Synthesis and Characterization of Ag/FeOOH and Ag/Fe$_2$O$_3$ derived from Iron Ore Tailings

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Abstract

This work is an experimental study on nano-crystalline Ag/FeOOH and Ag/Fe$_2$O$_3$ powder derived from the iron ore tailings. Iron ore tailings is a mineral waste contains 15- 20% Fe$_2$O$_3$ remaining mostly SiO$_2$. Iron is extracted out as FeCl$_3$ by hydrochloric acid digestion of iron ore tailings. The obtained aq. FeCl$_3$ solution was precipitated as ferric hydroxide by using different reagents such as aq.NH$_4$OH, aq. NaOH and Urea. Urea hydrolysis was carried out at 95 °C while in other two cases heating was not employed. Each ferric hydroxide obtained by the above three methods was divided into two portions. One portion of it was directly used as support for silver nanoparticles to obtain Ag/FeOOH. The other portion of FeOOH was calcined at 550 °C for 4 h to convert it into ferric oxide . These ferric oxides were then used as supports for silver nanoparticles to obtain Ag/Fe$_2$O$_3$. On observation, XRD pattern shows very broad diffraction peaks for the Ag/FeOOH samples and those peaks were identified for goethite phase. But Ag/Fe$_2$O$_3$ samples show very sharp diffraction peaks which were well matched with hematite phase. Raman Spectra of various Ag/FeOOH and Ag/Fe$_2$O$_3$ samples have shown very prominent Raman bands at various region between 200-1400 cm^{-1}. These bands are identified for various modes of vibration for Fe-O. UV-visible (diffuse) spectra of Ag/FeOOH and Ag/Fe$_2$O$_3$ samples show two absorption bands appeared at the same position although the supports for silver were of two different kinds (FeOOH and Fe$_2$O$_3$). TEM picture of Ag/FeOOH and Ag/Fe$_2$O$_3$ samples prepared via urea hydrolysis show that silver nanoparticles are well dispersed/ supported on FeOOH and Fe$_2$O$_3$ matrix. The particle size of FeOOH is found to be 60-70 nm range whereas the particle size of silver nanoparticles supported on FeOOH is observed to be <10 nm. TEM image of Ag/Fe$_2$O$_3$ shows particle size of silver <10 nm and 90-100 nm for Fe$_2$O$_3$. TGA curve of uncalcined Ag/FeOOH prepared using sodium hydroxide shows weight loss at two stages; first stage is below 200 °C and second stage is between 400- 450 °C. They correspond to dehydration of physically adsorbed water molecule and dehydroxylation of FeOOH to form Fe$_2$O$_3$. The present work also showed that the obtained silver loaded ferric oxide hydroxide and ferric oxide possess antibacterial properties which can be exploited to kill bacterial growth in a given region.

Keywords: silver nanoparticle , dehydroxylation, urea hydrolysis, diffraction peaks

Introduction

The generation of tailings is estimated to be 10-25 wt.% of the total iron ore mined, thus amounting to around 18 million tons (MT) per year in India [1]. The concept of utilisation of solid wastes embraces the basic principles of recovery, recycling and converting to value added products. Recovery and recycling is a well-recognized process that again generates waste which results in a disposal problem. Hence the concept of converting the solid industrial waste

into value added products have been receiving considerable attention in recent years. As one of the most widely used metals iron is used extensively in machinery, structural engineering, automobiles, surgical equipment, etc.. Metallic iron is rarely found on earth as it is very reactive towards oxygen and water. Metallic iron gets oxidized in presence of oxygen to form iron oxides, so most of the iron ores exist in the form of oxides of iron. The oxidation states of iron in iron oxides are +2 and +3. Among these two, most stable oxidation state of iron is +3. Some of the iron oxides are found in nature as wustite (FeO), hematite (α-Fe$_2$O$_3$), maghemite (γ-Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$), etc. These oxides find application in various purposes. Nano sized iron oxide is used as catalyst [2]. It can be employed as an adsorbent in wastewater treatment . It has been reported that iron oxides can also be used as pigments, flocculants, gas censors, coatings, magnetic recording devices, etc. Iron oxides are used as toners and inks in xerography .Superparamagnetic iron oxide can be potentially used as a contrast reagent in magnetic resonance imaging (MRI) [3]. Iron can also form oxide hydroxides like goethite, akaganeite and lepidocrocite and they are widely used in water treatment for the removal of toxic ions [2].

The huge amount of tailings, a bi-product of iron ore processing industries, is stored in the form of massive ponds. They are not environment friendly, so several attempts have been made to utilize the tailings in an efficient manner. Iron ore tailings can be converted into value added products. It has been reported that iron ore tailings can be used to manufacture ceramic floors and wall tiles which can be used as building materials [4]. Tailings can be used to produce cement and due to its iron content, the conventional usage of iron powder can be eliminated [5]. Tailings having high silicon, potassium and sodium content can be used as a raw material for glass production . Tailings containing Zn, Mn, Cu, Mo, V, B, Fe, P etc. can be used in the production of trace element fertilizers . Iron ore tailings can be used to synthesize akaganeite and hematite nanoparticles which can be used in water purification.

Iron ore tailings contain about 26% of iron oxide [6]. If this iron oxide from tailings is extracted out for further use, the amount of waste generated can be reduced significantly. Therefore, in this work an attempt is made to extract iron from the tailings in the form of iron chloride and then convert it into hydroxide and oxide to use them as support for silver nanoparticles for its effective environmental applications. Ag/FeOOH and Ag/Fe$_2$O$_3$ samples obtained out of tailings are characterized through various sophisticated techniques and are tested for antibacterial properties.

Materials and methods

Preheated (900°C for 4 hours) iron ore tailing was used as a starting material to synthesize ferric chloride which was then converted into ferric oxide-hydroxide and ferric oxide. The acid used for the digestion of iron ore tailing was hydrochloric acid (HIMEDIA, about 35% pure). Ferric oxide-hydroxide was precipitated out from ferric chloride using different precipitating reagents such as NH$_4$OH, NaOH and urea. To anchor silver nanoparticles on ferric oxide hydroxide and ferric oxide, silver nitrate (AgNO$_3$) was used.

Iron is extracted out as FeCl$_3$ by hydrochloric acid digestion of iron ore tailings. The obtained aq. FeCl$_3$ solution was precipitated as ferric hydroxide by using different reagents such as aq.NH$_4$OH, aq. NaOH and urea. Urea hydrolysis was carried out at 95 °C while in other two cases heating was not employed. Each ferric hydroxide obtained by the above three methods was divided into two portions. One portion of it was directly used as support for silver nanoparticles to obtain Ag/FeOOH. For supporting silver nanoparticles on FeOOH, at first FeOOH powder was

dispersed in water under stirring condition and appropriate amount of aq. $AgNO_3$ solution was added to it drop-wise and its pH was adjusted to 9 by addition of aq. NH_4OH. The mixture was dried in oven at 170 ^{o}C for 4-5 hours. Ag/FeOOH obtained through aq.NH_4OH, aq. NaOH and urea are denoted as Ag/FeOOH-NH_4OH, Ag/FeOOH-NaOH and Ag/FeOOH-urea.

The other portion of FeOOH was calcined at 550 °C for 4 h to convert it into ferric oxide. These ferric oxides were then used as supports for silver nanoparticles. Silver loading on ferric oxides were done as in the case of FeOOH. The schematic representation of experimental procedure adopted for the synthesis of above samples is demonstrated in Figure-1.
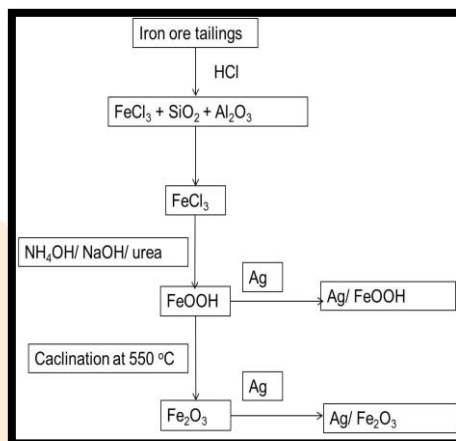
Figure- 1. Flowchart for preparation of Ag/FeOOH and Ag/Fe$_2$O$_3$

Characterization

After calcination, the structural, morphological, magnetic characterizations of the samples were performed by using several advanced experimental techniques. The X-Ray powder diffraction pattern were recorded in order to identify the inorganic phases present in the samples on a X-Ray Diffractometer (PANalytical, X'pert) equipped with Cu K-α radiation (λ = 1.54056 A) and it was operated at 40 kV and 30 mA. The laser Raman spectra were measured on a micro Raman spectrometer (RENISHAW in Via Raman Microscope) with an Ar- green laser beam (514nm) as an excitation source to identify the phases present in the sample. To know the optical absorption property of the sample, UV- Visible (diffuse reflectance) spectra were recorded for the Ag/FeOOH and Ag/Fe$_2$O$_3$ samples with the help of UV-visible spectrophotometer (Schimadzu) equipped with a diffuse reflectance attachment. The spectra were recorded from 800 to 200 nm wavelength at a scanning rate of 100 nm/min. The particle morphology, size and shape of Ag/FeOOH and Ag/Fe$_2$O$_3$ samples were observed under Transmission Electron Microscope (FEI, Technai) operated at 200 kV. The microscope was attached with facilities for observing selected area electron diffraction (SAED) pattern and EDS for elemental characterization. For TEM measurement, samples were dispersed in ethanol, sonicated and then were supported on a carbon coated copper grid. TGA of samples were done with the help of Mettler Toledo instrument (TGS/SDTA851^e). TGA curves of uncalcined ferric hydroxide samples were recorded from room temperature (30 ^{o}C) to 1000 ^{o}C at a heating rate of 20 degree/min to know its decomposition temperature. Antibacterial properties of the samples were tested with Escherichia coli and Staphylococcus aureus. For this, spot inoculations of samples were made

on the bacterium grown on petri plates. The zone of inhibition area was used as a semi quantitative measurement for the antibacterial property of the samples.

Result & Discussion

XRD patterns of iron ore tailings and its acid leached residues are shown in Figure-2. It reveals that both samples have shown very prominent diffraction peaks indicating for their crystallinity. It also shows the presence of hematite and quartz as major phase and corundum as minor phase in iron ore tailings. Whereas in case of acid leached residue, quartz phase was found to be as major phase and corundum as the minor phase. No diffraction peaks for hematite are found in the acid leached residue indicating that hematite is leached out as aq. $FeCl_3$ during HCl leaching/digestion at 95 °C.

XRD pattern shows very broad diffraction peaks for the Ag/FeOOH samples and those peaks were identified for goethite phase which was well compared with standard powder diffraction (JCPDS) file number 00-017-0536. But Ag/Fe_2O_3 samples show very sharp diffraction peaks which were well matched with JCPDS file number 00-032-0469 of hematite phase. The XRD pattern of some Ag/ FeOOH and Ag/ Fe_2O_3 samples are depicted in Figure-3. Further, existence of FeOOH and Fe_2O_3 were confirmed in Raman spectra.
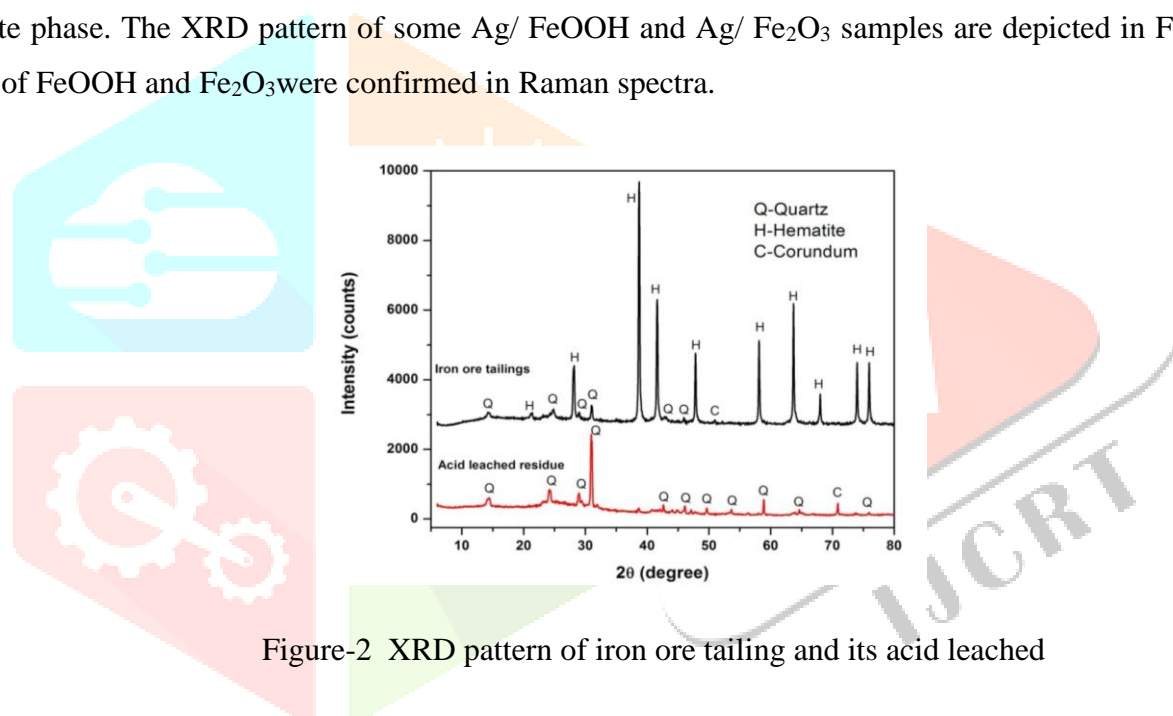
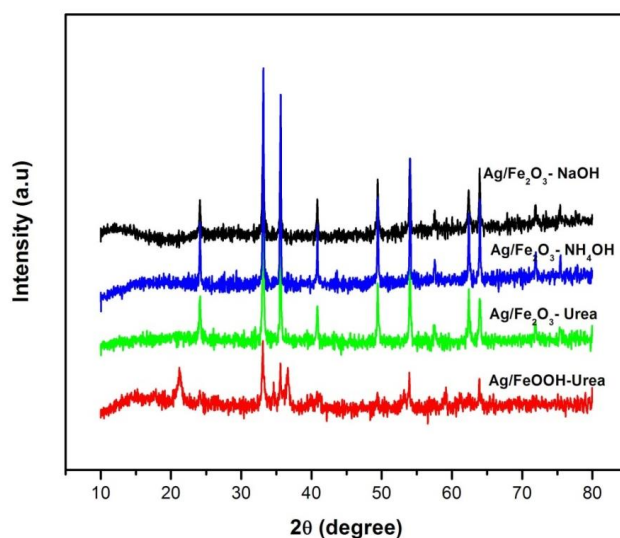Figure-2 XRD pattern of iron ore tailing and its acid leached

Figure-3   XRD patterns of some Ag/ FeOOH and Ag/ Fe_2O_3

Raman Spectra of various Ag/FeOOH and Ag/Fe_2O_3 samples are shown in Figure-4 and Figure-5 respectively. All samples have shown very prominent Raman bands at various region between 200-1400 cm^{-1}.
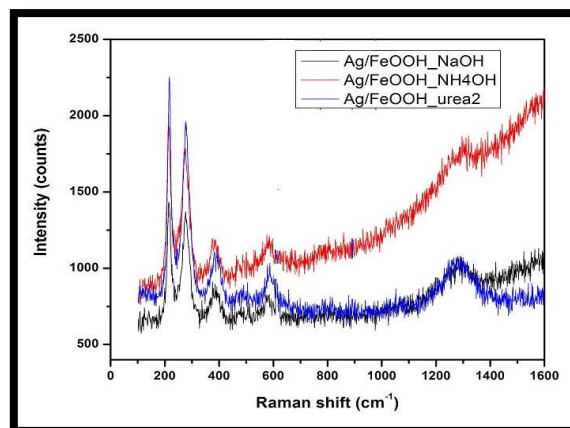

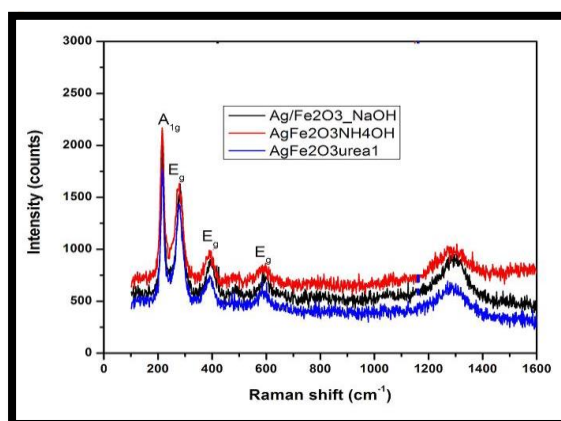Figure-4 Raman Spectra of various Ag/FeOOH samples

Figure- 5. Raman Spectra of various Ag/Fe2O3

UV-visible (diffuse) spectra of Ag/FeOOH and Ag/Fe_2O_3 samples prepared by various methods are shown in Figure-6 and Figure-7 respectively. It shows that all samples absorb at 425 and 580 nm wavelength region. The 425 nm band corresponds to the surface plasmon resonance line for metallic silver nanoparticles whereas 580 nm band is ascribed to the $FeOOH/Fe_2O_3$. The above two absorption bands appeared at the same position although the supports for silver were of two different kinds (FeOOH and Fe_2O_3). Further, it is observed that use of different precipitation reagents, such as NaOH, NH_4OH and urea does not bring any change in the spectra.
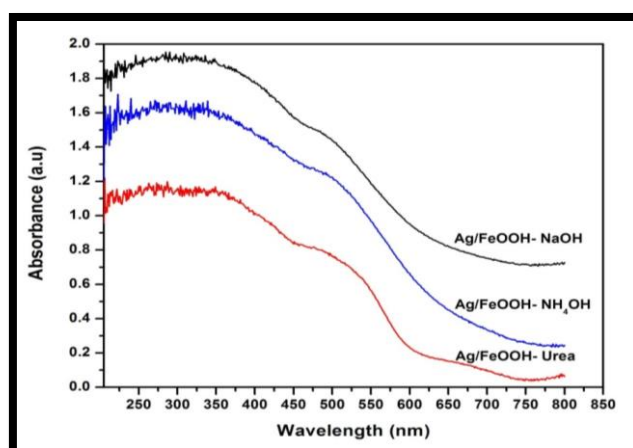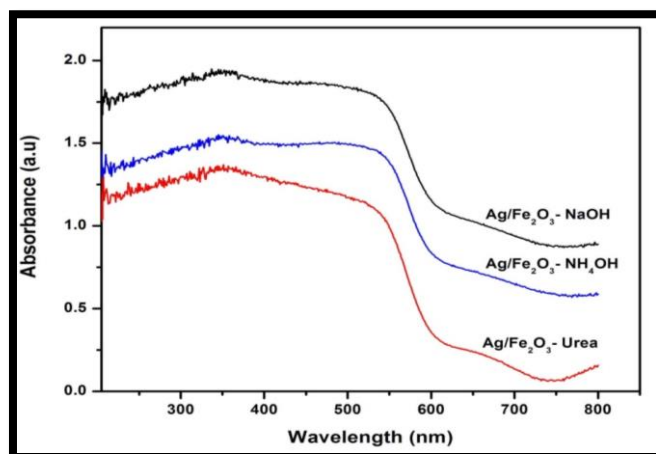
Figure- 6. DRS of various Ag/FeOOH samples

Figure- 7. DRS of various Ag/Fe2O3 samples

TEM picture of Ag/FeOOH and Ag/Fe_2O_3 samples prepared via urea hydrolysis are depicted in Figure- 8 and Figure- 11 respectively. They show that silver nanoparticles are well dispersed/ supported on FeOOH and Fe_2O_3 matrix. The particle size of FeOOH is found to be 60-70 nm range whereas the particle size of silver nanoparticles supported on FeOOH is observed to be <10 nm. The corresponding SAED pattern shows diffraction rings for metallic silver nanoparticles as well as FeOOH phase. The identified ring patterns for silver and FeOOH phases are indexed in Figure- 9. EDS spectrum shows peaks corresponding to Ag, Fe and O. The peaks observed for C and Cu are due to the carbon coated Cu grid used. The EDS spectrum is shown in Figure- 10.

TEM image of Ag/Fe_2O_3 shows particle size of silver <10 nm and 90-100 nm for Fe_2O_3. It is interesting to note that Fe_2O_3 particles have porous structure which can increase the surface area. The SAED pattern shows diffraction rings for metallic silver nanoparticles as well as Fe_2O_3 phase. The ring patterns for silver and Fe_2O_3 are shown in Figure- 12. EDS spectrum shows peaks for Ag, Fe and O. The peaks observed for C and Cu are due to the use of carbon coated copper grid. The EDS spectrum is shown in Figure- 13.
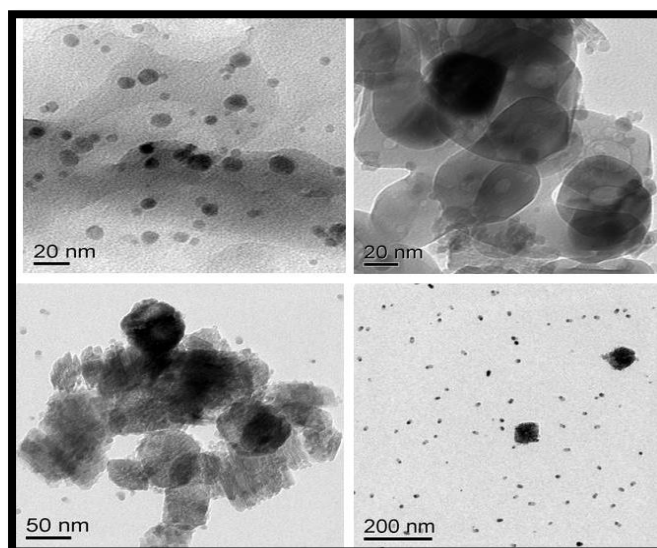

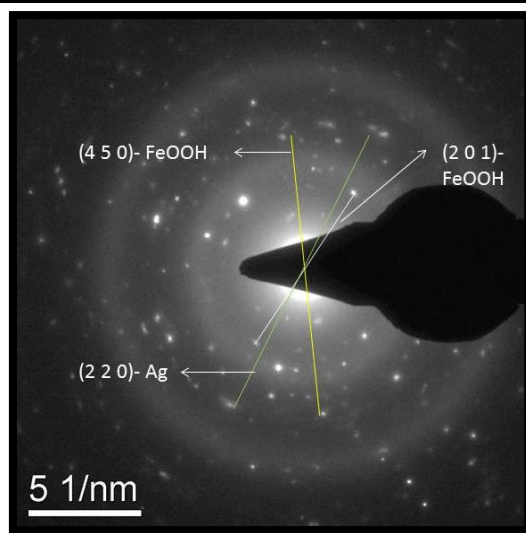Figure- 8.   TEM pictures of Ag/FeOOH prepared by urea hydrolysis

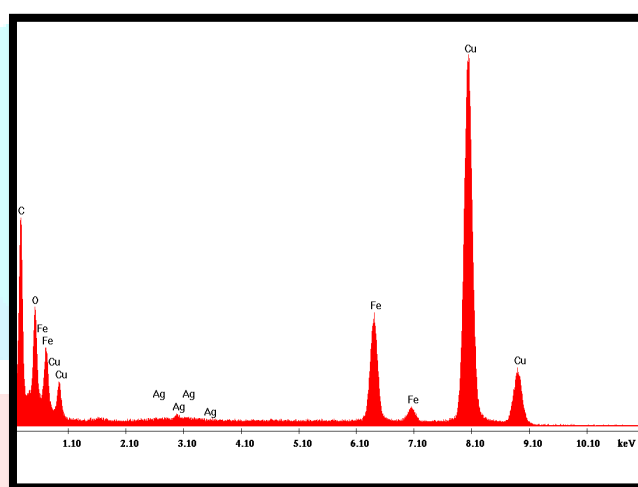Figure- 9. Selected Area Electron Diffraction (SAED) pattern of Ag/FeOOH prepared by urea

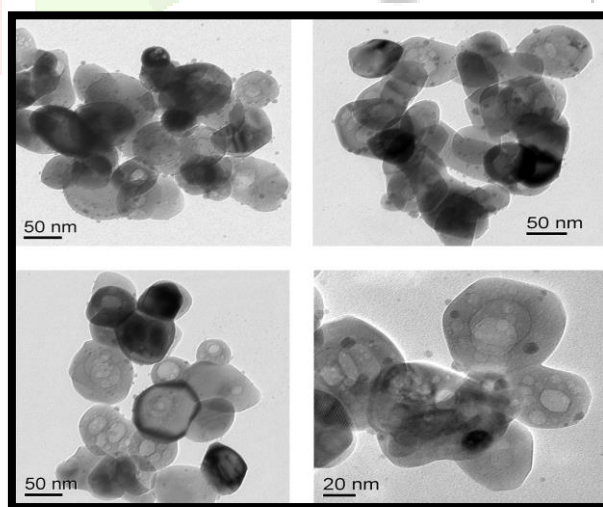Figure- 10. EDS spectrum of Ag/FeOOH sample prepared by urea

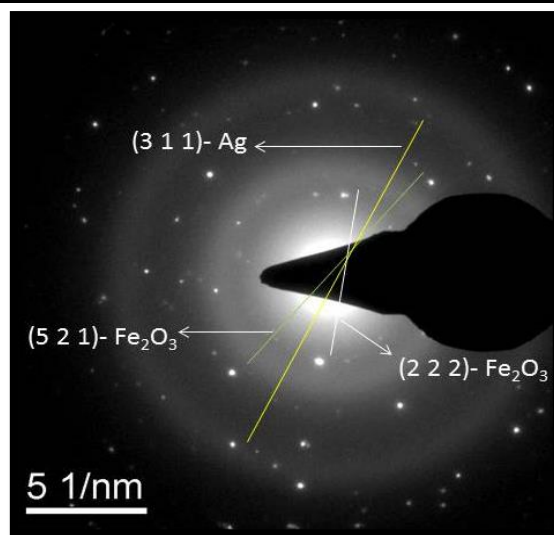Figure- 11. TEM   pictures of Ag/Fe_2O_3 prepared by urea hydrolysis

Figure- 12.   Selected Area Electron Diffraction (SAED) pattern of Ag/Fe$_2$O$_3$ prepared by urea hydrolysis
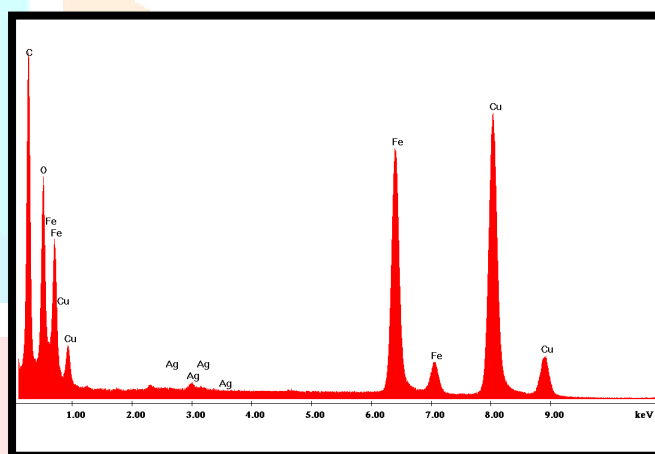

Figure- 13.   EDS spectrum of Ag/Fe$_2$O$_3$ prepared by urea hydrolysis

TGA curve of uncalcined Ag/FeOOH prepared using sodium hydroxide is shown in Figure- 14. It shows weight loss at two stages; first stage is below 200 ºC and second stage is between 400- 450 ºC. They correspond to dehydration of physically adsorbed water molecule and dehydroxylation of FeOOH to form Fe$_2$O$_3$. The DSC curve of the sample is shown in Figure- 15.
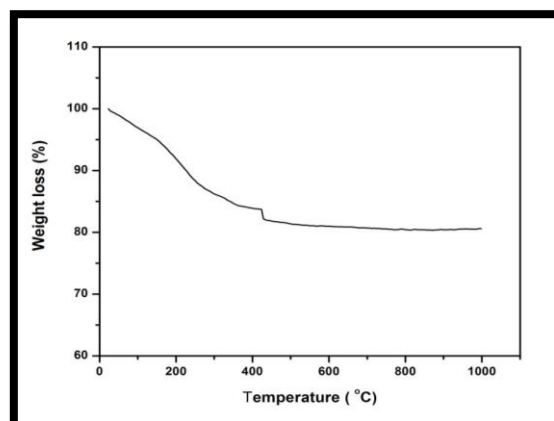

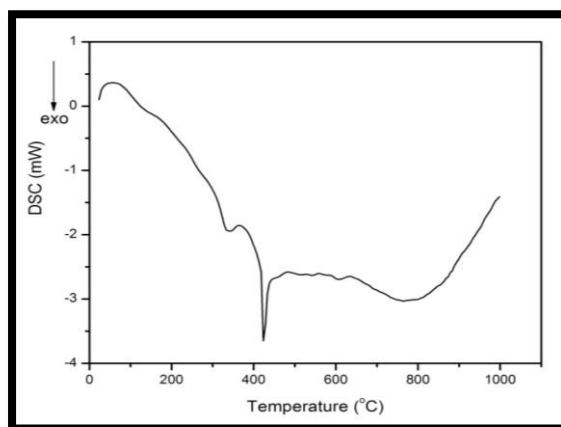Figure- 14. TGA curve of Ag/FeOOH- NaOH

Figure- 15. DSC curve of Ag/FeOOH- NaOH

Ag/ FeOOH as well as Ag/ Fe_2O_3 samples are exhibiting excellent antibacterial properties against Escherichia coli and Staphylococcus aureus. But the sample is more effective in killing Staphylococcus aureus (gram positive bacteria) than Escherichia coli (gram negative bacteria). The spot inoculation of Escherichia coli and Staphylococcus aureus is shown in Figure- 16 and Figure- 17 respectively. The labeling of samples is done as: 1-Ag/ FeOOH- NaOH, 2- Ag/ FeOOH- NH$_4$OH, 3- Ag/ FeOOH- urea, 4- Ag/ Fe_2O_3- NaOH, 5- Ag/ Fe_2O_3- NH$_4$OH, 6- Ag/ Fe_2O_3- urea
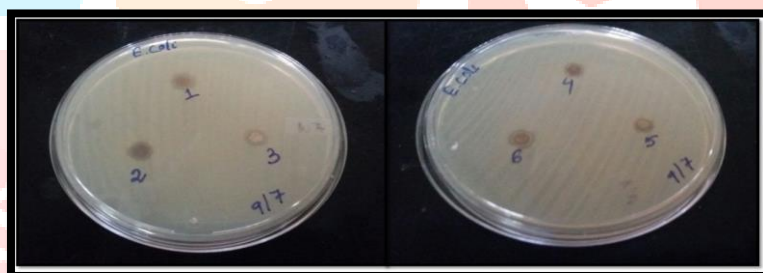

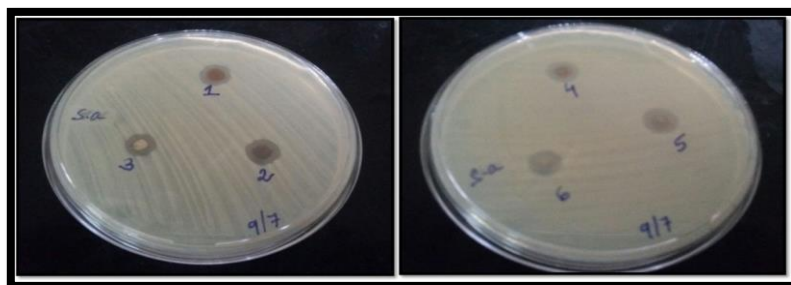**Figure- 16. Spot inoculation of sample with Escherichia coli**

Figure- 17. Spot inoculation of sample with Staphylococcus aureus

Conclusion

Ag/FeOOH and Ag/Fe_2O_3 powder derived from the iron ore tailings , are prepared successfully by chemical co-precipitation and urea-hydrolysis methods . XRD pattern shows very broad diffraction peaks for the Ag/FeOOH samples and those peaks were identified for goethite phase. But Ag/Fe_2O_3 samples show very sharp diffraction peaks which were well matched with hematite phase. Raman Spectra of various Ag/FeOOH and Ag/Fe_2O_3 samples have

shown very prominent Raman bands at various region between 200-1400 cm^{-1}. TEM picture of Ag/FeOOH and Ag/Fe$_2$O$_3$ samples prepared via urea hydrolysis show that silver nanoparticles are well dispersed/ supported on FeOOH and Fe$_2$O$_3$ matrix. The particle size of FeOOH is found to be 60-70 nm range whereas the particle size of silver nanoparticles supported on FeOOH is observed to be <10 nm. Further the obtained silver loaded ferric oxide hydroxide and ferric oxide possess antibacterial properties which can be exploited to kill bacterial growth in a given region. In summary, value addition to waste is successfully employed in this investigation. Hence, thought can be given to prepare more materials by using this mineral waste.

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