Synthesis and Characterization of Pigment Grade Red Iron Oxide from Mill Scale

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Authors' contributions

This work was carried out in collaboration between all authors. Author MSQ designed the study, wrote the protocol and wrote the first draft of the manuscript. Author MLR managed the analyses of the study. Authors JK and NS managed the literature searches. Authors SA and BB managed the characterization of the product. Author AJMTN wrote the final manuscript. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

This work aims at conversion of mill scale to produce value-added pigment grade red iron oxide by multi-step process, such as milling, acid treatment, mixing with redox reagents and calcination. In all steel re-rolling industries, mill scale is a solid waste material produced as a result of hot rolling of steel. Scales are formed due to oxidation of steel at high temperature. It can't be used along with iron ore or bar or plate, because products obtained by using this scale contain unwanted defects of scale pitting resulting brittleness. In Bangladesh, they are mainly dumped in landfills which results environmental pollutions and other serious problems. In this study, the experimental conditions like amount of sulphuric acid and type of redox reagents were investigated in order to determine the optimal ones. The phase of as-prepared red oxide was characterized using X-ray diffraction (XRD) analysis and morphology and the particle size was characterized by scanning electron microscopy (SEM) and particle size analyzer. The results revealed that mill scale waste can be successfully

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converted into value-added pigment grade red iron oxide having purity 95.3 percent with satisfactory oil absorption value (29.99%) and other physical properties needed for pigment which makes the mill scale as an alternative source of iron for the preparation of pigment grade red oxide. The prepared sample was found to be hematite phase having rhombohedral crystal structure from x-ray diffraction analysis.

1. INTRODUCTION

Due to ever-tightening environmental regulations, the recycling of wastes generated by steel re-rolling industry has become an important issue. In addition, as iron ores are depleting day by day, productive research work is essential to reuse the secondary raw materials produced as a by-product and waste materials in re-rolling industries.

In the steel-making process, during the heating of steel slabs at high temperature, their top layer becomes oxidized to iron oxide. This oxide is called "mill scale". During the rolling of slabs, by using a shower of water, mill scale is easily removed from the surface [1-4].

Earlier, mill scale was used in steelmaking process as an oxidizer in a conventional electric arc furnace. However, to improve melting and oxidation processes, the modern electric arc furnaces are designed with oxygen lancing system which is more efficient than mill scale practice [5]. A small portion of mill scale is used by cement plants. In that case, the mill scale does not blend uniformly with the other feed stock materials due to its greater density than any of the blending components and finally causes a greater variation in the blend used as kiln feed [6].

Unfortunately, to recycle iron from the mill scale in mass, no technology has been implemented [7]. The bulk of mill scale waste generated from steel re-rolling industries is dumped in landfills which results in leaching of some fractions of heavy metals into soil and groundwater, thus polluting the environment. The bad effects on the environment as well as continuous demand for more landfills necessitate the need for more productive utilization of mill scale.

Although the mill scale is considered as waste material in all steel re-rolling industries, it may be used as valuable secondary raw material because of its properties like the stable chemical composition, high iron content and low impurities.

With the current demand for ever-increasing steel production, the production of mill scale is increasing rapidly. The high iron content of mill scale with its low impurities makes it an excellent alternative source for the preparation of red iron oxide pigment.

Iron oxide pigment is largely used in coatings, construction materials and other applications due to its chemical stability, long durability, low costs and non-toxicity [8-10]. In recent years, the recycling of iron-containing solid waste in iron oxide preparations has become a hot research topic [11-14]. The reasons are, it can potentially improve value-added products as well as save natural resources and save the environment from the pollution. Red iron oxide pigment has hematite (α-Fe_2O_3) phase. In industrial anticorrosion coatings, it is currently used as one of the best antirust pigment and anticorrosive medium because of its unique flake structure and better performance. Red oxide pigment is commonly prepared by calcination of costly ferrous sulphate in excess of air [15]. Compared with this method, the developed method that converts waste mill scale is a low-cost technique and suitable for the mass production. However, there exist few methods concerning the preparation of red oxide pigment from waste mill scale [16].

In this study, an attempt has been made to prepare valuable pigment grade red oxide with desired properties and yield. The factors affecting the yield and quality of the red oxide pigment were studied in order to fix the optimum condition. To the best of our knowledge, no such work has so far been reported.

2. METHODOLOGY

2.1 Materials and Reagents

Locally procured and analytical grade reagents were used in this study. The chemicals used for the preparation of pigment grade red iron oxide were Sulphuric acid (H_2SO_4) 95-98% (Sigma-

Aldrich Germany), Sodium nitrate ($NaNO_3$) ≥99.0% (Sigma-Aldrich Germany), Sodium hydrosulphite ($Na_2S_2O_4$) ≥82% (RT) (Sigma-Aldrich Germany) and Hydrazine hydrochloride ($NH_2NH_2.HCl$) 97% (Sigma-Aldrich Germany). The mill scale used in this study was obtained from a local steel re-rolling industry. The main chemical composition of collected mill scale is given in Table 1.
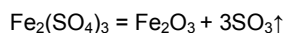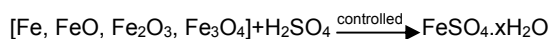
Table 1. Chemical analysis of the air-dried mill scale

Component	Content (*wt. %*)
Fe	74.21
Mn	1.04
P	0.02
Si	0.43
Cu	0.13
Ni	0.09
Moisture	0.01
Others	24.07

X-ray diffraction patterns recorded for the mill scale sample which was previously dried at 100ºC are shown in Fig. 1. In this figure, it is found that it contains many more diffraction lines than those recorded in the diffraction data file for Hematite phase. The additional diffraction lines

are identified as Magnetite (Fe_3O_4) (ICSD No.01-075-0449) and Wüstite (FeO) (ICSD No.01-085-0625).

2.2 Fabrication of the Pigment Grade Red Oxide

As outlined in Fig. 2, mill scale was ground to 100 mesh using ball mill. It was then allowed to react with the requisite amount of 9M sulphuric acid in a reaction vessel for a fixed period to convert it into sulphate salts. The reacted mass was then mixed with redox reagents at a definite molar ratio followed by heating and calcined at a definite temperature and for definite time period keeping the rate of temperature raising 10°C/min. During fabrication, the following reactions take place.

$$[Fe, FeO, Fe_2O_3, Fe_3O_4]+H_2SO_4 \xrightarrow{controlled} FeSO_4.xH_2O$$

$$6FeSO_4.H_2O = 2Fe_2O_3 + Fe_2(SO_4)_3 + 3SO_2\uparrow + 6H_2O\uparrow$$

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3\uparrow$$

The resultant calcined mass was then cooled, ball milled, washed with water several times to free from soluble impurities and separate red oxide from unreacted mass, filtered, dried at 80°C and pulverized. The effect of experimental factors like amount of sulphuric acid and type of redox reagents were investigated.
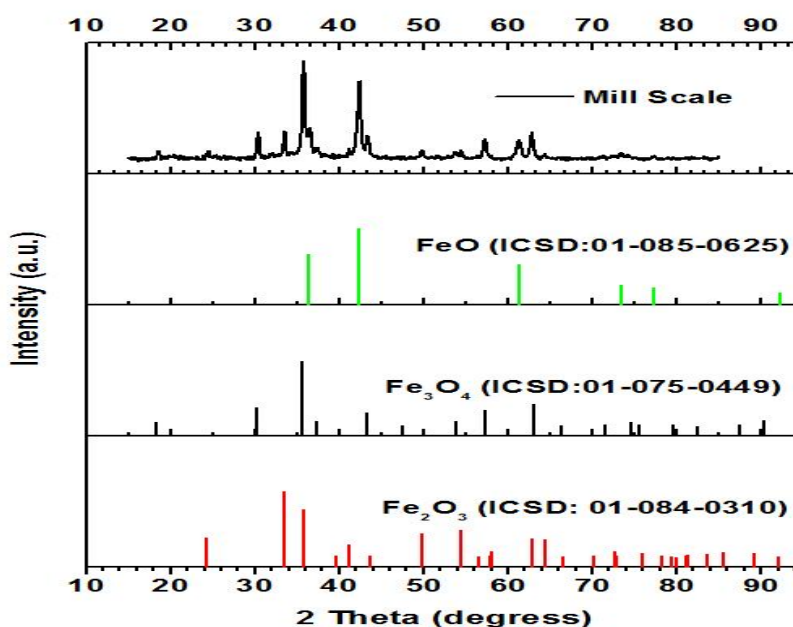

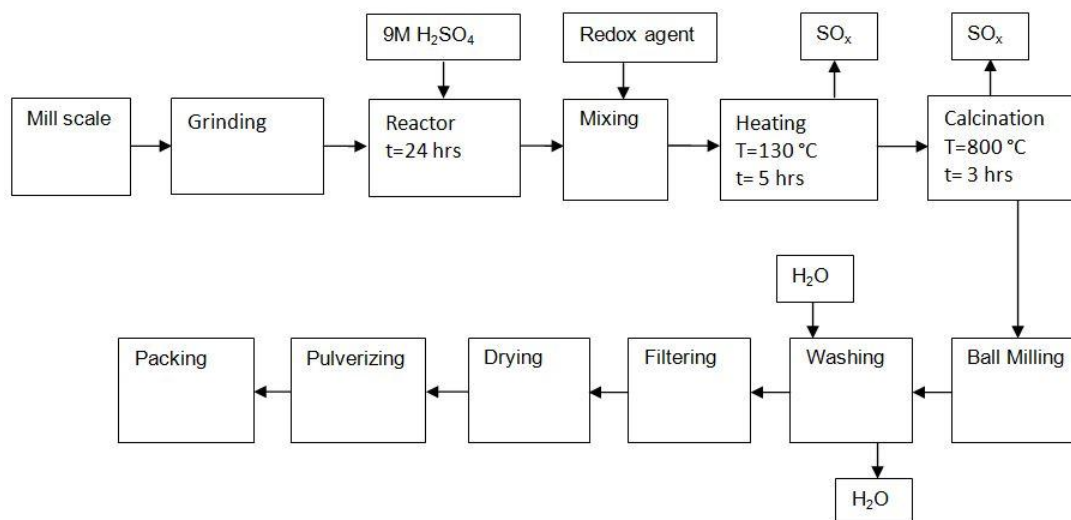**Fig. 1. XRD patterns of the mill scale dried at 100°C**

Fig. 2. Flow sheet for the preparation of red oxide from mill scale

2.3 Analytical Methods

X-ray diffraction (XRD) analysis was performed using Bruker D8 Advance X-ray diffractometer using Cu Kα (1.5406 Å) radiation. The diffraction patterns were recorded in the range of 10° to 90° having scanning speed of 2°/minute. Scanning electron microscope (PHENOM PRO, Netherlands) was used to observe the morphology and mean particle size. Particle size distribution was observed using Malvern Mastersizer 3000, UK. Optical properties like gloss and brightness were determined by using Dr Lange reflectometer (Refo-3) at angle 60° and at wavelength 570 nm. The concentrations of ferric ions were determined by chemical analysis of the liquids according to standard UV-Vis spectrophotometric methods by using a UV-Visible spectrophotometer (UV-2201, Shimadzu, Japan). The results were the mean values of the three experiments using the same sample. The oil absorption value of red oxide products was measured according to the ASTM D0281-95R02. Other physical properties like spreadability [17], water wettability [17], pH value of aqueous suspension [17], sieve residue [17,18], hiding power [17,18], density [19], atmospheric curing stability [17,18] were carried out according to the standard procedures.

3. RESULTS AND DISCUSSION

3.1 Effect of Amount of Sulphuric Acid

To investigate the effect of the amount of sulphuric acid, eight experiments were performed with iron to sulphuric acid molar ratio ranging from 1:1.20 to 1:2.87 using 9M solution of sulphuric acid while the molar ratio of iron to redox reagent ($NaNO_3$) was fixed at 1:0.026. The percent of conversion on the basis of iron, percent content of Fe_2O_3 and oil absorption value of red oxide pigment prepared under different iron to sulphuric acid molar ratio were given in Table 2. According to Table 2, it was observed that when the molar ratio of iron to sulphuric acid reached 1:1.91, the percent of conversion on the basis of iron was significant. Table 2 also showed that the product which was obtained at 1:2.39 molar ratio of iron to sulphuric acid had a good purity (97.8%), good oil absorption value (24.97%) and economical conversion of this series (51.072%) on the basis of iron. Considering all the above shown results and economic background, the optimal molar ratio of iron to sulphuric acid was 1:2.39.

3.2 Effect of Type of Redox Reagents

Table 3 shows the results of nine experiments that were performed using different redox reagents in single or mixed form to study the effect of redox reagents while the molar ratio of iron to sulphuric acid was fixed at 1:2.39 and that of iron to redox reagents was fixed at 1:0.026. In case of mixed redox reagents, five different molar ratios of sodium nitrate to hydrated sodium hydrosulphite (1:3, 1:2, 1:1, 1:0.5 and 1:0.33) were taken and the results are shown in Table 3. The corresponding characteristic parameters presented in Table 3 showed that among the

Table 2. Effect of molar ratio of iron to sulphuric acid on the yield and Fe_2O_3 content in the preparation of red oxide

The molar ratio of iron to sulphuric acid	Colour (visual observation)	The content of Fe_2O_3 (*wt%*)	Oil absorption (*wt%*)	Percent of conversion
1:1.20	Deep maroon	97.440	25.01	32.666
1:1.44	Deep maroon	97.260	20.31	37.395
1:1.68	Deep maroon	96.940	21.98	38.897
1:1.91	Deep maroon	97.650	27.47	48.343
1:2.15	Deep maroon	97.980	26.65	49.375
1:2.39	Deep maroon	97.800	24.97	51.072
1:2.63	Deep maroon	97.790	24.72	51.078
1:2.87	Deep maroon	97.780	24.63	51.082

applied redox reagents, sodium hydrosulphite dihydrate ($Na_2S_2O_4.2H_2O$) produces the glossiest product with the highest yield. But this product has a loss on ignition of 4.1 percent. Sodium nitrate produces almost same percent yield but less bright sample than sodium hydrosulphite. But this sample has a loss on ignition of only about 1 percent. As found in the case of gloss, the same effect was observed in the case of brightness as both gloss and brightness are related to the reflectance value at a different angle of light incident. Mixed redox reagents had no significant effect on gloss and brightness. The same effect was observed when no redox reagent was used. With an emphasis on the gloss and brightness, the sample prepared with sodium hydrosulphite as redox reagent was subjected to characterization for phase, particle size and physical properties.

Fig. 3 showed the XRD patterns of red oxide pigment synthesized using sodium hydrosulphite dihydrate as a redox reagent. It was found that this product has a pureα-Fe_2O_3 (hematite) phase with a rhombohedral crystal structure having lattice parameter a=5.0360Å, b=5.0360Å, c=13.7816Å. The recorded diffraction peak intensities matched very well with the diffraction data file (PDF: 01-076-8400) of standard α-Fe_2O_3 (hematite phase). The diffraction peaks recorded from the plane of (012), (104), (110), (024), (116), (122), (214), and (300) attributed to hematite (α-Fe_2O_3) formation.
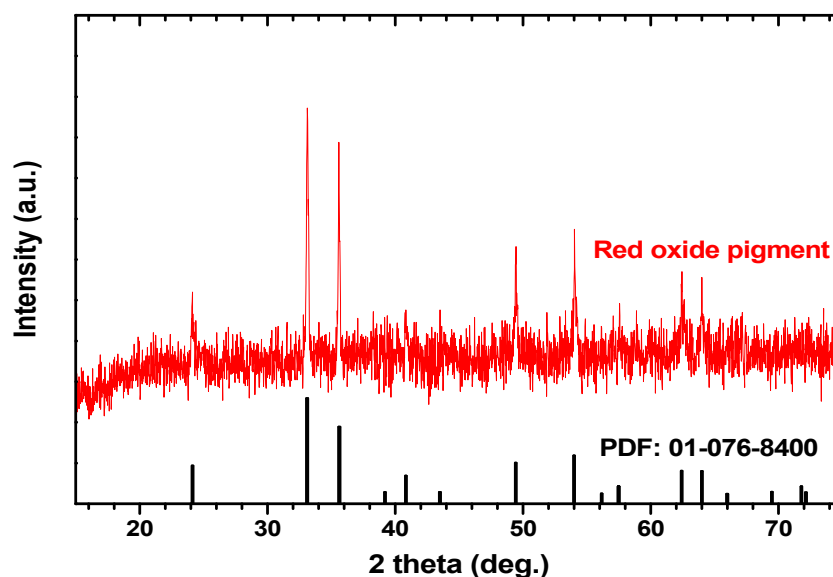

Fig. 3. XRD patterns of the prepared red oxide

Table 3. Effect of redox reagent on the yield and Fe$_2$O$_3$ content in the preparation of red oxide

Name of redox reagents	Gloss	Brightness	Loss on ignition, LOI at 1000 °C, 0.5 hr (*wt%*)	Colour (visual observation)	The content of Fe$_2$O$_3$ (*wt%*)	Oil absorption (*wt%*)	Percent of conversion on the basis of iron
Sodium nitrate	0.80	66.66	0.900	Deep maroon	97.800	24.97	51.072
Sodium hydrosulphite dehydrate	1.00	83.33	4.100	Deep maroon	95.300	29.99	51.599
Hydrazine hydrochloride	0.55	45.83	2.550	Deep maroon	96.040	29.15	48.979
Without redox reagent	0.50	41.66	1.880	Deep maroon	91.051	20.15	36.624
Mixed redox reagent-1	0.56	46.66	3.300	Black tinted maroon	95.925	26.67	51.467
Mixed redox reagent-2	0.43	35.83	3.030	Black tinted maroon	96.133	24.96	51.424
Mixed redox reagent-3	0.46	38.33	2.510	Black tinted maroon	96.550	33.07	51.326
Mixed redox reagent-4	0.50	41.66	1.970	Black tinted maroon	96.970	29.16	51.248
Mixed redox reagent-5	0.50	41.66	1.700	Black tinted maroon	97.170	28.28	51.203

Molar ratios of NaNO$_3$ to Na$_2$S$_2$O$_4$.2H$_2$O maintained in the mixed redox reagents -1, 2, 3, 4 & 5 were 1:3, 1:2, 1:1, 1:0.5 and 1:0.33 respectively
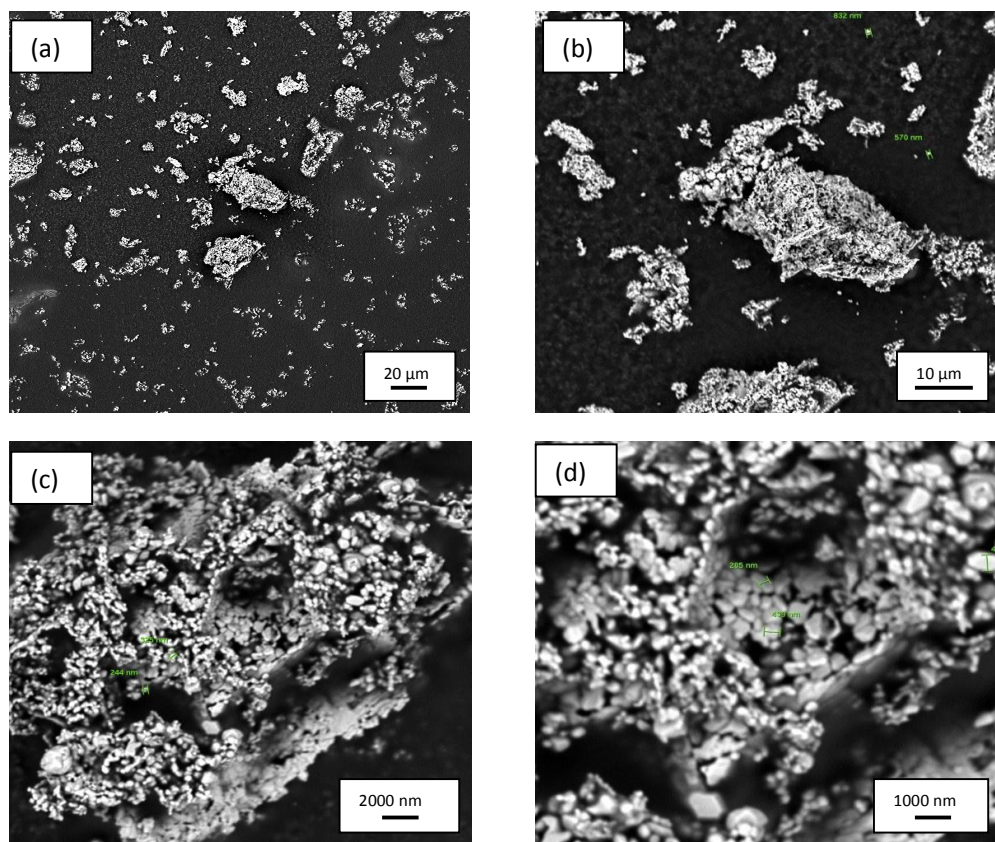
Fig. 4. SEM images of prepared red oxide at different magnifications

The SEM micrographs of red oxide pigment synthesized using sodium hydrosulphite dihydrate as a redox reagent in Fig. 4 exhibited uniform flakes which were crystalline but agglomerated. From particle size distribution analysis, shown in Fig. 5, it was found that 10 percent particles have average volume equivalent spherical diameter 3.28 µm, 50 percent have 20.3 µm and 90 percent have 41.4 µm. Also, the uniformity of the particle size which influences the gloss and brightness potential was in a satisfactory narrower range of 10-45 µm. Specific surface area of the prepared sample was 709.2 m^2/kg. The predominant particles which formed the agglomeration were within the range of about 200 nm to 600 nm as outlined in the SEM images (Figs. 4c and 4d).

Table 4. Properties of red oxide synthesized from mill scale under optimal conditions

| Property	Bayer standard (Bayferrox 110)	Local commercial sample	Synthesized sample
Iron content as Fe$_2$O$_3$ (*wt. %*)	98.09	97.30	95.30
Density *(g/ml)*	5.968	4.4787	6.9165
Oil absorption value (*wt. %*)	28	19.77	29.99
Hiding power	52	93.33	67.69
pH of aqueous suspension	6.30	6.20	6.4
Water soluble matter (*wt. %*)	0.432	0.441	0.3
Volatile matter at 105°C (*wt. %*)	0.255	0.306	0.112
Loss on ignition, LOI at 1000°C, 0.5 hr (*wt%*)	1.23	1.50	4.1
Residue on sieve (*wt. %*)	0.02 (45 µm)	0.01 (45 µm)	0.02 (45 µm)
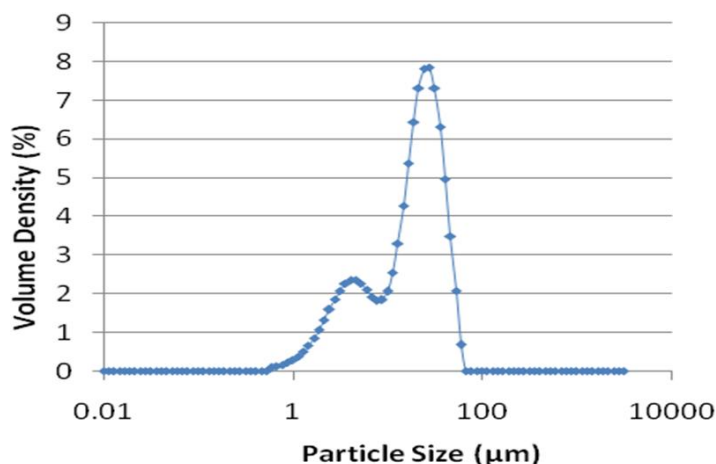
Fig. 5. Particle size distribution of prepared red oxide

3.3 Comparative Study of the Synthesized Red Oxide

Taking into account all the above discussion, optimal parameters of red oxide pigment synthesized from mill scale were 1:2.39 iron to sulphuric acid molar ratio and sodium hydrosulphite dihydrate as redox reagent. The characteristic properties (spreadability, water wettability, pH value of aqueous suspension, density, sieve residue, oil absorption value, Loss on ignition, hiding power, atmospheric curing stability) of red oxide pigments prepared under the optimal parameters were compared with Bayer standard (Bayferrox 110) and local commercial sample. The results which have numerical values are shown in Table 4 and found in satisfactory ranges. The other physical properties like spreadability, water wettability, atmospheric curing stability (both humidity and light) were found to be comparable with Bayferrox 110 by naked eye comparison.

4. CONCLUSION

Preparation of pigment grade red oxide was successfully carried out using mill scale as raw materials by means of the multi-step processes of milling, acid treatment, mixing with redox reagents and calcination. The optimum technological parameters which produce the glossy and bright product are 1:2.39 iron to sulphuric acid molar ratio and sodium hydrosulphite dihydrate as redox reagent. Red oxide pigment as-synthesized under the optimum condition is a uniform flake, deep maroon, and has a good purity of about 95.3%. Moreover, the prepared pigment grade red oxide met the required properties of iron oxide pigment. For recycling of iron from mill scale, the multi-step process for red oxide synthesis may be a viable alternative for mill scale consumption.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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