

Synthesis of Iron Oxide Yellow from Spent Pickling Solutions

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Abstract. This paper demonstrates a simple environment-friendly synthesis route of iron oxide yellow (α -FeOOH) using spent pickling solutions as raw material. After abundant laboratory experiments, we finally pinned down the best procedure. The research showed that α -FeOOH nanometer material with average diameter of 50nm and average length of 400 nm was prepared at the optimal technique. And the FeOOH content of the sample was as high as 90%, which is higher than the 86% of GB/T1863-2008. The structure, morphology and size distribution of the product was characterized by X-ray diffraction (XRD), Transmission electron microscope (TEM), Scanning electron microscope (SEM) and Malvern laser particle analyzer, respectively. The test results show that all the indices of as-prepared iron oxide yellow are completely in conformity with and even better than national primes standard.

1. Introduction

As we all know, pickling is an essential surface cleaning treatment for chemically removing a scale layer of iron oxides on steel surface. If discharged directly without previous treatment, the spent pickling solutions would do great damage to environment due to their high concentrations of iron and residual acid which are hazardous. Different processes have been reported for the treatment of steel pickling waste liquid in literatures which include: neutralization/precipitation^[1], hydrothermal method^[2,3], spray roasting^[4,5], spray pyrolysis^[6], electrolytic precipitation/deposition^[7,8], coprecipitation^[9,10], ion exchange technique^[11], acid pressure leaching^[12], electro-dialysis/membrane separation^[13]. There is no doubt that these approaches recover acid and metallic values respectively. However, most operation conditions of these methods are demanding, complex and costly, so it is hard to accomplish industrialization when taking practical application into consideration. Therefore, it is imperative for us to find an effective method to take full advantage of iron ion dissolved in disposal pickling solutions.

However, iron oxide yellow pigment, also known as goethite (α -FeOOH), as one of the most widely used and profitable material which exhibit various merits including good dyeing force, excellent covering power, heat-proofing, acid resistance, resistance to solvent, non-poison, anti-rust, ect, has aroused a wide range of concern of different fields. These outstanding properties make iron oxide yellow receives considerable interest among

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researchers for the potential application in the areas of coating, ceramic, plastic, robber as well as cosmetics, food, adhesion agent. From this point of view, it appears that research on the preparation of iron oxide yellow pigment is not only significant but also a rewarding and deserving causes. So far, many measures have been developed to fabricate goethite (α -FeOOH) such as forced hydrolysis^[14,15]; microemulsion^[16]; chemical precipitation^[17,18]; the sol-gel method^[19]; electrodeposition^[20,21]; the hydrothermal technique^[22], etc. Recently, with growing concern of environment protection and with the increase by a large quantity of demand for iron oxide yellow pigment, more and more manufactures begin to turn to grope for new ways to produce more competitive products by using low-cost raw materials such as spent pickle liquor, pyrite cinder. Though some achievements have been made, it is still hard for them to manufacture high-quality goethite (α -FeOOH). Our group has been engaged in working on the treatment of waste acid for years. After persistent efforts, we finally succeeded in discovering a novel approach to transform spent pickling solutions into worthwhile and profitable product, namely iron oxide yellow. The result revealed that high quality goethite can be gained under appropriate conditions. The properties of the product perfectly meet national primes standard of GB/T1863-2008.

Not only can this procedure utilizes ferrous iron dissolved in the spent pickle liquors to produce high value-added material, that is iron oxide yellow, but also eliminate the contamination resulted from spent pickling solutions, which poses a serious threat to our ecological environment owing to its high metal content and destructive caustic. Hence, if this process could be advocated throughout the country, it would result in considerable economic and environmental benefits.

2. Experimental

The chloride pickling liquors were obtained from a large-scale steel factory in Hebei. The spent pickling liquors were reduced by iron power or scrap iron so that ferric iron in the spent pickling liquors was reduced to ferrous iron first. After the waste acid reacted completely with scrap iron, the reduced mixture was filtered. Then $\text{NH}_3 \cdot \text{H}_2\text{O}$ was slowly added into the constant well-stirred filtrate at 60°C until the pH of the final solution was adjusted to the desired pH 5.0, where most impurities, such as Si, Al, Mg, Bi, Cr, would turn into precipitate that could be removed by filtered. The filtrate was diluted with water to 0.3mol/L of Fe^{2+} , into which twenty-five percent $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added dropwise until the pH of reaction system reached 7.2. Next, air was bubbled into the solution for about 3 hours at a stirring speed of 400 rpm when the low temperature was limited within $10\sim 30^\circ\text{C}$, ferric yellow crystal seed was gained. The second oxidation of ferric yellow crystal seed, which has temperature optima of $75\sim 85^\circ\text{C}$ and air flow rate optima for reaction of $0.1\sim 0.12\text{ m}^3/\text{h}$, resulted in the formation of ferric yellow by a stir treatment of the mixture at the speed of 400 rpm for about 7h. Ferric yellow was then filtered and washed with distilled water many times to eliminate residual CL. The single phase α -FeOOH with excellent pigment property was prepared when as-prepared ferric yellow was exposed to dry in the oven at 75°C for 8 hours.

The morphology, structure and size distribution of the product were characterized by Transmission electron microscope (TEM) (100CX-II made by JEOL, Tokyo, Japan), Field emission scanning electron microscope (FESEM, Nanosem 430), X-ray diffraction (XRD) (BDX-3300 made by Peking University Instrument Co., China), Malvern lazer particle analyzer (MASTERSIZE S MAM 5005 made by Malvern). The test results show that all the indices of as-prepared ferric oxide are quite up to and even better than national prime standard.

3. Results and Discussion

To demonstrate the influence of this cleaning treatment on the spent pickling liquors, table 1 shows the difference of content and ingredients between original spent pickling solutions and purified spent pickling solutions. The purification of waste acid can achieve the elimination of the main impurity ions in the case of Si, Al, Bi, Ni, Cr, for which the existence makes adverse effects to the quality of the product and the content must be limited in a certain range. From the experimental data we can infer that the concentrations of the other ions, especially for Si, Ni, Al, Mn, which have a great advantage to the synthesis of iron oxide yellow pigment, have dropped off sharply while the content of Fe²⁺ increased.

TABLE1 CHEMICAL ANALYSIS OF THE STARTING AND PURIFIED SPENT PICKLING LIQUORS

element	content before impurity/mg·mL ⁻¹	content after purification/mg·mL ⁻¹
Mn	2.8364	0.0782
Al	0.3196	0.0779
Bi	0.0096	-0.0052
Si	0.2602	0.1691
Ni	0.1084	0.0027
Mg	0.2062	0.0782
Ca	0.7968	0.4702
Cu	0.0315	0.0038
Cr	0.1324	0.0292

The specimen was identified with X-ray diffraction using Cu K α radiation ranging from $2\theta = 10$ to 80° at a scanning rate of $6^\circ/\text{min}$. Fig. 1a shows the X-ray diffraction (XRD) patterns of as-synthesized product. As we can see, the XRD peaks position of the synthesized sample matched quite well with the reported values from the standard card and the patterns correspond to goethite phase with orthorhombic crystal structure (α -FeOOH). From the picture, we can observe that shapes of the peaks are extremely sharp, which indicates the high crystallinity of the sample prepared by this method. And the FeOOH content of the sample was as high as 90%.

Fig. 1b exhibits line chart of size distribution of α -FeOOH product. From fig. 1b we can clearly see that the particle size distribution curves of the sample is sharp, which indicates the uniformity in size of goethite particles, and the particle size of the product is mainly between 150 and 400 nm. This is eligible for the iron oxide yellow standard.

Fig. 2 presents the SEM and TEM images of as-prepared α -FeOOH product. Fig. 2a and b show TEM images of the α -FeOOH at different magnifications. Fig. 2c and d show SEM images of the α -FeOOH at different magnifications. As can be seen, the morphology of the resultant α -FeOOH particles was approximately needle-like or spindle with average diameter of 50nm and average length of 400 nm, respectively. The aspect ratio of the corresponding product lies in the range of about 8-10. α -FeOOH particles have narrow and uniform particle size distribution.

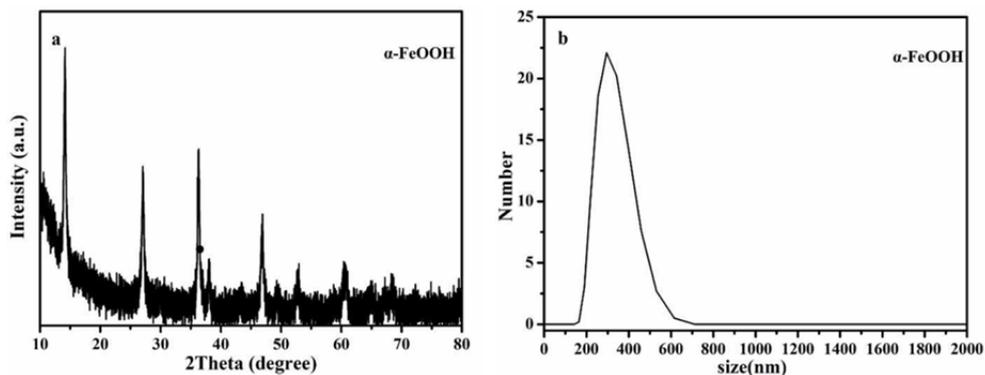


Fig. 1a X-ray diffraction patterns of α -FeOOH and fig. 1b size distribution of α -FeOOH. α -FeOOH was prepared at the optimal technique: preparation of ferric yellow crystal seed: $c\text{Fe}^{2+}=0.3\text{mol/L}$, $\text{pH}=7.2$, $t=3\text{h}$, temperature is 15°C , air flow rate is $0.1\text{ m}^3/\text{h}$; preparation of ferric yellow: $c\text{Fe}^{2+}=0.3\text{mol/L}$, $\text{pH}=2.4\sim 3.7$, $t=7\text{h}$, temperature is 80°C , air flow rate is $0.12\text{m}^3/\text{h}$.

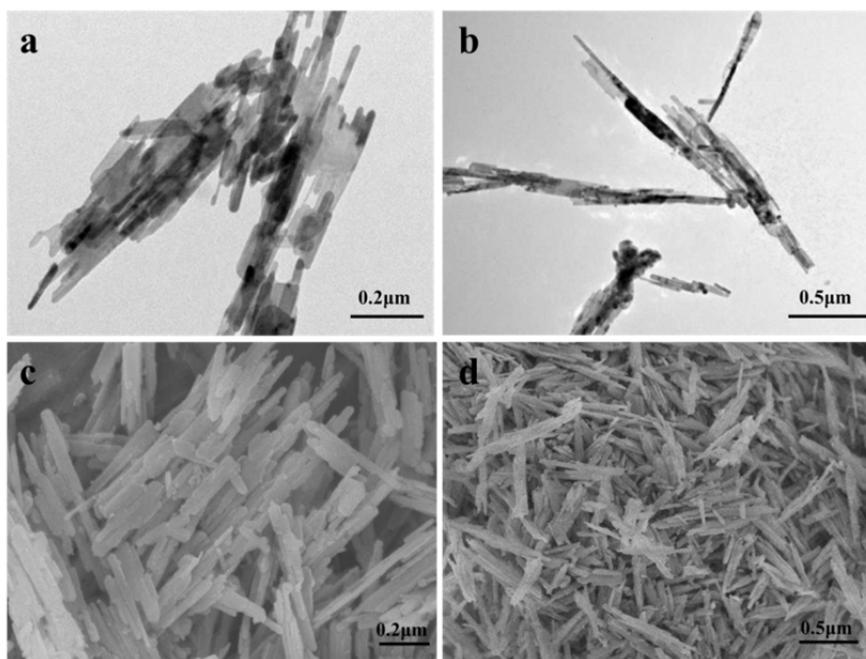


Fig. 2a and b TEM image of α -FeOOH sample; Fig. 2c and d SEM image of α -FeOOH sample. α -FeOOH was prepared at the optimal technique: preparation of ferric yellow crystal seed: $c\text{Fe}^{2+}=0.3\text{mol/L}$, $\text{pH}=7.2$, $t=3\text{h}$, temperature is 15°C , air flow rate is $0.1\text{ m}^3/\text{h}$; preparation of ferric yellow: $c\text{Fe}^{2+}=0.3\text{mol/L}$, $\text{pH}=2.4\sim 3.7$, $t=7\text{h}$, temperature is 80°C , air flow rate is $0.12\text{m}^3/\text{h}$.

4. Summary

A novel and environment-friendly route was proposed to translate steel pickling waste liquids into high value-added material, namely iron oxide yellow. After purification, the harmful ions in the solutions were greatly reduced which was believed to be favorable to

the preparation of desired product. α -FeOOH nanoparticles with orthorhombic crystal structure of goethite were successfully synthesized after the intermediate ferric yellow was exposed to dry in the oven at 75 °C for 8 hours. The as-synthesized nanometer FeOOH exhibits excellent pigment property that can be ascribed to the well monodispersity and narrow particle size distribution within 150- 400nm. The content of FeOOH in the resultant product was as high as 90%, which is perfectly meet national prime standard of GB1863-2008. Thus, it is likely to produce tremendous economic and environmental benefits if the process proposed by us can be implemented throughout the country.

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