

GREEN SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF IRON (III) COMPLEX OF UREA FROM HUMAN URINE AND IRON RUST

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ABSTRACT

This work presents a dry synthesis of Iron (III) complex with urea isolated from human urine and Fe (III) obtained from iron rust particles. Iron (III), PI (Purified iron rust), was isolated from iron rust in 10% hydrochloric acid, HCl and distilled water respectively. The complex was synthesized via dry-synthesis method using the melted urea as reaction medium. The isolated Fe (III) was characterized by elemental analysis which was done using XRF Cu-Zn method. The complex was prepared in a 1:4 metal to ligand (M-L) ratio. The stoichiometry of reaction indicate a 1:3 ratio of M-L (Fe-U). The complex was characterized by FT-IR, UV-vis, XRF and XRD spectroscopic techniques. The Fe (III) isolate and Fe-U complex shows percentage yields of 35.7% and ~92% respectively. The elemental and oxide composition of Fe and Fe₂O₃ (i.e., PI) were 40.387% and 57.753% respectively. The results obtained from the characterization of the iron-urea complex, IUC, indicate FT-IR result as symmetric and asymmetric frequencies with peaks of a combination band of V_s (NH) and V_{as} (NH), C=O and V (C-N) all stretched, XRD showed the crystal to be amorphous. The elemental and oxide composition of the Fe and Fe₂O₃ in IUC were 40.007 and 44.201 respectively. The results obtained revealed that useful complexes can be synthesized easily from waste materials, such as urine and iron rust particles, which complement Green chemistry.

Keywords: Urea, iron-rust, human urine, complexation, iron-urea complex

INTRODUCTION

Organometallic compounds, with their metal-carbon (M-C), lie at the interface between classical organic and inorganic chemistry in dealing with the interaction between inorganic metal species and organic molecules. In the related metal-organic compound area, in contrast, the organic fragment is bound only by metal-heteroatom bonds [1]

Iron is one of the most abundant elements on earth and widely known for its multifarious uses [2] Ferrous metal corrosion is the oxidation of iron metal from Fe to Fe²⁺, further to Fe³⁺, caused by electrons flowing from an anode (a point of positive polarity) to a cathode (a point of negative polarity) [3]. Almost every metal is susceptible to degradation. Rusting of iron and tarnishing of silver are common examples of corrosion. Corrosion is the deterioration or destruction of a substance (metals and alloys) or its properties as a result of an undesirable chemical or electrochemical reaction with the

environment. In simple terminology, the corrosion process involves the reaction of metals with environmental species. Corrosion is irreversible and degenerative and is related to the second law of thermodynamics. A considerable amount of damage is done by corrosion every year, which includes the damaging of iron rods for house decking, pipes/tubes, cars, grills, buses, railings, sinking of ships, falling off bridges, deterioration of statues, etc. Iron rust can be collected from corroded materials in the surrounding environment. Iron (III) can be isolated from rust particles of iron using dilute mineral acids. Purified rust, that is, Fe (III) can further be used to synthesize Fe-urea complex, which is the basis of this study.

Many coordination complexes in which the donor base is urea and the acceptor-acid is Fe (III) have been reported. There have also been millions of synthesized chemical compounds in existence worldwide, with hundreds still

being synthesized, the need to synthesize more complex, especially from waste materials is not out of place. Iron plays an important role in biological systems, because it forms complexes with molecular oxygen in hemoglobin and myoglobin [4]. Iron is also the metal used at the active sites of many important redox enzymes dealing with cellular respiration, oxidation, and reduction in plants and animals [5].

Studies have shown that industrial production of Metal-Urea complexes, MUCs with Fe, Co, Cu, Ni, Zn, Cd, and Pb elements causes substantial environmental pollution. Hence, the need for synthesis via other environmental-friendly methods of synthesis. Urea is an organic ligand that is both bidentate and tridentate. The dentition of urea is due to the presence of lone pairs of electrons in its molecule. It has the ability to coordinate with different metals to form different MUCs [21]. In the pharmaceutical industries, urea alongside some organic compounds is significantly used to synthesize some important compounds [7]. Urea may be prepared in the laboratory by action of ammonia with carbonyl chloride, alkyl carbonates, chloroformates or urethans. It is used for the manufacture of hydrazine in which urea is treated with alkaline sodium hypochlorite. The organic ligand (i.e., Urea) represents not only an important molecule in biology but also an important raw material in chemical industry [8]. Urea has also found its significance in the formation of several organometallic complexes.

Complexes of iron (III) with general molecular formula $[\text{Fe}(\text{L})_n]\text{X}_3$, L = Urea, $n = 4, 6$ and $\text{X} = \text{ClO}_4^-, \text{Cl}^-, \text{Br}^-$, has been determined [9].

Omar in 2012 [10], has reported iron-urea complex of stoichiometric molar ratio of 1:4 (M:U), (where M= Fe (II) and U = urea), which was in agreement with the general molecular formula $\text{FeCl}_2 \cdot 6\text{U} \cdot 3\text{H}_2\text{O}$ or $[\text{Fe}(\text{urea})_6(\text{H}_2\text{O})]\text{Cl}_2$. Charles in 1966 [11] showed that in urea complexes there may be donation from either the nitrogen or oxygen atoms. Eltayeb in 2000 [12], further reported that the infrared spectra of urea complexes revealed that urea forms nitrogen-metal bond of molecular formula, $[\text{Fe}(\text{urea})_6]\text{Cl}_3$ with coordination occurring from oxygen rather than nitrogen. Both $\text{FeCl}_2 \cdot 6\text{U} \cdot 3\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 3\text{U} \cdot 5\text{H}_2\text{O}$ have been prepared by mixing equal methanolic solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at room temperature, 60°C and 70°C respectively [13, 17]. Gabriela & Neculai in 2006 [14] have found that urea complexes formed in solid medium, that is, when urea is melted and used as reaction medium occurs with very good result. It was also established that the melted urea is a very good reaction medium, which in combination with other suitable organic ligand can serve to prepare a large number of compounds or complexes with different metals. It therefore implies that the dry-synthesis method, if used to synthesis urea complex gives a better yield. Urea ligand and iron (III) of this study were both obtained from so-called “environmental waste” materials: urine and iron rust particles. “Green synthesis” is used here to mean dry-synthesis or hazardous-free chemical materials.

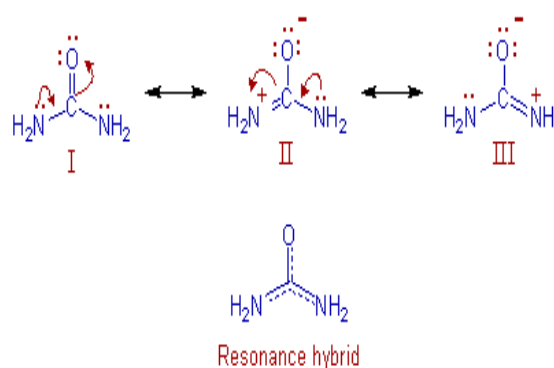


Fig 1: The Resonance Structure

<https://chemistry.stackexchange.com/questions/103472/shape-of-urea-molecule-around-n-atom>
[20]

EXPERIMENTAL

Materials and Methods

The materials used for this work include urea from human urine and iron (III) from iron-rust. Urea was obtained from a previous work by Gongden et al., in 2019 [15]. The urea was isolated from human urine by evaporating (or concentrating) urine sample, nitration of the urine concentrates to form urea nitrate and then purification of the urea nitrate followed by crystallization and re-crystallization. This is summarized in fig. 2 below.

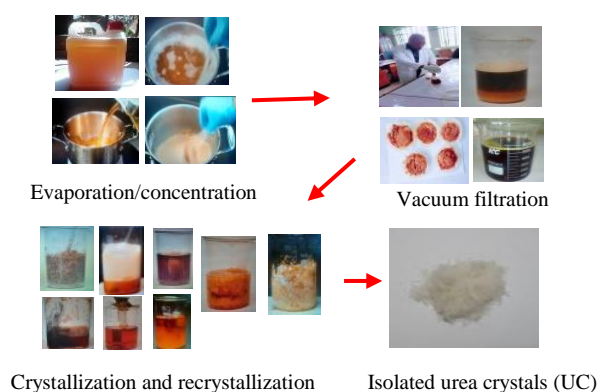


Fig 2: Isolation of urea from

Synthesis of iron-urea complex

The complexation of iron-urea complex, IUC was carried out following the method used by Neculai and Gabriela, Adel & Megahed, as modified [14, 17, 19]. The dry chemical-free synthesis method was applied to synthesize the complex. The complex was prepared in 1:4 (Metal-ligand) ratio. 4g of UC was first weighed accurately using the AR2130, Ohaus Cooperation, Japan Weighing Balance, into a clean-dry boiling tube. The boiling tube was covered with porcelain, to prevent any gas from escaping. The test tube was then suspended inside a 250 ml beaker containing about 150 ml water. The beaker was placed on top of hot plate at 125°C, slightly below the melting point of urea crystal. After about 15 minutes, when the UC was completely melted (plate 1a, 1b), 1g of the purified rust, PI was added. The temperature was kept under control between 115-125°C, below the decomposition temperature of urea, which is 133 - 135°C. The

The simple random sampling method was used to collect rust iron/iron rust particles from within the University of Jos Senior Staff quarters, in the Jos North Local Government Area of Plateau State, Nigeria. Iron-rust samples (particles) were collected from the rusting rods of old decking from the garages of houses within the University senior staff quarters. The iron-rust collected was scraped, crushed and sieved to a fine powder. About 200 grams iron rust (powdered) collected was stirred in 1500 ml of 8 % hydrochloric acid, HCl for about 3 minutes. The acid was then removed by filtration. The residue of the iron-rust was again washed in a beaker with another 1000 ml portion of 8% HCl, and then 500 L. It was then rinsed with 250ml of distilled water. The washed solution was further removed by filtration. The residue which was suspected to be iron (III) chloride, FeCl_3 , was labelled PI and then allowed to dry.

heating continued at 125°C for two more hours until no gases or steams were further emitted (plate 2a, 2b.). The reaction system (test tube) was then removed from the beaker and allowed to cool. After cooling, the complex was washed with small amounts of water and ethanol in order to remove the urea excess. The synthesized iron-urea complex, IUC, was further dried on CaCl_2 in a desiccator until the mass remained constant.

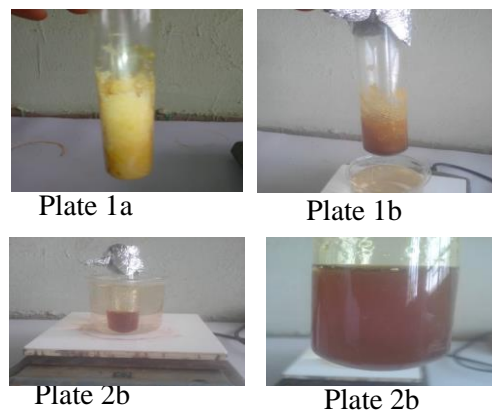


Plate 2: complexation of IUC

Characterization of iron-urea complex, IUC.

Instrumental methods were applied to characterize the isolated iron (III), PI and the complex, IUC formed. Elemental analysis of PI was carried out by XRF and FT-IR spectroscopy. Finally, the IUC obtained was further characterized spectrally using UV, FT-IR, XRF and XRD. These were all carried out at the SPECIAL LABORATORY SERVICES, No. 14, Forte Oil Station Polytechnic Road, Kaduna South, Kaduna State, Nigeria. Analysis for their physical properties were also carried out at the Post Graduate laboratory of the Department of Chemistry, Faculty of Natural Sciences, University of Jos Plateau State, Nigeria.

Procedures for the Instrumental Analysis

1. FT-IR

For functional unit determination, a Shimadzu Fourier transform Infrared Spectrophotometer- FTIR 8400 S was used. Samples were weight-in at 0.01 g and homogenized with 0.01 g KBr anhydrous by mortar agate. The mixtures were pressed by vacuum hydraulic (GrasebySpecac) at 1.2 psi to obtain transparency pellet. Scanned sample passed through infra-red, where its continuing wavelength was recorded by detector that connected to computer, gave the characteristic tested sample spectrum. The samples were scanned in the absorption area of 600 to 4000 cm^{-1} . The results of analysis consisted of chemical structure, molecular binding form and certain functional groups of tested samples as basic of spectrum type.

2. Spectrophotometer (UV-vis)

The T70 PG Instruments' UV-spectrophotometer was used to analyze the samples at different wavelength and absorption the spectrophotometer was first switched on and allowed to stabilize before the calibration was done using distilled

water and a black body. After calibration, the wavelength was set to 330nm and the corresponding absorption was displayed after pressing the key for absorption. This step was followed for other wavelengths until it got to 900 nm.

3. X-ray fluorescent (XRF)

The X-ray fluorescent (XRF) Nitron 3000 was powered on and allowed to stabilize for five minutes after initialization. The Cu-Zn method was chosen, which normally detects large amounts of elements and sesquioxides due to its intensity. The sample was placed on a sample holder, while the ray point was placed over it and the ray button was pressed to start taking the data. The data were collected in triplicates and this automatically took the average. This procedure was followed for all the samples to get the percentage chemical composition in oxide and elemental form.

4. XRD Procedure

The XRD was powered and from the panel, the voltage and current were set at 45kV and 40 mA. The temperature was set at 21-23°C. The computer system was switched on and the software of XRD was double clicked to run. The settings dialogue was clicked and all the required setting of power and temperature were checked to correspond to that of the XRD. The sample was poured into a sample holder and then placed in the sample chamber column. Then the door was shut and confirmed from the computer. The measurement setting was then set for scan axis as Gonio, start and end position were also set so is the angle and time of scan. The scan began and then stopped at the required time and the result was saved to a file.

RESULT AND DISCUSION

Percentage Yield of PI and IUC

Fig. 4 shows the steps and chemical reaction for the isolation of iron (III)

from iron rust with about 10% HCl solution.

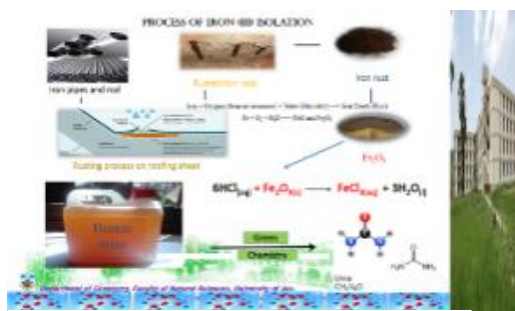


Fig 4a: Process of iron (III) isolation

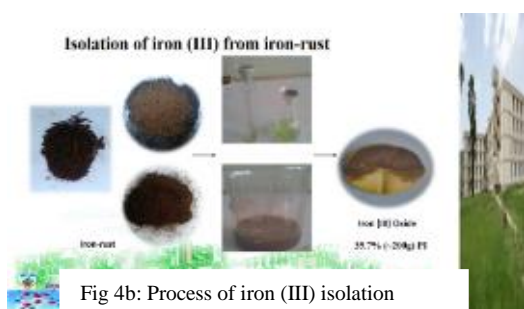


Fig 4b: Process of iron (III) isolation

The percentage yields of PI and IUC were calculated using the two formula below.

$$\% \text{ yield of PI} = \frac{\text{Mass of isolated Fe (III)}}{\text{Total mass of Iron}} \times 100$$

$$\% \text{ yield of IUC} = \frac{\text{Mass of IUC in g}}{(\text{UC} + \text{PI}) \text{ g}} \times 100$$

~92% (i.e., 9.2 g) yield of IUC was obtained from 10 g (i.e., 2 g PI and 8 g UC). This high yield of the complex was expected, because of the method used to synthesize the complex. The dry synthesis only required a direct combination of the metal and ligand. The loss of about 0.8g may be as a result of the escape of gas, possibly, CO₂ gas from the reaction medium. Though the yield of Fe (III), was low at about 35.7%, but it corresponded to about 35.5 g of isolated Fe (III) per 100 g of iron rust. However, the actual percentage composition of Fe (III) in PI is about 57.753% (table 1a).

Table 1: Result of the physical properties of UC and IUC

+ Slightly soluble; ++ soluble; +++ very soluble

Parameter	Sample UC	IUC
Water (27°C)	+++	+++
Ethanol (27°C)	++	+++
Methanol (27°C)	++	++
pH at (27°C)	5.70	8.10
Refractive Index (n)	1.321	1.433
Melting point (°C)	135-141	89-92
Electric Conductivity (S/cm) (27°C and atm pressure)	1.9 x 10 ⁻⁴	1.4 x 10 ³
Colour and particulate nature	White Powder	Brown

The physical property tests such as color, solubility and melting point were determined for UC, PI and IUC. The results are given in Table 4. Both UC and IUC are soluble in water, ethanol and methanol. This result agrees with the report of [10]. The melting point range of UC and IUC are 135 – 140°C and 89-92°C respectively. The electrical conductivities of UC and IUC showed that it is a non-electrolyte, while IUC was a good electrolyte. The pH values of UC and IUC are 5.70 and 8.10 respectively. The pH result shows that the complex formed is slightly alkaline.

Plate 3: IUC complex

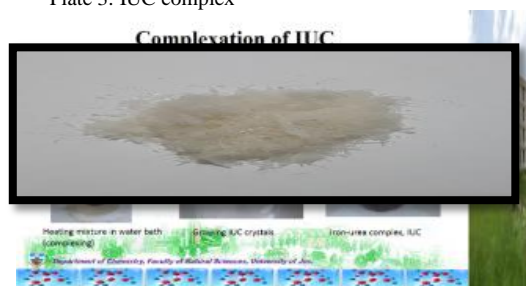


Plate 4: UC appearance

UV-vis spectra result of UC and IUC

The UV-vis spectrum (Fig 5) of the UC, shows a peak absorbance of 3.095 at wavelength of 212.80 nm. The crystal is found to be transparent in the region between 300 and 230 nm, while two distinct peaks were observed at 238 nm and 215 nm respectively for IUC (Fig 6). The slight difference may be attributed to the difference in their appearance (plates 3 & plate 4) respectively. The high absorbance of 3.095 (Table 2) of UC may be due to the transparent nature of the solution of

the sample, which must have allowed a higher transmittance of light through the sample. However, it could be that the presence of Fe (III) in the complex, IUC had resulted in a brown colouration (Fig 7), which may have produced the slightly high wavelength of 215 nm and a low absorbance of 0.944. The second peak (Peak 1 of Fig 7), nevertheless, showed a low absorption of 0.906 at a wavelength of 238nm.

Table 2: UV-vis Spectra results of U and IUC

No.		UC	IUC
1.	Wavelength (nm)	212.80	238.00
	Absorbance	3.095	0.906
2.	Wavelength (nm)	-	215.50
	Absorbance	-	0.944
3.	Wavelength (nm)	-	
	Absorbance	-	

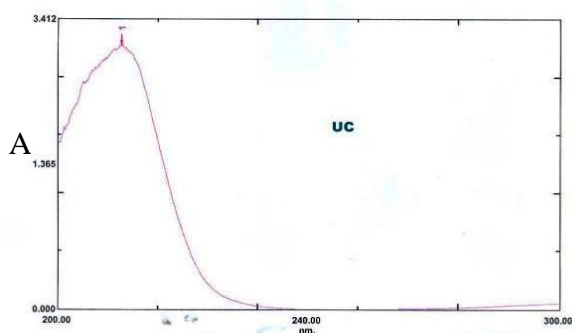


Fig 4: UV-vis spectrum of UC

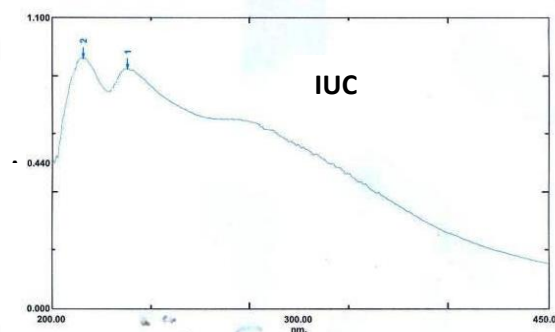


Fig 5: UV-vis spectrum of, IUC

FT-IR spectra analysis of UC and IUC

The FTIR spectra of the UC and IUC, were recorded on FTIR-ATR (Shimadzu 8400S model) utilizing KBr disc process and all samples were scanned over a range of 750-4000 cm^{-1} . The FT-IR spectra of UC and IUC are shown Figs 6 & 7. The FT-IR spectrum of the IUC showed a dual peak at 2924.18 and 2862.46 cm^{-1} resulting to the symmetric stretch which required slightly more energy (2924.18 cm^{-1}) for a transition. The second peak however is an antisymmetric stretch, which

requires slightly less energy (2862.46 cm^{-1}). The symmetric and antisymmetric coupling observed at these energies may be due to the vibration of neighboring bonds in the complex, which corresponded to the vibrational mode of N-H group of a secondary amide [16, 18]. The bands which corresponded to $-\text{NH}_2$ stretching of UC and IUC were 3394.83 and 3417 cm^{-1} respectively (table 5).

The characteristic vibrational frequency of urea, UC, has been reported in the literature of

previous work [15]. An intense sharp peak occurred each, at 1527.67 and 1612.14 cm^{-1} for UC and IUC respectively (fig 6 and 7). The peaks were attributed to the presence of the carbonyl functional group. The peak corresponding to $\nu\text{C-N}$ was observed at 1033.88 for UC. However, the introduction of Fe (III) from PI must have caused a shift in the frequency of CUI to 1018.45 cm^{-1} . The presence of peak at 2924.18 and 2862.46 cm^{-1}

corresponds to N-H bending of both free –NH₂ and N-H of semicarbazone group [18]. These frequencies were indications that there could be an $n^*-\sigma$ transition of the double bond of C=O. The identified functional groups in UC and IUC₁ crystals were systematically assigned with the corresponding wavenumber, in table 4. The prominent shifts in the vibrational frequencies of IUC indicated the incorporation of Fe (III).

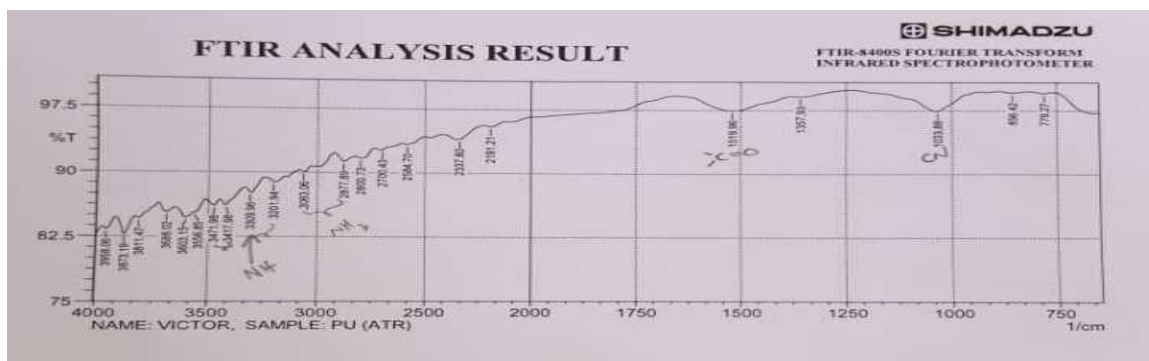


Fig 6: FTIR Spectrum for UC

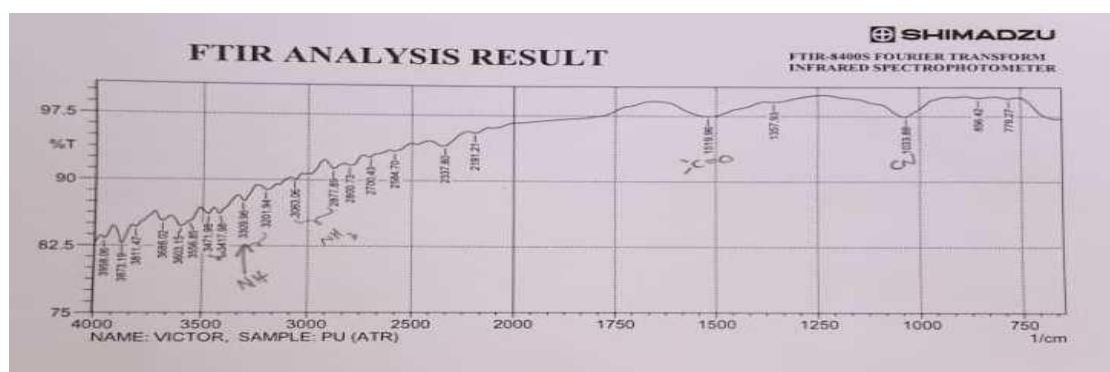


Fig 7: FTIR Spectrum for IUC

Table 3: Characteristic FT-IR frequencies and tentative assignments of urea UC and IUC

Reference	UC (cm^{-1})	Intensity (%T)	IUC ₁ (cm^{-1})	Intensity (%T)	Band Assignments
3422–3320 (m)	3487.42 3394.83	84.893 85.431	3417.98 3263.66	77.830 77.678	$\left. \begin{array}{l} \nu_s (\text{NH}_2) \\ \nu_{as} (\text{NH}_2) \end{array} \right\}$ stretch
3000 – 2800 (sh)	Combination band		2924.18 2862.46	70.706 76.917	$\left. \begin{array}{l} \nu_s (\text{NH}) \\ \nu_{as} (\text{NH}) \end{array} \right\}$ stretch
1700–1510 (s)	1527.67	96.389	1612.54	83.333	C=O stretch
1250–1020 (m)	1033.88	98.347	1018.45	49.847	ν (C-N) stretch

vs: very strong, m: medium, s: strong, sh: shoulder, w: weak

Elemental analysis of PI and IUC

The XRF spectra results of the elemental analysis of IUC and PI (Figs 8 & 9) shows distinct peaks of elements present. These elements and their oxides are recorded in table 4 and table 5 respectively. The elemental composition of Fe was 40.387% before complexation (Table 4a). This result indicated that a good amount of the iron metal which is of interest is present in the iron isolate. Chloride ion was also present in about 1.311%. ‘Bal’ which means balance, represents other component, such as radioactive isotopes, Nitrogen, Hydrogen, etc, which could not be detected by the machine.

It was observed that after complexation the composition of Fe atom reduced very slightly by 0.380%. This slight decrease may be due to the interaction of Fe³⁺ with

the lone pairs of electrons of the urea ligands. The oxide composition of PI and IUC are given in tables 5a and 5b respectively. The oxide composition of PI was 57.753%, indicated that good percentage of Fe³⁺ was isolated from the iron rust. However, there was a relatively high drop in the iron (III) oxide composition of ICU of about 13.552% after complexation. This drop was however expected, due to the possible coordination of the urea molecules with the Fe³⁺ from the oxide. Chloride composition of both PI and IUC did not change. The reason for this could plausibly be that it neutralises the +3 charge from Fe³⁺. The result also suggests the presence of anionic specie outside the coordination sphere of the complex as illustrated in the chemical equation below:

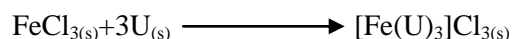


Table 4: Elemental composition of isolated iron (III) PI, and Ironurea complex, IUC using XRF Cu-Zn method

Table 4a: Elemental composition of isolated iron, PI

Table 4b: Elemental composition of Ironurea Complex, IUC

ELEMENT	PI	ELEMENT	IUC
OXIDE	PI	OXIDE	PI
Bal	55.814	Bal	21.701
CuO	0.064	CuO	0.064
NiO	0.011	NiO	0.957
Fe ₂ O ₃	57.753	Fe ₂ O ₃	57.753
MnO	0.225	MnO	0.225
S	0.183	S	0.172
Cr ₂ O ₃	0.078	Cr ₂ O ₃	0.078
Cl	1.311	Cl	1.311
TiO ₂	0.208	TiO ₂	0.208
CaO	0.179	CaO	0.179
Al ₂ O ₃	0.679	Al ₂ O ₃	0.679
Sn	0.003	Sn	0.003
MgO	0	MgO	0
Sb	0.044	Sb	0.039
ZnO	0.083	ZnO	0.083
SiO ₂	2.048	SiO ₂	2.048
TOTAL	61.328	TOTAL	61.328
Bi	< LOD	Pb	0.047
TOTAL	99.988	Bi	< LOD
		TOTAL	99.988

Table 5: Oxide Composition of isolated iron (III) PI & iron-urea complex, IUC using XRF Cu-Zn method.

Table 5a: Oxides of PI

OXIDE	PI
CuO	0.064
NiO	0.011
Fe₂O₃	57.753
MnO	0.225
Cr₂O₃	0.078
TiO₂	0.208
CaO	0.179
Al₂O₃	0.679
MgO	0
ZnO	0.083
SiO₂	2.048
TOTAL	61.328

Table 5b: Oxides of IUC

OXIDE	IUC
CuO	0.064
NiO	0.011
Fe₂O₃	44.201
MnO	0.225
Cr₂O₃	0.078
TiO₂	0.258
CaO	0.299
Al₂O₃	0.509
MgO	0.001
ZnO	0.083
P₂O₅	13.552
SiO₂	2.048
TOTAL	61.328

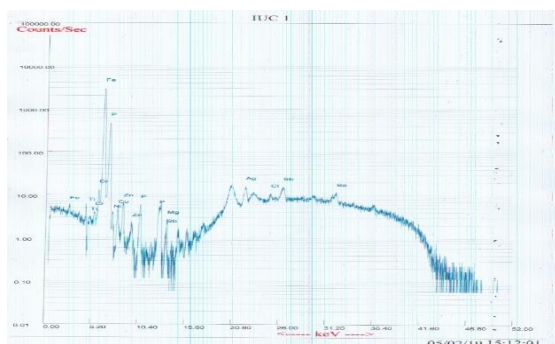


Fig 8: XRF Spectrum for IUC

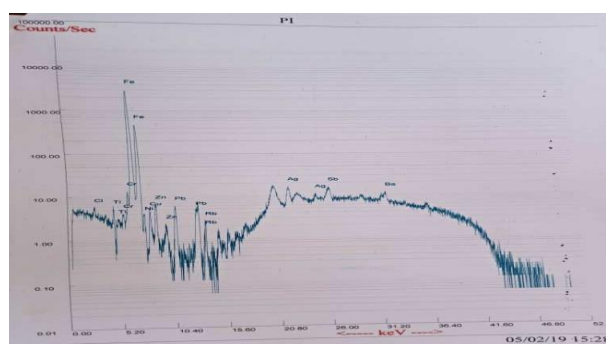


Fig 9: XRF Spectrum for PI

Result of XRD analysis

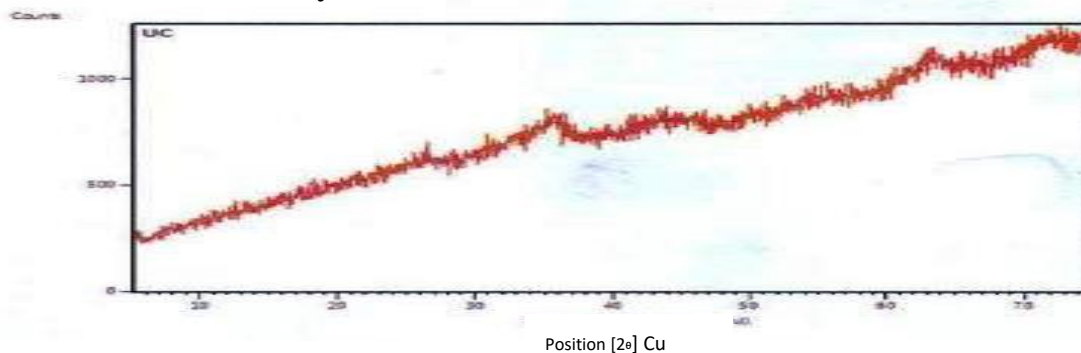


Fig 10: XRD spectrum of IUC

The XRD of IUC was carried out (Figs 10) and the results of the spectrum showed that it is an amorphous solid.

Proposed Structure of IUC

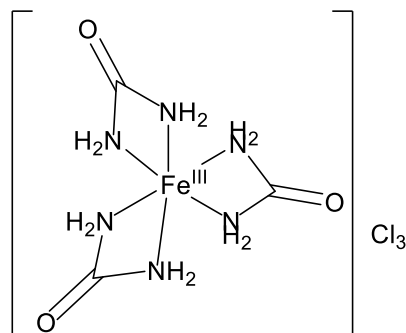


Fig. 11: Proposed structure of iron-urea complex.

CONCLUSION

The present work provided a green synthesis method to synthesize Iron (III) complex of urea from human urine and iron rust. The complex was characterized using several conventional techniques like FT-IR, UV-vis, XRF and XRD. The detailed characterizations by FT-IR and XRF revealed that the synthesized IUC coordination occur via Fe-N site. The XRD result shows IUC to be amorphous. The stoichiometry of reaction indicated a 1:3 ratio of M-L (Fe-U). Urea,

which served as the ligand, supplied six lone pairs of electrons through the nitrogen atoms. The isolated urea which has already been reported in a previous work by Gongden et al., was said to have been characterized by ¹H-NMR, ¹³C-NMR, UV-vis and FT-IR. This new approach introduced a new route for efficient green synthesis of organometallic complexes from environmental waste, which also played an important role in reduction of environmental pollution and use of toxic chemicals in synthesis of Iron-urea complexes.

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