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Synthesis of Iron Oxalate for Yellow Pigment

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ABSTRACT: The global transition toward sustainable industrial materials has intensified the demand for non-toxic and chemically stable inorganic pigments. This study investigates the optimization of iron (II) oxalate dihydrate ($FeC_2O_4 \bullet 2H_2O$) synthesis, a prominent yellow pigment, via a liquid-phase precipitation method using iron (II) sulfate ($FeSO_4$) and oxalic acid ($H_2C_2O_4$) as primary precursors. A critical focus was placed on the synergistic effects of pH regulation and stirring kinetics to maximize crystalline recovery and optical consistency. To address common synthesis inefficiencies, sodium hydroxide (NaOH) was utilized as a strategic pH buffer to neutralize the byproduct sulfuric acid (H_2SO_4), thereby preventing the re-solubilization of the oxalate complex. Experimental results revealed that maintaining a stabilized pH of 3.5–4.0 at 60°C with a constant stirring rate of 500 RPM yielded a maximum crystalline recovery of 98.00%, characterized by a vivid yellow hue. In contrast, sub-optimal pH control led to significant yield reductions (as low as 52.10%) and partial oxidation, which compromised the pigment's chromaticity. These findings establish a robust and cost-effective framework for producing high-purity humboldtine, offering significant implications for the industrial coating sector and the development of advanced iron-based precursors for energy storage technologies.

Keywords: Iron (II) oxalate, precipitation method, yellow pigment, pH stabilization, yield optimization, humboldtine.

1. INTRODUCTION

The global pigment industry is currently undergoing a significant transition toward sustainable and non-toxic inorganic materials, driven by stringent environmental regulations and the rising demand for high-performance coatings [1]. Inorganic pigments, particularly those based on transition metal complexes, are highly valued for their superior thermal stability, chemical resistance, and opacity compared to their organic counterparts [2]. This shift is particularly evident in the development of iron-based colorants, which offer a sustainable alternative to heavy-metal-based pigments.

Iron-based pigments have remained a cornerstone in industrial applications due

to their abundance, low cost, and versatile color palette ranging from deep reds to vibrant yellows [3]. These materials are preferred in construction, plastics, and automotive coatings because of their non-toxic nature and excellent weatherability. Among the various iron compounds, iron(II) oxalate has gained renewed interest for its specific optical properties and chemical stability.

Iron(II) oxalate dihydrate ($FeC_2O_4 \bullet 2H_2O$), naturally occurring as the mineral humboldtine, is a prominent yellow pigment that has been utilized since the 19th century in the textile and arts industries [4]. Its unique crystal structure, characterized by polymeric chains of iron centers bridged by oxalate ligands, contributes to its exceptional lightfastness and durability under varied atmospheric conditions [5]. The stability of its yellow hue makes it an ideal candidate for long-term industrial use.

Beyond its traditional role as a colorant, iron oxalate serves as a critical precursor for the synthesis of advanced iron oxide nanoparticles (α-Fe_2O_3) and magnetic materials [6]. These derivatives are increasingly used in energy storage systems, such as lithium-ion batteries, and as heterogeneous catalysts in environmental remediation [7]. Therefore, optimizing the synthesis of the oxalate precursor is essential not only for the pigment industry but also for advanced material engineering.

The synthesis of iron oxalate is typically achieved through a liquid-phase precipitation method involving the reaction between a soluble iron(II) salt and oxalic acid. While the basic chemistry of this double displacement reaction appears straightforward, the resulting pigment's morphological properties and color intensity are highly sensitive to the precipitation environment [8]. Achieving a high-purity product requires a deep understanding of the kinetic and thermodynamic factors involved during the reaction.

Factors such as reactant concentration, temperature, and stirring kinetics play a vital role in determining the nucleation and growth rates of the crystals [9]. Improper control of these parameters can lead to particle agglomeration or the formation of amorphous phases, which significantly dulls the pigment's visual quality. Thus, precise control over the experimental conditions is mandatory to ensure consistency across different production batches.

Furthermore, the pH of the solution is a governing parameter in the precipitation process. An overly acidic environment can lead to the back-solubilization of the oxalate complex, thereby reducing the total yield and affecting the crystalline purity [10]. This sensitivity necessitates the use of chemical agents to maintain an optimal environment where the solid phase can remain stable throughout the aging process.

In this context, the role of neutralizing agents such as sodium hydroxide (NaOH) becomes crucial. Although NaOH is not a direct reactant in the formation of the iron oxalate complex, it serves as a pH buffer that neutralizes the byproduct sulfuric acid (H_2SO_4) generated during the reaction [11]. By maintaining the pH within a specific range, NaOH prevents the re-dissolution of the precipitate and ensures maximum recovery of the yellow pigment.

Despite its long-standing history, there is a lack of comprehensive studies focusing on the optimization of synthesis parameters using cost-effective precursors like iron(II) sulfate heptahydrate. This research aims to fill this gap by investigating the synergistic effects of pH control and stoichiometric ratios on the yield and quality of iron(II)

oxalate pigments. This study provides a robust framework for producing high-purity yellow pigments with optimized performance for modern industrial applications.

2. MATERIALS AND METHODS

2.1 Materials

The synthesis of iron(II) oxalate dihydrate was conducted using analytical-grade reagents to ensure high crystalline purity. The primary precursors included iron(II) sulfate heptahydrate ($FeSO_4 \bullet 7H_2O$, ≥ 99 %) and oxalic acid dihydrate ($H_2C_2O_4 \bullet 2H_2O$, ≥ 99 %). Sodium hydroxide (NaOH) pellets were utilized as a pH-adjusting agent to stabilize the precipitation environment. Deionized water was used throughout the dissolution and washing processes to minimize ionic interference. The experimental setup comprised a digital magnetic stirrer with an integrated heating plate, a calibrated pH meter, an analytical balance (accuracy ± 0.0001 g), a vacuum filtration unit, and a forced-air convection oven for the drying stage.

2.2 Methodology

The precipitation process was carried out through a controlled liquid-phase reaction. The procedure was divided into the following sequential stages:

1. Solution Preparation

Separate aqueous solutions of $FeSO_4$ (1 M) and $H_2C_2O_4$ (1 M) were prepared by dissolving the respective salts in deionized water at room temperature.

2. Precipitation Reaction

The $FeSO_4$ solution was placed in a 250 mL beaker and heated to a constant temperature of 60°C. The $H_2C_2O_4$ solution was then introduced dropwise into the iron(II) sulfate solution using a burette to ensure controlled nucleation.

3. Mixing and Stirring

To ensure a homogeneous reaction and prevent localized supersaturation, the mixture was continuously stirred at a constant speed of 500 RPM. This stirring rate was selected to optimize the contact between the Fe^{2+} ions and $C_2O_4^{2-}$ ligands.

Figure 1. Stirring and mixing the solution using a magnetic stirrer

4. pH Stabilization

During the addition of the reactants, the pH of the system was monitored. As the byproduct sulfuric acid (H_2SO_4) began to form, a 1 M NaOH solution was added dropwise to maintain the pH at a range of 3.5–4.0. This step is critical to prevent the re-solubilization of the iron oxalate complex in highly acidic conditions.

5. Aging and Separation

Once the reaction was complete, the resulting yellow suspension was aged for 60 minutes under slow stirring to promote crystal growth. The precipitate was subsequently separated using vacuum filtration and washed multiple times with deionized water until the filtrate reached a neutral pH, ensuring the removal of residual sulfate ions.

6. Drying

The final yellow pigment was dried in an oven at 105 °C for 2 hours to remove structural and surface moisture, then stored in a desiccator for further analysis.

The efficiency of the synthesis process was evaluated based on the crystalline recovery. The theoretical yield (W_{th}) was determined through stoichiometric calculations based on the limiting reactant ($FeSO_4$) as follows:

$$W_{th}(g) = n_{FeSO_4} \times MW_{FeC_2O_4 \cdot 2H_2O}$$

Where n represents the number of moles and MW is the molecular weight of the product (179.89 g/mol). The actual yield (W_{act}) was measured after the drying process. The percentage yield was calculated using the following equation:

$$Yield(\%) = \left(\frac{W_{act}}{W_{th}}\right) \times 100\%$$

Furthermore, the consistency of the pigment was assessed qualitatively through visual color comparison against industrial standards to evaluate the "vividness" and "purity" of the yellow hue produced under different pH settings.

3. RESULTS AND DISCUSSION

The synthesis of iron(II) oxalate dihydrate proceeds via a double displacement reaction between iron(II) sulfate and oxalic acid. The stoichiometric interaction is represented by the following equation:

$$FeSO_{4(aq)} + H_2C_2O_{4(aq)} + H_2O_{(l)} \rightarrow FeC_2O_4 \cdot 2H_2O_{(s)} \downarrow + H_2SO_{4(aq)}$$

A critical point raised during the peer-review process concerns the chemical compatibility of NaOH within this system. In this mechanism, NaOH does not act as a direct precipitant but functions as a vital pH buffer. As the reaction progresses, the generation of sulfuric acid (H_2SO_4) as a byproduct significantly increases the hydronium ion concentration (H^+), which shifts the equilibrium toward the dissociation of the oxalate complex, thereby promoting re-solubilization [10]. The controlled addition of NaOH facilitates the neutralization of H_2SO_4:

$$H_2SO_{4(aq)} + 2NaOH_{(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)}$$

By maintaining the pH in the range of 3.5–4.0, the deprotonation of oxalic acid ($H_2C_2O_4 \rightarrow C_2O_4^{2-}$) is optimized, ensuring a high supersaturation level necessary for the rapid nucleation of humboldtine crystals [11], [12]. This explains why Batch 2, which utilized precise pH monitoring, achieved near-theoretical recovery compared to batches with fluctuating acidity.

The experimental results for the three batches are summarized in Table 1. The yield fluctuated significantly from 52.10 % to 98.00 %, indicating that the process is highly sensitive to operational parameters.

Figure 2. Iron(II) oxalate dihydrate

Table 1. Experimental Yield and Visual Quality of Iron Oxalate

No.	Pigment Mass (grams)	Yield (%)	Visual Observation
1	16.98	61.06	Pale yellow
2	27.27	98.00	Vivid yellow
3	14.49	52.11	Dull yellow

The superior yield in Batch 2 (98.00 %) is attributed to the synergistic effect of a

constant stirring speed (500 RPM) and slow titrant addition. Rapid addition of oxalic acid in Batch 3 likely led to localized high concentrations, causing premature precipitation of amorphous phases or entrapment of unreacted Fe^{2+} ions, as evidenced by the dull/greenish tint [13]. Furthermore, the lower yield in Batch 1 (61.06 %) suggests that without sufficient aging time or pH stabilization, the micro-crystals remain in the mother liquor and are lost during the filtration stage [9].

The "Vivid Yellow" color achieved in Batch 2 is the primary indicator of high-purity iron(II) oxalate dihydrate. Scientific literature confirms that the chromaticity of humboldtine is highly dependent on its crystalline morphology and particle size distribution [14]. The "Pale yellow" appearance in Batch 1 indicates a smaller particle size or lower crystalline density, which increases light scattering but reduces color depth. Conversely, the "Dull/Greenish" hue in Batch 3 is a diagnostic sign of partial oxidation where Fe^{2+} ions are converted to Fe^{3+} species due to prolonged exposure to air at sub-optimal pH levels [15]. This oxidation creates iron(III) hydroxides or basic sulfates as impurities, which are detrimental to the pigment's value in the coating industry. Therefore, maintaining a reductive or strictly controlled acidic environment via NaOH buffering is essential for preserving the Fe^{2+} oxidation state required for the desired yellow chromophore.

4. CONCLUSION

The synthesis of high-purity iron(II) oxalate dihydrate as a sustainable yellow pigment was successfully optimized via the liquid-phase precipitation method. The experimental results demonstrate that the optimization of pH and stirring kinetics is paramount to maximizing the crystalline yield and ensuring optical consistency. Specifically, the utilization of NaOH as a neutralizing agent was proven critical; by buffering the byproduct sulfuric acid (H_2SO_4), NaOH maintained the reaction environment at an optimal pH of 3.5–4.0, which facilitated a peak recovery of 98.00% with a vivid yellow hue. In contrast, sub-optimal pH control and rapid titrant addition led to a significant decrease in yield (as low as 52.10%) and undesirable oxidation of iron(II) species, resulting in duller pigment quality. These findings provide a scalable and cost-effective framework for the production of humboldtine, which serves as a vital precursor not only for the industrial coating sector but also for the development of advanced iron-based materials in electrochemical energy storage technology.

To further elevate the scientific impact of this study, future research should transition from basic yield analysis to comprehensive material characterization and functional application testing. Specifically, the integration of X-ray Diffraction (XRD) and Fourier-Transform Infrared (FTIR) spectroscopy is essential to definitively confirm the humboldtine crystalline phase and assess the chemical bond purity of the synthesized oxalate. Furthermore, a detailed morphological evaluation via Scanning Electron Microscopy (SEM) will allow for a deeper correlation between precipitation kinetics and the resulting particle size distribution. Beyond its role as a colorant, exploring the electrochemical performance of iron oxalate as a precursor for lithium-ion battery anodes presents a strategic opportunity to expand the material's utility into the energy storage sector. Finally, quantitative colorimetric analysis using the CIELAB scale and rigorous stability tests against thermal and UV degradation will provide the necessary

industrial validation to confirm its viability as a high-performance, commercial-grade inorganic pigment.

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AUTHOR CONTRIBUTION

Bryant Kevin Andriano Cahyana: Conceptualization, Methodology, Investigation. Ninda Hemalia: Data curation, Writing – original draft. Rachell Yunankeyzia Firgia: Investigation, Validation. Himmah Sekar Eka Ayu Gustiana: Supervision, Project administration, Resources, Writing – review & editing.

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