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Synthesis and Evaluation of Iron (III)-Red Onion Skin Extract Azo Complexes as Pigments for Surface Coatings in Oilfield Environment

A. A. Akaho[1*], U. J. Chukwu[2] and O. Akaranta[1,2]

[1]World Bank Africa Centre of Excellence for Oilfield Chemicals Research, University of Port Harcourt, Nigeria.
[2]Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria.

Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Red Onion skin extract (ROSE) -azo compound of 2-aminobenzoic acid and Iron (III) metal complex of the azo compound (Fe-ABmROSE) were synthesized and characterized using FT-IR spectroscopy, UV-Visible absorption spectroscopy and Scanning electron microscopy. The IR Spectra showed the values of N=N- stretching frequency of 1496.81cm^{-1} at 1500 cm^{-1} in ABmROSE. This stretching frequency is absent in the Fe-ABmROSE. This is an indication of the involvement of the N=N- bond in coordination to the metal. ABmROSE shows an absorption maximum at 560.1 nm. This band was shifted to 310 nm in Fe-ABmROSE. This suggests an interaction between the Fe and the azo compound.

Keywords: 2-aminobenzoic acid; red onion skin extract; Fe-ABmROSE; complex; diazotization.

**Corresponding author: E-mail: akaho.azabaze@aceuniport.org;*

1. INTRODUCTION

Flavonoids are a big family of over 6,500 hydroxylated polyphenolic compounds that carry out very useful functions in plants [1,2]. They are classified into 12 major subclasses based on their chemical structures. Six of these: anthocynanidins, flavan-3-ols, flavonols, flavones, flavanones and isoflavones are of dietary significance. Glycosylated flavonols (bound to at least one sugar molecule) are the most widely distributed flavonoids in the diet and they are reported to have antioxidant, antiviral and anti-bacterial anti-microbial, anti-carcinogenic and anti-fungal properties [3,4,5,6,7]. Some epidemiological studies show that foods rich in flavonoids protect against cardiovascular diseases. Some epidemiological studies show that foods rich in flavonoids protect against cardiovascular diseases.

Onion (*Allium cepa*), the second most important vegetable extensively eaten throughout the world is found in every home and it is the richest source of flavonoids and organosulphur compounds [8,9]. The outer parts of the onion bulb known as onion peels or onion skin are usually thrown away as wastes and this may raise environmental concerns if they are not correctly disposed. Onion skins are known to contain the highest concentrations of a polyphenolic compound called "quercetin" and other flavonoids [10,11,12]. In addition to its anti-oxidative, anti-apoptosis and anti-inflammation properties (Alrawaiq & Abdullah, 2014), studies have shown that quercetin and other flavonoids are good metal chelators [13,14,15,16]. Extracting very important constituents from onion skin is not only economically beneficial but environment friendly.

Quercetin is a polyphenolic compound with five hydroxyl groups which are used for bonding with metals or other compounds. The word quercetin is derived from the Latin word *quercetum*, which means oak forest. The German nutrition expert, Prof. Stephan C. Bischoff, "Quercetin is a most promising compound in disease prevention and therapy" [17]. Quercetin is found in many fruits, vegetables and leaves and the highest levels of quercetin have been found in onion (Allium cepa), Asparagus (Asparagus officinalis) and red lettuce (Lactuca sativa), [11,12]. Quercetin forms complexes with metals in solution [18,19]. It has been reported to have inhibitory properties [20]. The ability of quercetin to chelate with metals is credited to the presence of the five hydroxyl groups at positions 3, 5, 7, 3', 4' and a carbonyl group at position 4 as shown on Fig. 1. The metal chelating properties of quercetin could be enhanced with the introduction of azo (N=N) functional groups in the structure. This could be achieved via coupling reaction with aromatic diazonium salts. The proposed reaction mechanism and products for the synthesis of diazonium salt and coupling with "quercetin rich" red onion skin extract are shown on scheme 1 and equation 1 respectively.

Azo compounds are highly coloured and the presence of the N=N- provides lone pair of electrons that can be donated to a metal to form complex compounds [21]. Jarad et al. reported that azo compounds have been extensively utilized in the textile industries. Metal chelates of azo compounds have been highly studied for their antimicrobial, anticancer and analytical applications. Slabbert [22] confirmed that Azo compounds form complexes with metals. The synthesis and characterization of Ni(II) and Cu(II) complexes of four azo compounds have been carried out. Their coordination behaviours were studied using analytical tools [23]. Azo dyes are used in many industries including food, cosmetics, textiles, pharmaceuticals, and leather tanning [24].

It has been established from literature that both quercetin and azo dyes are metal chelators. The thrust of this work therefore was to synthesis and characterize azo-metal complex of quercetin derived from Red Onion Skin Extract (ROSE).

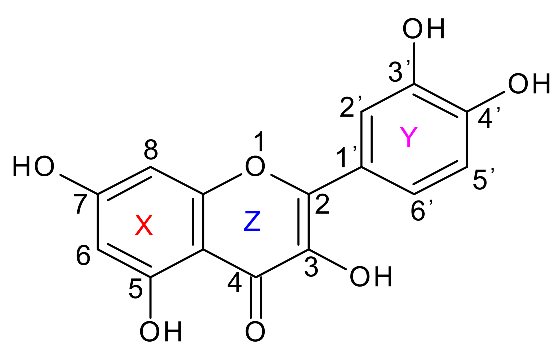


Fig. 1. Structure of quercetin

2. EXPERIMENTAL

Red Onion skins were sourced by peeling the dry skin of red onion bulbs. 2-aminobenzoic acid, methanol, acetone, sodium hydroxide, sodium nitrite and Iron (III) salts were of analytical grade and were purchased from Sigma Aldrich. Infra-red spectra were obtained using KBr discs on a Shimadzu 8400S FTIR spectrophotometer in the region of 500-4000cm$^{-1.}$ Ultra violet spectra were carried out using Cary 50 Bio UV Spectrophotometer within the wavelengths of 200-800 nm. Scanning Electron microscopy of the samples was done using SEM. JEOL JXA 6400. The pH was measured using a pH meter and melting points determined using Gallen kemp melting point apparatus.

2.1 Collection and Pretreatment of Red Onion Skin (ROS)

Red onion skins were collected from Fruit Garden market in Port Harcourt, Nigeria. The skins were cleaned and dried. The dried skins were powdered using Binatone blender, sieved to a mesh size of 355µm and stored in dry, air-tight containers. They were used in the extraction process following the method according to Manasa et al. [9] with slight modification.

2.2 Chemical Modification of Red Onion Skin Extract (ROSE)

The red onion skin extract (ROSE) was modified using benzenediazonium chloride, an aromatic diazonium salt. The salt was synthesized by diazotization reaction of 2-aminobenzoic acid according to the method of Myek, Adesina and Batari, (2014) with slight modification.

2.2.1 Synthesis of the Benzenediazonium salt.

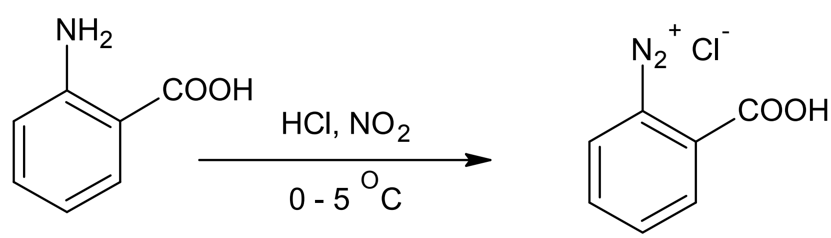
Method of Myek et al. [25] was used with slight modification. 1.37 g (0.01 mol) of 2-aminobenzoic acid was dissolved into 45 mL of distilled water. 12 mL of concentrated hydrochloric acid was slowly added while stirring. The resulting solution was cooled in an ice-bath at 0-5ºC. 5 mL of cold $NaNO_2$ (0.01 mol, 0.7g) was added drop wise while stirring and maintaining the temperature between 0-5ºC. After the addition, the reaction mixture was stirred for another 2-3 minutes. The resulted solution was benzenediazonium chloride. The reaction equation for the synthesis of the diazonium salt is shown by scheme 1.

2.2.2 Preparation of modified red onion skin extract of benzenediazonium salt (ABmROSE)

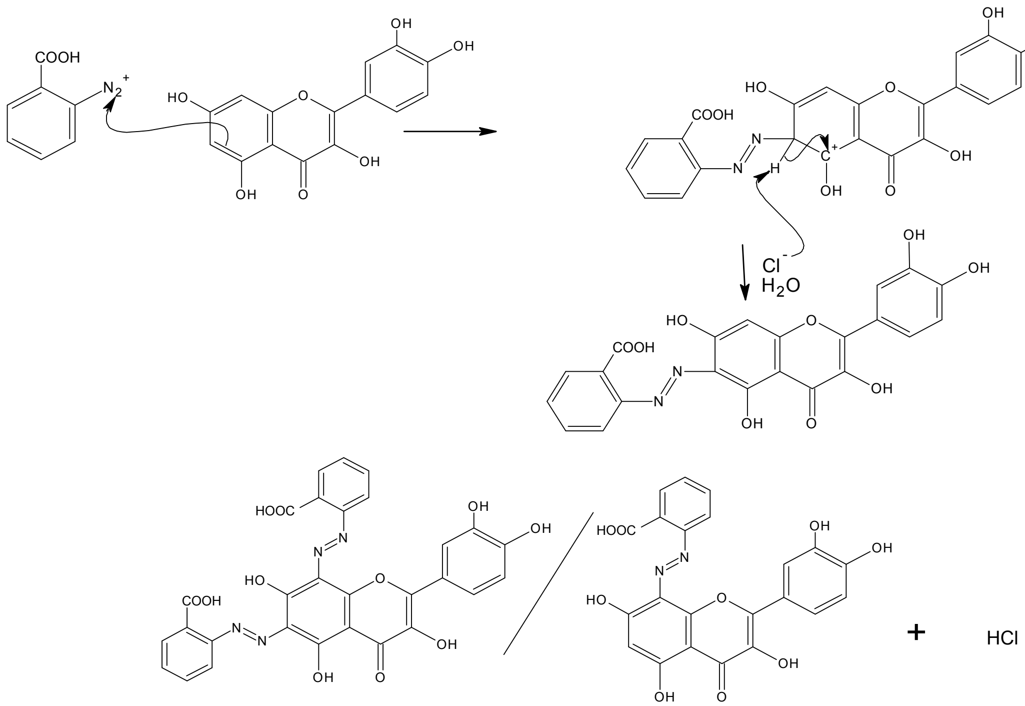
An alkaline solution of ROSE was prepared by dissolving 3.02 g of ROSE into 30 mL of 10% sodium hydroxide solution in a 250 mL beaker. The resulting solution was cooled in ice-bath at 0-5ºC. 2-aminobenzoic acid modified red onion skin extract (ABmROSE) was prepared by slowly adding the benzenediazonium chloride solution to the alkaline solution of red onion skin extract while stirring at 0-5ºC. After addition, the reaction mixture was stirred for another 10 to 15 minutes to ensure the reaction goes to completion. The resulting precipitate was filtered using suction filtration apparatus, washed with small amount of cold water and dried at ambient temperature for 3-5 days.

2.2.3 Preparation of metal complex ABmROSE

The method of Mishra et al. [26] was adopted with slight modification. In a two necked round bottom flask equipped with an electromagnetic stirrer and thermometer, 0.9g (0.002 mol) of red onion skin extract modified with 2-aminobenzoic acid salt (ABmROSE) was dissolved in 5cm^3 of methanol for 10 minutes. The colour of the solution was reddish brown. 0.65g (0.002 mol) of Iron (III) chloride was added quickly in the reaction mixture. The colour of the solution turned to dark brown. It was stirred for two hours, then filtered and the filtrate evaporated at room temperature. The resulting dark coloured product was washed with methanol and dried in a vacuum desiccator.



Scheme 1. Synthesis of diazonium salts of 2-aminobenzoic acid



Equation 1. Proposed mechanism for the modification of UROSE with diazonium salt of 2-aminobenzoic

3. RESULTS AND DISCUSSION

3.1 Chemical Characterization

An azo compound was synthesized by coupling diazotized 2-aminobenzoic acid with onion skin extract. Its metal complex was produced by reacting the azo compound which serves as a ligand with Iron (III) chloride. The Infra-Red spectra of the azo compound and its metal complex were obtained. The appearance of the azo band (1450-1600cm^{-1}) confirmed the presence of the azo group (N=N) in the azo compound and in its metal complex [27]. Figs. 2 and 3 are the FTIR results of ABmROSE and Fe-ABmROSE.

The IR spectra showed the value of N=N stretching frequency for ABmROSE to be 1411.94cm^{-1} with an area of 19.06 while Fe-ABmROSE has stretching frequency at 1408.08cm^{-1} with an area of 24.084. This is an indication of the involvement of the N=N bond in coordination to the metal. The O-H stretching frequency decreased from 3402.54cm^{-1} in UROSE with an area of 300.428 to 3456.55cm^{-1} in ABmROSE and Fe-ABmROSE. The area under the peak for Fe-ABmROSE (34.754) is larger than that of ABmROSE (26.3). Change in the position of O-H shows that it is involved in coordination between the azo compound and its metal complex [27]. The FTIR shows that N=N and N=C bonds are present in the azo compound and in its metal complex. The Scanning Electron Microscopy for the compounds formed had different morphologies, indicating that they are indeed new products.

Table 1. Physical characterization

Compound	Colour	Melting Point/^{0}C	Yield%	Soluble in	Insoluble in
UROSE	Red	102-105	/	M ,E, EA, Ac	H, H_2O
ABmROSE	Brick Red	78-80	74.2	M, E, EA, Ac	H, H_2O
Fe-ABmROSE	Dark Brown	>370	75.3	M, E, EA, Ac	H, H_2O

Where M= Methanol, E= Ethanol, EA= Ethyl ether, Ac=Acetone, H=Hexane

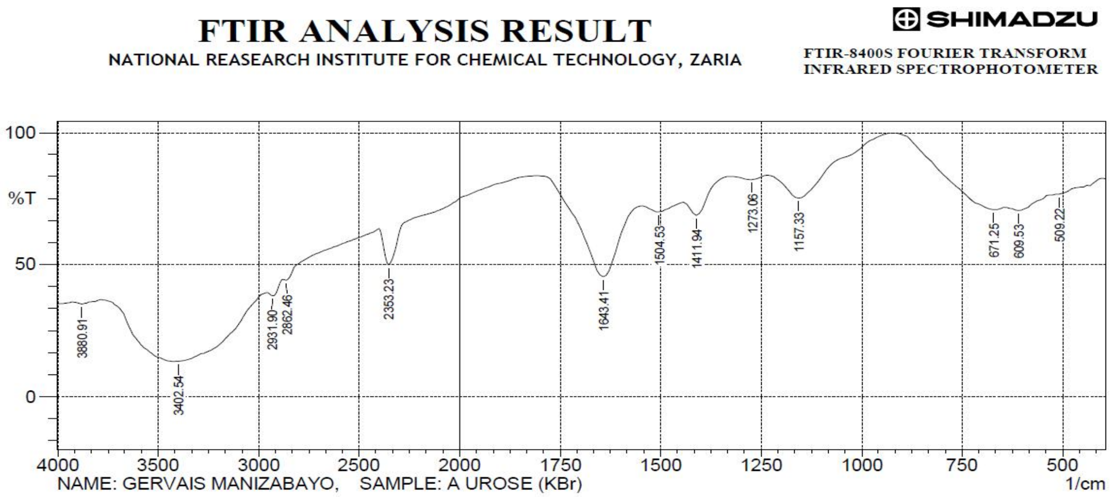


Fig. 2. Infrared spectrum of unmodified onion skin extracts (UROSE)

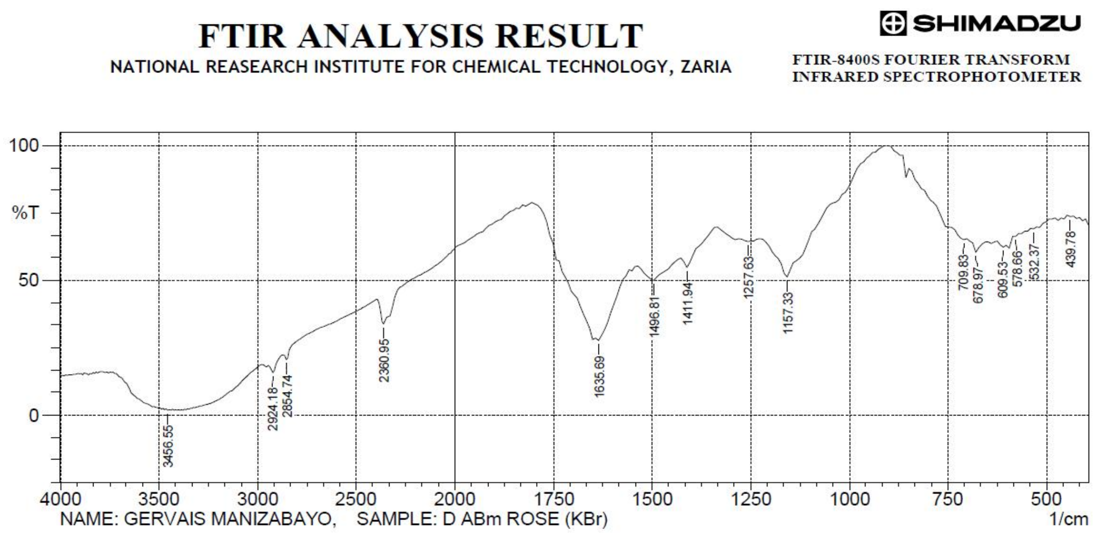


Fig. 3. Infrared spectrum of ABmROSE

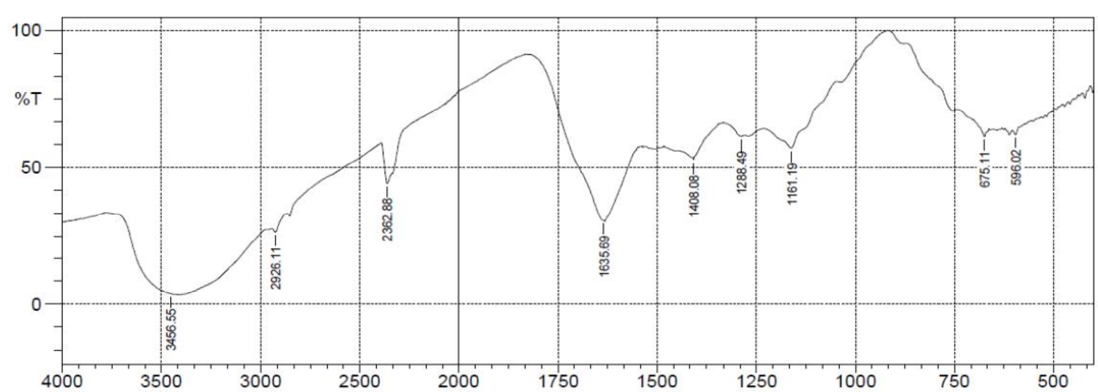


Fig. 4. Infrared spectrum of Fe-ABmROSE

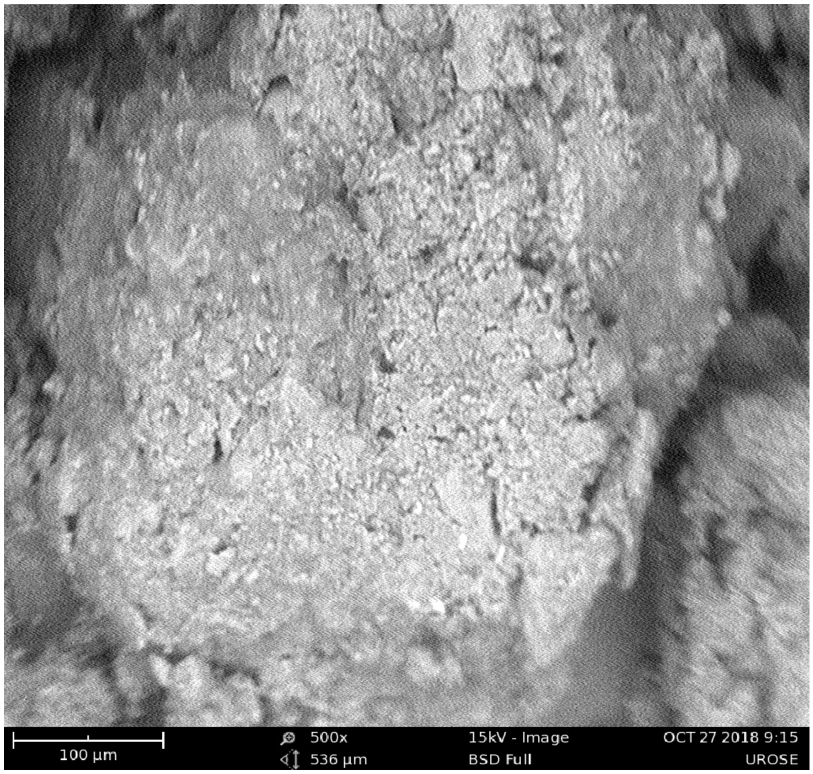


Fig. 5. Scanning electron microscopy of UROSE

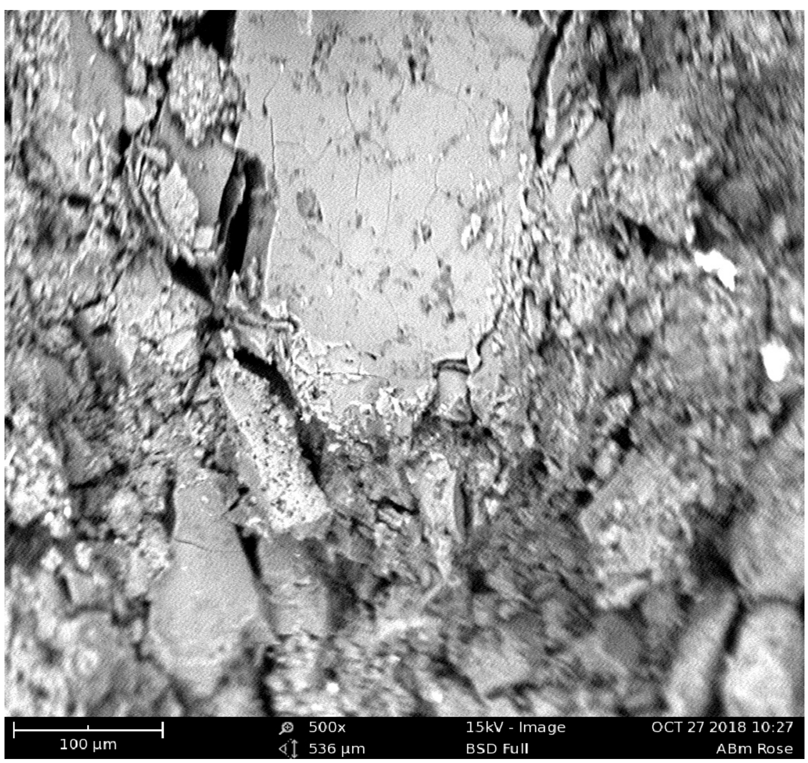


Fig. 6. Scanning electron microscopy of ABm ROSE

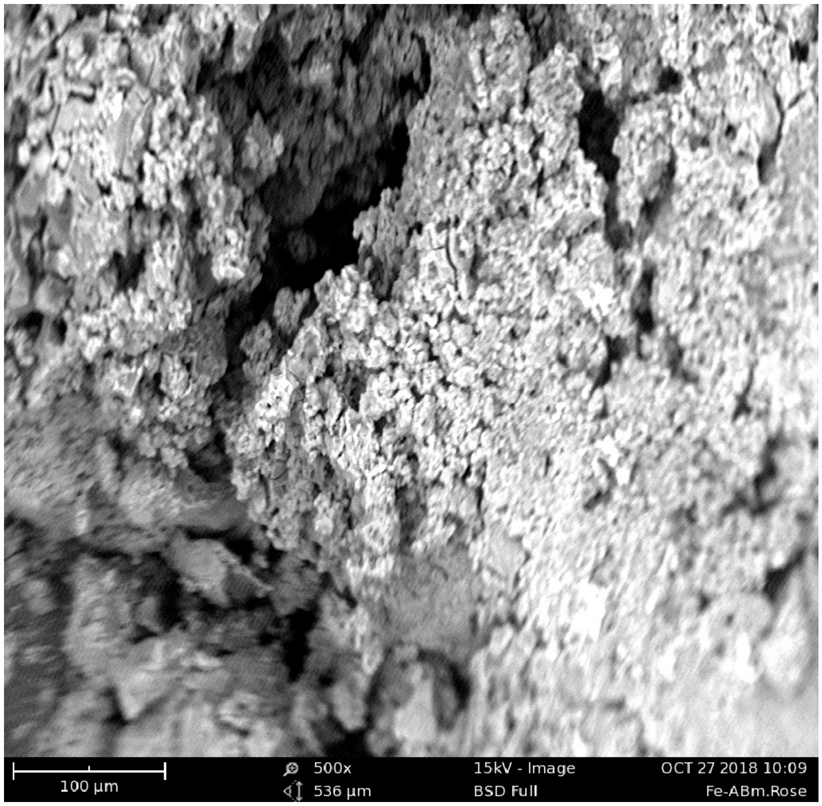


Fig. 7. Scanning electron microscopy for Fe-ABmROSE

The metal complex has melting point higher than 370ºC while ABmROSE melts between 78-80ºC. This is an indication that the metal complex is preferable in applications where very high temperature is required. The azo compound and metal complex are insoluble in water and hexane but soluble in other organic solvents. The colours also attest that they are different product.

4. CONCLUSION

We were able to synthesize an azo compound by coupling diazotized 2-aminobenzoic acid with red onion skin extract which has quercetin as its major constituent. Its Iron complex was also synthesized. They were characterized using FTIR and UV-Visible spectrophotometers. It is on the basis of the FTIR results that the structures of the compound and metal complex were proposed.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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