Hydrophobic mineral pigment by surface engineering

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Abstract: *A inorganic mineral pigment is designed out of a mineral by-product namely jarosite, and its characteristics have been studied and reported. For the current study, we obtained the jarosite directly from the mining industries. The immobilization of hazardous materials like Sulfur, Zinc, Lead, and Cadmium from the Jarosite is done by surface modification. Leaching out of those elements can be avoided by introducing hydrophobic nature to the Jarosite.*

Key Words: *Inorganic Colorant; Jarosite: Mining Waste; Hydrophobic.*

1. INTRODUCTION:

Development of high-value industrial products from inorganic mining wastes is a great concern to the industries. Processing of high purity Zn alloys from zinc ore through hydrometallurgy route [1]discharge voluminous amount of inorganic wastes which is named as jarosite[1]. Chemically which is sodium and sulphate impurities containing iron silicate. It is amild yellow colored powder, broadly categorized into iron silicate sulphate family. Depending on the origin of the mining, jarosite contains impurities such as lead, cadmium and arsenic and hence this by-product is classified as hazardous and shows high acidic nature, and is of P^H value <3. The safe disposal of the Jarosite was not possible in its original form. Jarosite shows*R*3*m* space group and rhombohedral symmetry with hexagonal cell and parameters *a* ~ 7.29 Å, *c* ~ 17.16Å Z~3Å. Jarosite industrial waste is earlier explored for the sintered glass ceramics.

The waste is aimed to be transformed into a hydrophobic inorganic colorant for multifunctional applications. From the XRF studies, we confirmed that the jarosite used in this study contains toxic ions, which are in mobile phase. One of the simple and viable technique is to provide a water-repellent polymer layer over the surface of jarsoite where a polymer layer can inert the toxic substances from the jarosite and prevent the leaching out of the hazardous ions. Since thin polymer layer may degrade over the time, it is ideal to transform the jarosite into a hydrophobic material before any use. In the current study, colour adsorption property of jarsoite is first investigated to obtain range of inorganic-colorants at room temperature and also in neutral p^H. For this, a simple adsorption technique is followed. Subsequently, surface treatment is made to make the jarosite hydrophobic. Reports indicate, that the iron sulphate hydroxide is hydrophobic and the iron sulphate hydrate is hydrophilic [3,11]. Therefore, in this work, surface modification of the Jarosite is carried out.

2.MATERIALS AND METHODS:

Jarositeis supplied byBinani Zinc Pvt. Ltd, Ernakulam, Kerala, India.Tetraethyl orthosilicate(TEOS) is from Aldrich(98% purity). Toluene (99.5%)isused as solvent(Fisher Scientific). Blue, magenta, orange, and yellowinorganic stains are fromthe Asian Paints.

Jarosite waste is sieved and ball milled to uniform particle size, Inorganic colour stains having different ratios (2%,4%,6%,8%,10%,and 12% by wt)are incorporated into the jarosite with 50% water for getting homogenous colour dispersion. It is again dried in sunlight and hand milled using mortar and pestle. Surface modification ismade using Stearic acid, TEOS and Toluene. Solutions are prepared, in varying percentage (5%,10%,15%,20%,25%,30%,35% & 40%) of Stearic acid in the TEOS/ Toluene (3:4 in ml) mixture containing definite amount of the jarosite (5g). The jarosite paste with the surface modifier solution is stirred well, and coated over a glass plate by dip coating method and allowed to dry.Contact angle data for finding water repellent capacity of the sample is noted. The study reveals the optimization of the sample with minimum amount of Stearic acid for maximizing the contact angle.

Preliminary characterizations of the jarosite are done by X-Ray Fluorescence Spectroscopy (XRF), X-ray Diffraction (XRD) Spectroscopy. The surface morphology of the jarosite sample is studied by the Scanning Electron Microscope (SEM). The Laser Diffraction Particle size analyzer (Beckman coulter, LS13320) determines the reduced size of the jarosite. The surface modifier solution is used to develop the hydrophobic nature of the Jarosite by introducing nonpolar groups (alkyl) on the jarosite surface. Nonpolar groups with jarosite binding are examined by FTIR analysis ,the contact angle measurement is used to determine the water repellency of the surface modified jarosite pigment.

3. RESULTS AND DISCUSSION:

The preliminary characterization of the jarosite is conducted with XRF, XRD,particle size analysis and morphological studies. The received jarosite from the industry as such is used for XRF study.Table 1.1 shows that the major parts of the jarosite contains Fe_2O_3, SO_4 together with other metal oxides,from the XRF data, it is confirmed that the given jarosite is iron sulfated, in which44.756% is Fe_2O_3.The jarosite contains lots of toxic materials such as PbO, SO_3,As_2O_3etc.

Compound	Concentration	Compound	Concentration
Fe_2O_3%	44.756%	SrO%	340.5ppm
SO_3%	33.357%	TiO_2%	968.2ppm
SiO_2	6.292%	MnO	0.136%
CaO	5.103%	MgO	0.116%
In_2O_3	0.108%	In_2O_3	0.108%
PbO	2.948%	NiO	138.4 ppm
Cu0	0.754%	Ga_2O_3	149.6 ppm
Al_2O_3	1.418%	La_2O_3	120.8 ppm
k_2O	0.224%	Rb_2O	78.7 ppm
ZnO	3.890%	V_2O_5	19.6 ppm
Eu_2O_3	770.0ppm	As_2O_3	631.6 ppm
IrO_2	336.2ppm	BaO	294.9 ppm

Table1.1: Elemental mapping by X-ray Fluorescence (XRF) of Jarosite

The Powder X-ray Diffraction is used to confirm the mineral phase. Which is measured within the angle range $2\theta = 20^\circ - 90^\circ$. All the crystalline peaks are matching well with the Jarosite Ref.Code 00-022-0827. It is potassium iron sulfate hydroxide with chemical formula $KFe_3(SO_4)_2(OH)_6$, which shows the Rhombohedral crystal structure.

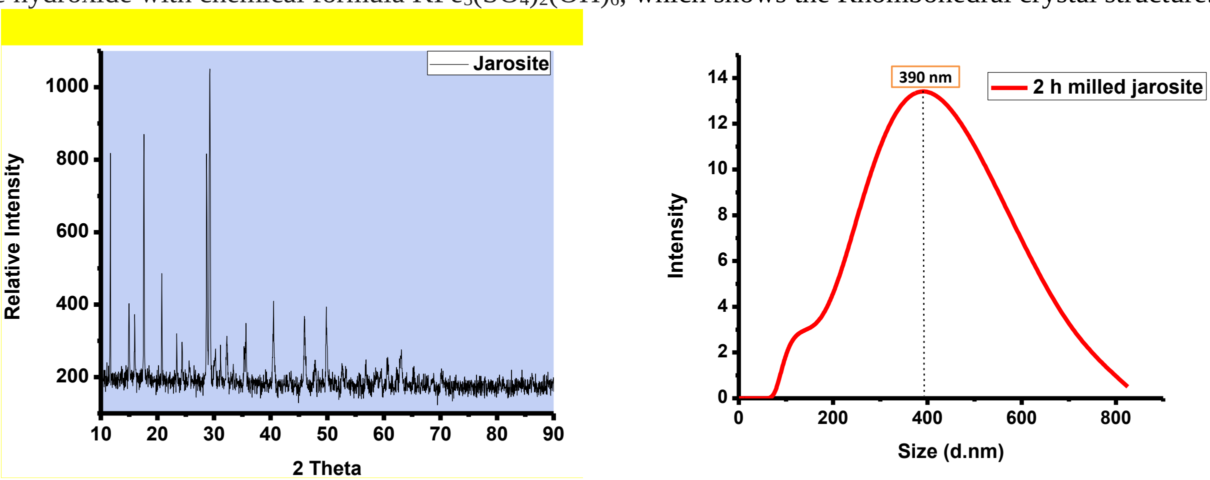

Fig.1.1 XRD Pattern of jarosite and particle size distribution of ball milled jarosite

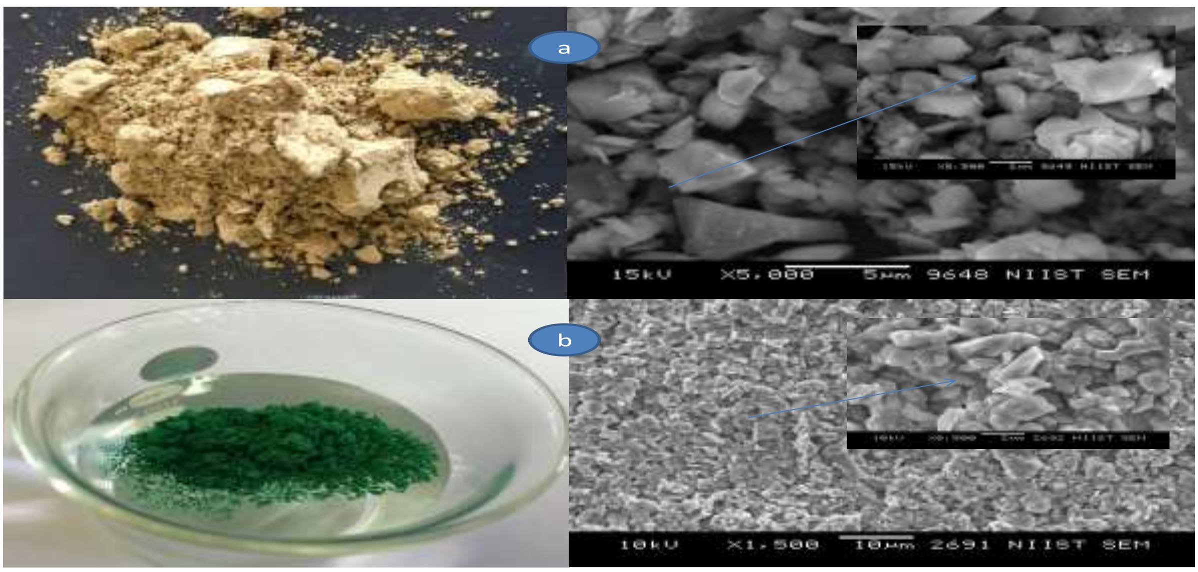

Fig.1.2 SEM images of (a) microstructure Jarosite particles (b) microstructure of surface modified Jarosite pigment

The microstructure analysis of the Jarosite reveals that most of the particles are irregular in shape with multiple humps and most of the particles have a flaky appearance. Its surface is smooth but irregular in shape.SEM images of jarosite indicate that most of the particles are above 2 micron size values, but the surface modified Jarosite pigment (fig1.2.b) shows that it has fused flaky structure, This may be due to the influence of surface modifier solution. Particle size of the jarosite is analyzed, which shows that most of the Jarosite particles are of 390 nm size.Compared with other minerals, the above particle size is better. This may be due to the presence of Fe_2O_3, which is capable for segregation.
Hydrophobicity is one of the most important requirements for the Jarosite pigment, because Jarosite contains lot of toxic materials which are loosed out in water. Contact angle measurements are used for finding water repellency of the material. Table 1.2 shows the contact angle values of samples with different percentage of Stearic acid. It is clear that10% Stearic acid is only required for getting good results. Higher concentration of will not be better cured. At this concentration, it becomes hydrophobic with a contact angle as high as 108°.

Sample	Stearic acid (g)	TEOS (ml)	Toluene (ml)	Jarosite (g)	Contact angle (Degree)
S1	0.25	3	4	5	97
S2	0.5	3	4	5	108
S3	0.75	3	4	5	105
S4	1	3	4	5	104
S5	1.25	3	4	5	98
S6	1.5	3	4	5	97
S7	1.75	3	4	5	92
S8	2	3	4	5	90

Table 1.2 varying compostion of Stearic acid and its contact angle values

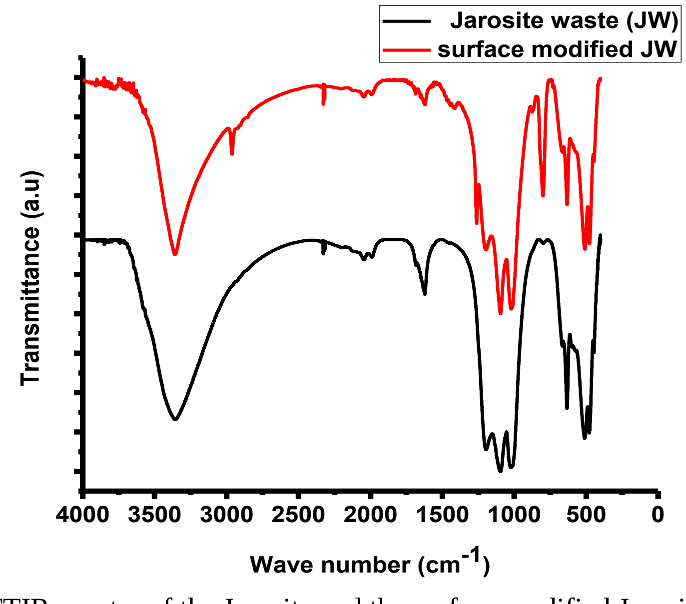

Fig 1.3: FTIR spectra of the Jarosite and the surface modified Jarosite pigment.

Fourier Transform Infrared (FTIR) analysis is give the chemical interaction between surface modifier and Jarosite, which confirmes the chemical modification successfully done on Jarosite pigment. A strong and broad peak in the region 3000 to 3500 cm-1 represents the O-H groups. Jarosite shows a broad peak in this range but surface modified jarosite pigment shows same peak with short width, which means that the surface modifier solution helps to reduce O-H groups from the jarosite. A peak at 1228.10 cm^{-1} confirms the presence of Fe-O-Si bond. A peak at 2966.68 cm^{-1} shows the presence of alkyl ($-CH_3$) groups. The polar groups like alkyl groups are introduced on Jarosite surface. The surface modification of Jarosite is successfully done and is verified through FTIR analysis.

4. CONCLUSION:

Jarosite is a hazardous waste material produced from Industries. We are successfully modifying its surface via surface engineering. The Surface modification of Jarosite with PDMS and TEOS/stearic acid, we got an excellent result of Super hydrophobicity. Modified surface then analysed by using SEM, XRD, FTIR,Contact angle and Particle size analyser. These studies shown that PDMS & Stearic acid has a better combination and the surface is protected without toxicity. In future these materials are used to make hydrophobic surface, which is effectively low coast, less hazardous, eco-friendly.

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