d–d transitions; the redistribution of electrons among orbitals that are mainly localised on the metal atoms or charge-transfer (CT) transitions involving the metal d-orbitals. Typically, the bands above 300 nm and below 850 nm, involve the motion of electrons from an essentially ligand-based orbital to an essentially metal-based. This makes a charge to be transferred from one atom to another. In general, it is referred to as ligand–to–metal charge–transfer (LMCT). CT bands are observed if the energies of empty and filled ligand-and metal-centered orbitals are similar. It occurs within the visible or near UV region of the spectrum; this is in line with other research Amira *et al.* [18]. Thus the kinetic studies were done using UV-visible spectrophotometry and at the established wavelength of maximum absorbance for molybdenum blue solution.

Characterization of the dissolved organic matter, DOM samples

The DOM samples were characterized by measuring the content of their humic materials. In achieving this, 300 ml each from the DOM samples were freeze-dried using a freeze drier, after which the DOM samples were characterized by UV-visible and FTIR spectrophotometers [11, 14].

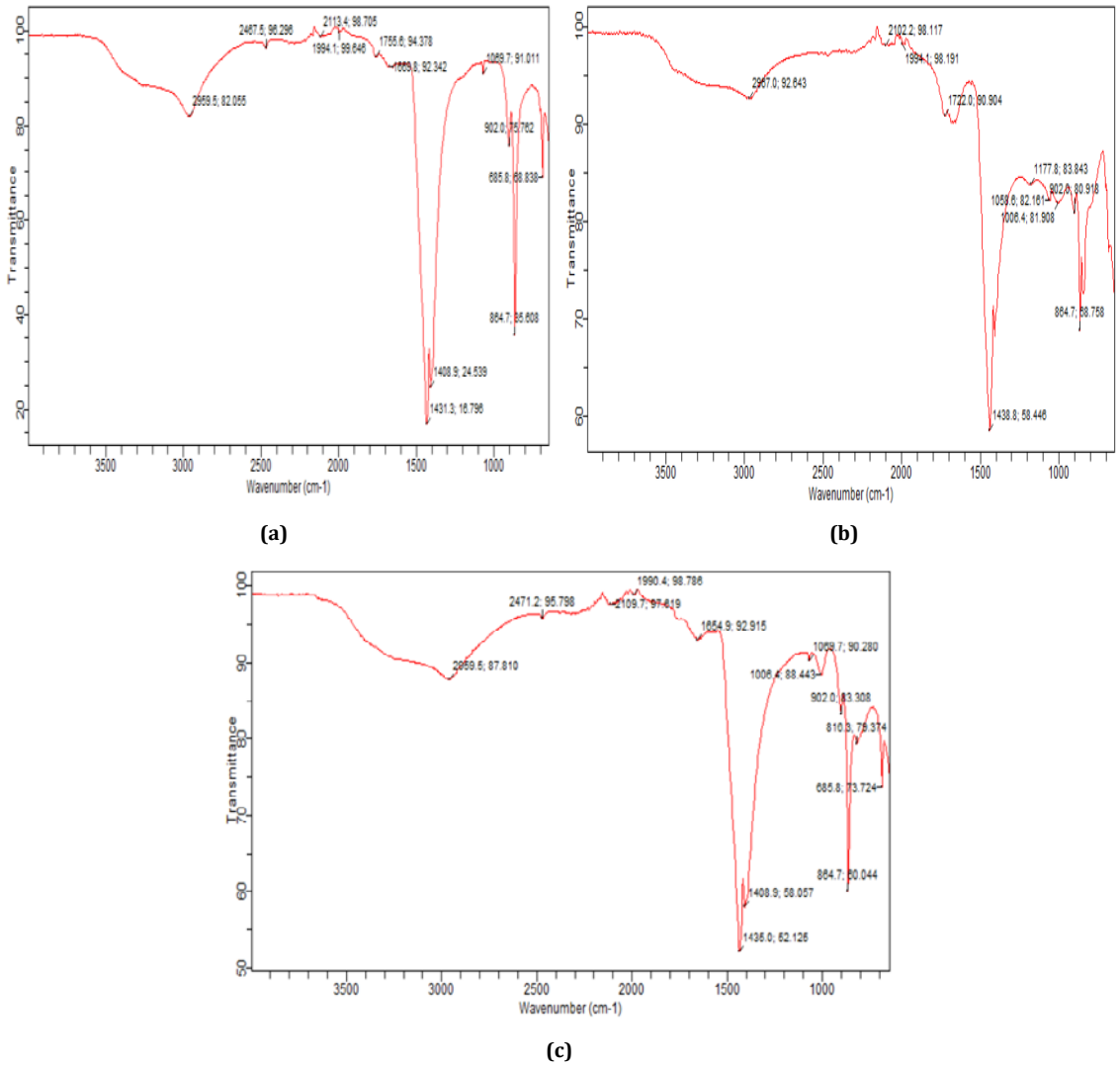
From fig. 1b, it can be seen that the wavelength of maximum absorption was found as 250 nm DOM(SD), 256 nm DOM(GH) and 260 nm DOM(RH) as presented in table 1. In all cases, the UV-visible spectra have shown similarities in the peaks. The UV-visible spectra data of the DOM samples were recorded in ethanol in the wavelength range 200-600 nm at ambient temperature (298–300 K), using a 1.0 cm quartz cell, reference was pure water. Samples were diluted to maintain the maximal response as reported by Shie-Jie [19].

The characteristic energy of a transition and the wavelength of radiations absorbed are properties of a group of atoms rather than of electrons themselves. The group of atoms producing such absorption is called a chromophore [20]. The electronic spectra data of humic materials have λ_{max} at 254 nm [21]. These UV-visible spectral data from the DOM samples might have been contributed by phenolic, aromatic carboxylic, and polycyclic aromatic compounds of the humins [19]. The bands may be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [19, 20].

IR spectra of these DOM samples are being presented in fig. 2; table 1 has the spectra data for these bands. They have a variety of bands typical of those for humic materials (humic and fulvic acids) as reported by Shie-jie *et al.* [19], Silverstein *et al.* [20] and Helal *et al.* [22]. The major absorption bands are found in the regions of 2500–3500 cm^{-1} and 650-770 cm^{-1} (O-H stretching and out of plane bending groups), 2500–3500 cm^{-1}, 1350–1470 $cm^{-1}$and 690–900 cm^{-1} (C–H stretching, deformation, and bending and ring puckering respectively), 1650–1800 cm^{-1} (C=O stretching of COOH), 1620–1680 cm^{-1} (alkene/aromatic C=C stretching), 970–1250 cm^{-1} (C–O stretching of alcohols/phenols) 880–995 cm^{-1} and 1395–1440 cm^{-1} (=C–H out of plane bending/C-O-H bending). These spectra show the predominance of OH and COOH groups which are the most characteristic features of humic materials. It is obvious that the IR results are in good agreement with the other characterization findings as reported by Shie-jie *et al.* [19], Silverstein *et al.* [20] and Helal *et al.* [22].

Based on the FTIR and UV-visible spectrophotometer analysis, it can be said that those samples {obtained from groundnut husk (GH), rice husk (RH) and sawdust (SD)} contained DOM that also evidently oxidized As(III) to As(V) {as there was a molybdenum blue complex, formed between

As(V) and ammonium molybdate in an environment of hydrazine sulfate-evident in the blue colour formation}. Also, the similarity of these absorption bands indicated that many similar structural and functional groups existed in the DOM from all the agro wastes.



(a) **(b)**

(c)

Fig. 2: Infra-red spectral of the dissolved organic matter, DOM obtained from (a) sawdust (b) groundnut husk and (c) rice husk

Table 1: UV-visible and Infra-red spectral data of the dissolved organic matter, DOM from sawdust, groundnut husk and rice husk

λ_{max} (nm)/Infra-red frequencies (cm^{-1})	DOM sawdust	G/nut husk	Rice husk
λ_{max}	250.00	256.00	260.00
$\upsilon_{(O-H)}$ (COOH)	2959.5	2967.0	2859.5
$\upsilon_{(C-H)}$ (SP^3)	2959.5	2967.9	2859.5
$\upsilon_{(C=O)}$	1755.6	1722.0	1654.9
$\upsilon_{(C=C)}$	-	-	1654.9
$\upsilon_{(-C-O-)}$ (alcohol/phenols)	1069.7	1058.6	1069.7
$\upsilon_{(CH_2 \text{ and } CH_3)}$	1408.9	1438.8	1408.9
$\upsilon_{(=C-H)}$	902.0	902.0	902.0
$\upsilon_{(C-H)}$ (arene)	864.7	864.7	864.7
$\upsilon_{(O-H)}$ (phenol/alcohols)	685.8	-	685.8
$\upsilon_{(C-O-H)}$	1431.3	1438.8	1435.0

Effect of the initial concentration (volume) on the rate of reaction

Dissolved organic matter (DOM) is known to serve as both an electron donor and electron acceptor during redox reactions, which is an important factor influencing As biogeochemistry in the environment as reported by Wittbrodt and Palmer, [23] and Redman *et al.*, [24]. The DOM comprises humic substances whose classification is based on their solubility in water and composition as; Humins, Humic acids and Fulvic acids. Various agricultural waste products, including; wood sawdust, rice husk and groundnut husks were used as sources of biochar and/or organic matter, which were seen to oxidize As(III) to As(V), [as seen in the formation of molybdenum blue salt:-a product of ammonium molybdate(VI) with As(V) ions (in

the environment of hydrazine sulphate)]. This observations agreed with other researchers who carried out studies on similar work Xiaoling *et al.*, [11], Niedzielski1 and Siepak [7] and Rao *et al.* [8].

The amount of DOM in the samples was determined by the Walkley-Black titrimetric method [10, 12], and was found to contain approximately 0.2592 % DOM from groundnut husk, DOM(GH), 0.2640 % DOM from rice husk, DOM(RH) and 0.2933 % DOM from sawdust, DOM(SD). The percentage weight/volume carbon of these sampled agro wastes were found to be of the order; DOM(SD)>DOM(RH)>DOM(GH).

The intensity of the colour of the molybdenum blue complex is significantly affected by the concentration of hydrazine sulphate in the solution and the concentration of ammonium molybdate(VI), which forms a complex with As(V) ions as reported by Hammes *et al.* [14]. The effect of concentrations of ammonium molybdate and hydrazine sulphate on the formation of molybdenum blue complex was optimised by varying the volumes of 2.5 % ammonium molybdate solution and 0.5 molL^{-1} hydrazine sulphate, and found as 2 ml: 1 ml ammonium molybdate to hydrazine sulphate.

The rate of oxidation of AsO_2^- by DOM was considered and table 2 has the k_{obs} values of these reactions. The reaction rate was found to increase with an increase in volumes of the DOM, but there was no observable rate at 10 ml. The non-observable rate of reaction at very low weight/volume percentage(s) could be because the time range for our reactions were not long enough to notice what has taken place. Again, reactions proceed at a faster rate when concentrations are high because of increased effective collisions resulting in a faster rate of reaction [30], hence oxidation of AsO_2^- by 10 ml percentage weight/volume DOM could not have been possible within the period. Similarly, the rate of oxidation of As(III) by DOM is higher with DOM(SD) compare with DOM(GH) and DOM(RH) as DOM(SD) is found to have a higher percentage weight/volume dissolved organic matter.

Table 2: Pseudo-first order, k_{obs} data for the oxidation of AsO_2^- ion by dissolved organic matter, DOM obtained from sawdust, groundnut husk and rice husk

V (cm³)	k_{obs} (s^{-1}) AsO_2^-/DOM sawdust	G/nut husk	Rice husk
10.00	0.000	0.000	0.000
20.00	0.001	0.000	0.000
30.00	0.001	0.001	0.001
40.00	0.002	0.001	0.001
50.00	0.003	0.002	0.002

Effect of pH on the rate of oxidation of As(III) by DOM

The speciation of metal ions (including As) is a function of pH fig. 3, as reflected in the reaction rate for the oxidation of AsO_2^- by DOM. Table 3 has the values of the rate of reactions, where the rate of reactions increased with an increase in pH; that is, at higher pH there are more of the AsO_2^- ($H_2AsO_3^-$) ions in solution which could collide faster with the DOM, resulting to more effective collisions and the redox exchange process occurred at a faster rate and the rate increased [23, 26, 27]. The redox reaction [oxidation of As(III) by DOM] can be expressed in Equation 3, as reported by Xiaoling *et al.* [11] as;

$$HAsO_2 + 3OH^- + DOM \rightarrow H_2AsO_4^- + \text{reduced DOM} + H_2O \quad \ldots\ldots\ldots (3)$$

Equation 3 indicates the involvement of hydroxyl ions in the oxidation of As(III) by DOM. Hence, as the pH changed from 2-8–10, there is an increase in hydroxyl ions concentration and the rate turn to increase as shown in table 3.

Table 3: Pseudo-first order, k_{pH} data for the oxidation of AsO_2^- by dissolved organic matter, DOM (mL) at varying pH

pH	k_{pH} (s^{-1}) AsO_2^-/DOM sawdust	G/nut husk	Rice husk
2	0.000	0.000	0.000
4	0.000	0.000	0.000
6	0.001	0.001	0.001
8	0.001	0.001	0.001
10	0.002	0.002	0.002

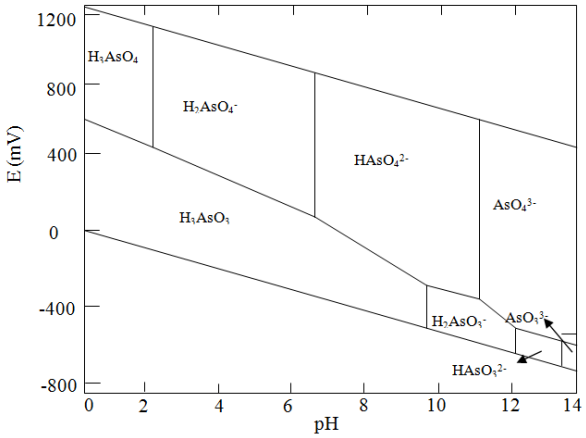


Fig. 3: E-pH diagram for As in an aqueous environment at 25 °C and 1 bar total pressure [10, 26]

Effect of ionic strength on the rate of oxidation of As(III) by DOM

The rate constant of an ionic reaction depends upon the ionic strength of the solution. But, this "primary kinetic salt effect" may be understood qualitatively in terms of favorable interactions between the reactants and activated complex and the ionic atmosphere of charged ions that surround them in solution [28, 29]. The oxidation of AsO_2^- ion by DOM was monitored at varying ionic strength. Table 4 has k_I values of the reactions, which showed a fairly constant rate with varying ionic strength. The independence of the reaction rates on the change in ionic strength suggests that the intermediates are likely a union of two reactants (AsO_2^- and DOM(SD), DOM(GH) DOM(RH)). The negative change in entropy of activation for the reactions (table 6) further supports the formation of the binuclear complex at the activated complex [30]. Furthermore, since the reactions are between AsO_2^- and DOM whose ionic charge is not established and this may, in a simple picture, cause no change in the rate constant with change in ionic strength of the reaction as it is observed in table 4 [28, 29].

Table 4: Pseudo-first order, k_I data for the oxidation of AsO_2^- ion by DOM (ml) at varying ionic strength (0.005–0.021 molL^{-1} $NaNO_3$)

I (molL^{-1})	K_I (s^{-1}) AsO_2^-/DOM Sawdust G/nut husk	Rice husk	
0.005	0.001	0.002	0.001
0.009	0.001	0.001	0.001
0.013	0.001	0.001	0.001
0.017	0.001	0.001	0.001
0.021	0.001	0.001	0.001

Effects of temperature on the rate of oxidation of As(III) by DOM

The results of temperature dependence studies for the oxidation of AsO_2^- ion by DOM, showed an increase in rate as the temperature increased, table 5 has the pseudo-first-order rate constants for these reactions but, there is no observable rate at 288 K and 293 K in all cases of the DOM samples. The activation energy, Ea, enthalpy change, ΔH and entropy change, ΔS for the oxidation reactions are contained in table 6 as obtained from Arrhenius/Eyring's plots. A high E_a value signifies that the rate constant depends strongly on temperature [27] and that a slow reaction would have high energy of activation [31].

The calculated values of activation parameters from these plots (for oxidation of AsO_2^- by DOM) gave high energy of activation as shown in table 6, indicating the temperature dependence of the oxidation of AsO_2^- ion by DOM. This is not much supported by the fact that the enthalpy change for the reaction is negative, indicating that the reaction is exothermic and spontaneous. Moreover, the free energyΔG for the reactions were found to hav e values in the range (-8.43532 kJ mol^{-1}) at 308 K to (-71.46408 kJ mol^{-1}) at 288 K, the values are indicative of the spontaneity of the oxidation of AsO_2^- ion by DOM [15, 31]. Furthermore, the oxidation of AsO_2^- ion by DOM(SD), DOM(GH) and DOM(RH) was considered at 0 °C (273 K). The results showed an increased reaction rate in all cases at this temperature or the reactions rates were comparable to the rate of the reactions at say 30 °C (303 K)–35 °C (308 K), the increased reactions rates at this temperature compared to the aqueous phase (or other temperatures) could likely be due to the freeze concentration effect [11]. The concentrations of DOM, protons and AsO_2^- were high in the ice grain boundary region (that is, at 273 K), which accelerated AsO_2^- ion oxidation. A similar effect was noticed by Xiaoling *et al.* [11]. Thus, concentrating either protons or DOM in the aqueous phase had a similar effect as carrying out the reaction in the ice phase. Therefore, the accelerated oxidation of AsO_2^- in the ice phase could most likely be ascribed to the freeze concentration of both $H^+$and DOM [11].

Table 5: Pseudo-first order, k_T data for the oxidation of AsO_2^- by DOM (ml) at varying temperatures (273, 288–308 K)

T (K)	K_T (s^{-1}) AsO_2^-/DOM Sawdust G/nut husk	Rice husk	
273	0.002	0.002	0.001
288	0.000	0.000	0.000
293	0.000	0.000	0.000
298	0.001	0.001	0.001
303	0.001	0.001	0.001
308	0.003	0.002	0.002

Table 6: Activation parameters (activation energy, enthalpy change and entropy change) of the oxidation reaction between □□□$_□^-$ and DOM

Nature of Reaction	Activation energy, Ea KJmol^{-1}	Enthalpy change, ΔH kJmol^{-1}	Entropy change, ΔS Jmol^{-1}K^{-1}
AsO_2^-/SD	83.31	-80.85	-32.59
AsO_2^-/GH	52.60	-50.08	-135.21
AsO_2^-/RH	52.60	-50.08	-135.21

CONCLUSION

The oxidation of AsO_2^- ion by DOM has been reported, and the study has demonstrated that oxidation of the toxic metal ion As(III) to the less toxic form As(V) by DOM is feasible and fast. The use of DOM to oxidize the metal ions has also given us an alternative approach (greener approach) to the prevention of environmental pollution as these agro wastes are found to be lethal the environment causing one hazard and another. The DOM obtained from the agro wastes (that served as reductants) are of little or no monetary value (charge) and are obtained from renewable sources as wood is sawed frequently, groundnut and rice are cultivated yearly in Nigeria.

AUTHORS CONTRIBUTIONS

Boniface T. Iorhuna: He is the main author and coordinated the article, Raymond A. Wuana: He is the major supervisor of the work done by the other three of the authors, Stephen G. Yiase: He oversaw the laboratory work for the article, Timothy T. Awuhe: He carried out seventy percent of the results discussion, Ernest Isaac: He helped in carrying out the laboratory analysis.

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AUTHORS CONTRIBUTIONS

All the authors have contributed equally.

CONFLICT OF INTERESTS

Declared none

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