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Hydrometallurgical Processing of Brazilian Iron Ore Tailings for the Synthesis of Pigments

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Abstract

The aim of this study was to investigate the synthesis of iron oxide pigments from IOT. The sample of IOT was obtained through mining activity of the Quadrilátero Ferrífero in the state of Minas Gerais, Brazil. The procedure was carried out by hot acid leaching with hydrochloric acid (HCl) which allowed the recovery of about 95% of the iron in a liquor. The iron-based pigments—red (IBP_R), black (IBP_B), and yellow (IBP_Y)—were synthetised from the liquor by selective precipitation, crystallisation, and thermal procedures. The pigments were characterised by particle size distribution, mineral and chemical compositions, as well as colourimetric properties. The process of synthesis was successful and the procedure was shown to maximise the utilisation of mineral resources and minimise the environmental, social, and economic impacts associated with IOT disposal.

Keywords

Iron Ore Tailings, Pigments, Iron Oxide, Waste Management, Hydrometallurgy

1. Introduction

Iron ore tailings (IOT) are generated in large amounts and are almost entirely disposed of in piles or dams with several associated socio-environmental risks [1] [2] [3]. Tailings reduction, dry tailings disposal, and conversion of IOT into value-added products are all of interest for the iron ore industry [4]. The use of IOT in the civil construction sector has been one of the great targets and investigations comprise the utilization as a material to make cement and concrete [2] [5] [6] [7] roads [8], ceramics [9], and pigments [10].

Moreover, iron-based pigments (IBP) are largely used in the industry; the global iron oxide pigment market moves billions of dollars and is constantly ex-

panding. They are important inputs in several segments, such as in those used in construction, ceramics, and paint, and have been used since ancient times because of their chemical stability, non-toxicity, and cost benefit. Different colours can be obtained including yellow, orange, red, brown, and black [11] [12] [13] [14] [15].

These pigments can be natural or synthetic. Natural IBPs are obtained by milling ochres, and are commonly marketed at low costs. In contrast, synthetic IBPs can be used as standardised materials with repeatable properties in terms particle size distribution, mineral composition, and colour, competing directly with natural IOPs in many colour applications and attending exclusively to the part of market that requires high quality standards [16]. The global IOPs market moved more than $2 billion in 2020, with strong growth expectations for the coming years, driven mainly by the development of the construction sector [17].

In the literature review, we did not identify studies involving the synthesis of pigments from IOT. In the case of the study of Galvão *et al.* [10], the IOT was used as a pigment in its raw state, subjected only to drying and lump breaking. In order to contribute to this scenario, we investigated the synthesis of the IBPs in red (hematite), black (magnetite), and yellow (goethite) attained from the liquor by hot acid leaching of an IOT with hydrochloric acid (HCl). The objective was to validate whether the acid leaching product can be used for such purpose. The results are discussed in terms of the hydrometallurgical route and the context of iron ore mining.

2. Experimental Setup

2.1. Iron Ore Tailings (IOT)

The IOT sample used in this study came from a mine in the Quadrilátero Ferrífero (QF) located at coordinates 20˚25'37"S 43˚52'29"W. The residue was collected after the thickening stage of the tailing following the magnetic concentration of the iron ore. The IOT presented a size distribution of 0.07 - 300 μm and a specific surface area of 10.6 $m^2 \cdot g^{-1}$. The X-ray analysis of the material showed the presence of quartz and hematite as major crystalline components and goethite, kaolinite, and biotite as minor components. The elemental composition determined by X-ray fluorescence provided the following results: Si—31.05%, Fe—16.98%, Al—1.59%, Ti—0.07%, Mn—0.02%, Mg—0.0038%, and P—0.04%.

2.2. Reagents and Materials

The reagents applied in this study were all of analytical grade. Acid leaching was carried out with HCl (37%), supplied by Quimica Moderna (Barueri, SP, BRA). Sodium hydroxide (NaOH) was supplied by Dinamica (Indaiatuba, SP, BRA), nitric acid (HNO_3; 65%) by Quimica Moderna (Barueri, SP, BRA), and potassium hydroxide (KOH) by Sigma-Aldrich (São Paulo, SP, BRA). Deionized wa-

ter was used in the preparation of all solutions. Filtration was always carried out with quantitative filter Unifil.

2.3. Leaching and Synthesis of IBPs

The leaching of iron from the IOT was carried out under the conditions established by Almeida [3]: HCl concentrations of 10.8 mol·L^{-1}, a temperature of 80˚C, a two-hour leaching time, and solid/leaching-solution ratio of 1.8 kg of IOT for 3 L of water. After leaching the assembly sample was filtered and the liquor produced was analysed via inductively coupled plasma optical emission spectrometry (ICP-OES) to identify the elemental composition of the soluble metals using a Perkin Elmer Optime, model OPTIMA 8300 DV. Following, the solid residue was washed three times with deionised water (in a volumetric ratio 1:2 solids to water) to remove the ferric chloride adhered to the particles and this water was discarded.

The red pigment (IBP_R) was obtained by following the methodology of synthesis of Schwertmann and Cornell [12]. For this, 50 mL of the liquor had its pH adjusted to 3.6 through the addition of NaOH 4 M for iron precipitation as hydroxide. The precipitate was filtered and then diluted in 100 mL of a HNO_3 2 M solution. The new solution was then submitted for pH adjustments to 12.0 through the addition of a KOH 4 M solution. The set was kept in agitation and heated at 70˚C for 24 hours. After this period of time, the precipitate was centrifuged and washed three times with volumes of 50 mL of deionised water. After this cleaning procedure, the pigment was dried at 60˚C and stored in a plastic bag free of humidity.

For the production of the black pigment (IBP_B), a sample of the liquor of ferric chloride was first converted into ferrous chloride. The reduction of Fe^{3+} into Fe^{2+} was performed through the addition of commercial Fe^0 (as a low carbon steel wool) to the ferric chloride solution in an iron Fe^0:Fe^{3+} ratio of 1:1. The iron chloride and ferrous chloride solutions were mixed in a 2:1 Fe^{3+}/Fe^{2+} ratio and NaOH 4 M was added to increase the pH up to 12. Following the stabilisation of pH, the material was kept in mechanical agitation for 24 hours. Subsequently, the precipitated particles were centrifuged, washed, dried, and stored following the same procedures carried out for the red pigment.

The yellow pigment (IBP_Y) was synthetised according to the Schwertmann and Cornell methodology [12], adapting the concentrations of the reagents to the iron concentration available in the ferric chloride liquor. Under agitation, about 80 mL of NaOH 6 M was added to 50 mL of $FeCl_3$ to precipitate the iron as hydroxide. The precipitated material was filtered and diluted in 100 mL of a HNO_3 4 M solution. This new solution was kept in agitation for ten minutes to achieve homogenisation. The iron nitrate solution was placed in a 2000 mL volumetric flask that received 180 mL of KOH 4 M and about 1700 mL of deionised water. The solution was stirred and then, the flask was kept for about 60 hours in a previously heated oven and kept at a temperature of 70˚C. After this

period, a precipitate with a yellow tone was obtained and then centrifugated, washed, dried, and stored like the two other pigments.

2.4. IOP Characterisation

The particle size distribution of the pigments was measured by laser diffraction using a CILAS 1180 particle size analyser. The mineralogical composition was determined using an X-ray diffractometer, SIEMENS (BRUKER AXS), modelD-5000 (θ-2θ), equipped with a fixed Cu anode tube, operating at 40 kV and 25 mA, with an incident radiation of 1.5406 Å. The angular range analysed was from 3˚ to 80˚ 2θ with a step size of 0.02˚/3s using divergence and anti-scattering slits of 2 and 0.2 mm in the detector

Colourimetric characterisation was performed in the colourimetric system CIE Lab*. This analytical methodology can translate colours into numbers that make up a three-dimensional diagram represented by three axes that represent the clarity of the colour characterised by the parameter L* (L-100% is white and L-0% is black), the colours green and red by the parameter a* (−a, green/+a, red), and the colours blue and yellow by the parameter b* (−b, blue/+b, yellow). The CIELAB parameters of the primary colours (red, black, and yellow) were obtained using the RGB-CIELAB online converter, COLORIZER [18]. Each colourimetric measurement was performed in triplicate and the result presented corresponds to their mean.

3. Results and Discussion

The protocol adopted for leaching the iron from IOT was successful. It was possible to recover 95% of the iron available in the tailings. The liquor was analysed via ICP-OES for the elementary quantification of soluble metals. The main components identified were iron (112,800 mg·L^{-1}) and aluminium (1700 mg·L^{-1}). Other elements identified, but in a much lower concentration, were barium (9.9 mg·L^{-1}), lead (3.1 mg·L^{-1}), sulphur (2.9 mg·L^{-1}), copper (2.8 mg·L^{-1}), and chromium (2.2 mg·L^{-1}). The residue obtained after the leaching, filtration, and washing steps presented about 70% of initial IOT mass where SiO_2 was the major component, accounting for 90% of the material. This material could be a good source of silica and deserves further investigation.

The three IBPs synthetised are presented in **Figure 1** and their main characteristics are summarised in **Table 1**. The red, black, and yellow pigments presented size distributions between 0.04 - 2.00 μm, 0.04 - 38.00 μm, and 0.07 - 32.00 μm, respectively. X-ray diffraction analysis showed the presence of an amorphous phase with peaks indicating the presence of hematite in the red pigment and, in same way, an amorphous phase with peaks indicating the presence of goethite in the yellow pigment. In both situations, the crystallisation process was incomplete. The crystallisation was successfully attained in the synthesis of the black pigment, and magnetite was the only crystalline species identified.

Considering the CIElab parameters of the primary colours red (53.23, 80.11,

67.22), black (0, 0, 0), and yellow (97.14, −21.56, 94.48) obtained on the platform COLORIZER [18], we found that IBP_R was darker, less red and less yellow than the red colour. The IBP_B was lighter than the black colour, redder, and more yellowish. The IOP_Y was darker than primary yellow, redder, and less yellow. Correlating the colourimetric results on the Pantone platform [19], which is known worldwide for its colour system, we obtained the equivalences presented in **Figure 2**.

These results demonstrate the possibility of obtaining different pigments from IOT. The manipulation of process variables allows distinct products and colours compatible with market demands. However, it should be noted that the synthesis of pigments is sensible to the kind of chemicals chosen, concentrations applied, and the procedure in general [20].

In parallel, Brazil generates and disposes over 200 million tonnes of IOT per year. Considering the results of this study, 160 kg of iron can be obtained from a liquor for each metric ton of IOT. The conversion of the ferric liquor into pigments can generate, on average, up to 240 kg of red pigment (IBP_R), 310 kg of black pigment (IBP_B), and 280 kg of yellow pigment (IBP_Y) per mT, with iron contents of 65%, 51%, and 56%, respectively.

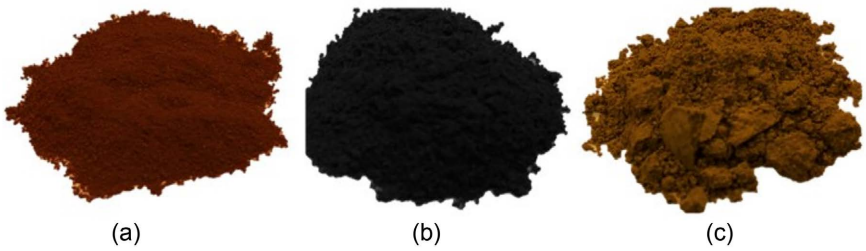

Figure 1. IBPs synthetised from the IOT; (a) IBP_R, (b) IOP_B, (c) IBP_Y.

Figure 2. Equivalence of pigments in colours. Source: Pantone (2021).

Table 1. Characteristics of the pigments produced.

		IBP_R	IBP_B	IBP_Y
Size distribution (μm)		0.04 - 2.00	0.04 - 38.00	0.07 - 32.00
Average diameter (μm)		0.28	7.14	5.04
Colourimetric parameters	L*	33.92	23.52	58.79
	a*	26.51	4.19	15.93
	b*	24.03	8.85	37.39

The appropriation of IOT to obtain pigments contributes to sustainability in mining, maximising the use of natural resources and adding value to the materials that are currently wasted. The benefits extend to the pigment industry, which has sought the development of processes and the incorporation of sustainable raw materials. The aspects of this study meet these demands, contributing to the insertion of materials into the circular economy and cleaner production practices in these important industrial sectors.

4. Conclusion

Different pigments can be obtained from iron ore tailings by means of hot acid leaching. The leaching process was performed with an iron recovery of 95% and production of a siliceous material with a SiO_2 content greater than 90%. Nano/micro iron oxide particles in the colours red, black, and yellow, with iron concentrations of 65%, 51% and 56%, respectively, could be synthesized from the iron rich liquor using conventional and well-established chemical procedures. However, the overall procedures involved several stages and different reagents, which reinforces the importance of seeking simplified alternative processes compatible with the great volume of wastes managed by the mineral processing industry.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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