

Production of Industrial-Grade Monoclinic Lead Chromate (PbCrO_4) from Indigenous Chromite ore for Paint Pigment Utilization

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Abstract

Decades of use have proven that lead chromate (PbCrO_4) powder is an excellent paint pigment material. Unfortunately, practically this entire superb chromate compound used for decorative systems, protective systems, and mass dyeing of paper and polymer materials is conventionally made using inorganic synthetic chromium salts. In this study, we reported a promising simple, low-cost lead chromate production route derived from chromite ore from Nigeria. The Nigerian chromite ore was roasted in a 1:1 NaOH salt and then leached with water at 60°C. Lead nitrate was added to the leached liquor to further co-precipitate it. The resulting precipitate was then cleaned in ethanol and oven dried for ten hours at 80°C. The experimental results showed that lead ion concentration, temperature and flow rate have large influence on lead chromate precipitation, and the precipitation data fit a diffusion model. The activation energy of lead precipitation obtained was 4.76 kJ/mol, and the reaction order was 0.873 nearly one in relation to the concentration of lead ion. Additionally, XRD, FT-IR, and SEM/EDS comparative investigation of the properties established which favourable paint pigment performance similar to that of commercial industrial lead chromate powder in a range of all established physicochemical properties clarified the developing direction of research on lead chromate synthesis from Chromite leached liquor.

Keywords: Chromite ore; Co-precipitation; Indigenous; Leaching; Lead chromate

Introduction

Lead (II) chromate, with the formula (PbCrO_4), is an important chromate chemical that occurs naturally as crocoite or crocosite [1]. PbCrO_4 typically appears in two crystal structures: stable monoclinic and unstable orthorhombic [2]. Because it possesses a bright yellow color and is essentially insoluble in water, it is used in paints under the name chrome yellow [3]. Lead chromate (PbCrO_4) powder has been used for decades, proving to be an ideal paint pigment. Regretfully, inorganic synthetic chromium salts have historically been used to

create practically this entire wonderful chromate compound, which is used for decorative systems, protective systems, and mass colouring of paper and polymer materials. Lead chromate (PbCrO_4) is a chemical that is commonly referred to as crocotite and is a valuable solid pigment with a monoclinic $\text{P}2_1$ structure that is utilized as a photosensitizer [4, 5]. Lead chromate is an important solid functional material with photo-electricity that is widely used in ornamental and protective applications, as well as for mass coloring rubber, elastomers, fibers, and plastics.[6–9]. In

addition, it has been used as a host material for light sensitizers, humidity-sensing resistors, and other uses.

Recently, a number of synthetic procedures, such as co-precipitation, crystallization, chemical diffusion through porous pores, electrodeposition, chemical fusion, and so on, have been used to create stable monoclinic lead chromate. However, intricate operations, time/energy consumption, and costly reagents appear to be an impediment to the commercialization of lead chromate synthesis. As a result, developing rapid, easy, and mild pathways for large-scale lead chromate production remains a significant issue. For this reason, it is essential to synthesize lead chromate with precise size and shape control for its intended applications. Few or no studies have been published to date on the synthesis of lead chromate from local mineral ores; nonetheless, several techniques have been used to achieve this goal, including: Lead chromate nanoparticles were synthesized via a chemical co-precipitation method by Davamani and Rani [10]. The results of the X-ray powder diffraction analysis gave well-crystallized, tetrahedral-shaped particles with an average size in the nano range (70–423 nm). Marcus et al. [11] describe a selectively adjustable process for creating PbCrO_4 nanorods and Pb_2CrO_5 microparticles by varying the parent mixture's pH when a PVP (poly(vinyl pyrrolidone)) surfactant is present.

The resulting PbCrO_4 nanorods are extremely homogeneous, with a length of 1.2–1.5 μm and an average diameter of 60–80 nm. They also come to the conclusion that the phase development of PbCrO_4 is significantly influenced by pH, or more specifically, the concentration of hydroxyl ions. Auraujo et al. [12] suggested a polymeric precursor method for

the manufacture of lead chromate (PbCrO_4) in another study. The samples' optical band gap was determined indirectly, and the green sample's monoclinic PbCrO_4 phase was visible in the XRD patterns. Using an ambient temperature solution process and no other additives, Xiang et al. [13] selectively produced orthorhombic and monoclinic PbCrO_4 , Pb_2CrO_5 , and $\text{K}_2\text{Pb}(\text{CrO}_4)_2$ nanocrystallites with varying morphologies. The results showed that changing the pH range and the molar ratio of $\text{Pb}(\text{Ac})_2$ and K_2CrO_4 can significantly alter the production of polymorphs and phases. This simple room temperature process is useful for the selective synthesis of lead chromate pigments with diverse phases and polymorphs, and it might be adapted to other inorganic systems. Pourmortazari et al. [14] investigated easy, rapid, and controllable precipitation approach for the manufacture of lead chromate nanorods in aqueous conditions. Taguchi robust design approach with L9 orthogonal array was used to optimize the experimental conditions for the syntheses. Various experimental parameters like, lead ion concentration and chromate ion concentration, were discovered to have important roles in determining lead chromate particle size. For a long time, researchers have been closely monitoring the usage of synthetic inorganic salts to make chromate salts due to their accessibility and, on occasion, low cost. There hasn't been much interest in synthesizing usable compounds from local mineral ores, such as lead chromate. As far as we know, our team is the only one that has used oxidative decomposition and water leaching to make monoclinic sodium chromate from chromite ore [15].

A typical lead chromate (PbCrO_4) was produced in this study adopting a

straightforward process of roast-leaching and co-precipitation using Nigerian chromite ore. The physicochemical and powder properties of the product after oven drying have been examined and studied. XRD, SEM/EDS, and FT-IR were also utilized to look into the structure and morphology of synthesized PbCrO_4 . The as-prepared PbCrO_4 exhibits good purity and a long thermal capacity.

Materials and Methods

Every chemical was utilized precisely as supplied, with no deviations in analytical purity. The leaching of chromite ore to create sodium chromate, which was utilized in this work, was previously documented by Ayinla et al. [15]. A total of 25, mL of sodium chromate leached liquid aqueous solution was added one by one to 5, 10, 15, 20, and 25 mL of 0.2 M $\text{Pb}(\text{NO}_3)_2$ aqueous solutions while agitating the mixture moderately. HCl and NaOH (1 mol L⁻¹) were used to change the liquids' pH to 5 or 11. The resulting mixtures were allowed to mature for ten hours at room temperature without being stirred. After centrifuging and repeatedly rinsing the products with 100% ethanol and distilled water, the products were vacuum-dried for six hours at 50 °C. The XRD line broadening method of particle size assessment was utilized in this work to evaluate the crystallite size of the powder sample. At STIC Cochin, the morphology of the powder samples was examined with a scanning electron microscope (SEM), utilizing a 'SHIMADZU' FTIR 8400S type spectrometer, infrared spectroscopic (IR) research on lead chromate powder was conducted utilizing the KBr approach. Based on the unique properties of the materials and their chemical composition, TG (Thermo Gravimetry) analyses were performed at different temperatures to investigate the behavior of the pigments during heating. A Netzsch STA 449

F5A was used to investigate the heating behavior of pigments. The TG and DSC curves were measured using alumina crucibles in a nitrogen atmosphere.

Results and Discussion

Leach Liquor Composition

The chemical components of leached solution as determined by atomic absorption spectroscopy (AAS) analyses is presented in **Table 1**. The AAS results emphasize the importance of metal ion concentration prior to precipitation in order to produce the synthesized inorganic pigments. Thus, the sodium chromate solution is mostly composed of chromium, aluminium, titanium, and vanadium. The iron generated from the leaching process is 0.22 gL⁻¹, and the remaining components do not surpass 1 gL⁻¹. The lead chromate pigment includes 73.2 percent lead and 23.6% chromium, with no more than 0.03 percent minor components.

Table 1: Atomic absorption spectroscopy analysis of used chromite ore leached liquor

Metal ions	Concentration gL ⁻¹
Cr	4.92
Al	17.80
Ti	1.95
V	1.40
Fe	0.22
Ni	0.15
Mn	0.06

The lead chromate synthesis yield optimization.

Optimization is a critical step in establishing a synthesis technique for nanoparticle formation. The purpose of this work was to investigate how certain experimental parameters affected the diameter of lead chromate and to identify the ideal experimental setup for the co-precipitation method of producing very fine lead chromate

(PbCrO₄) particles.

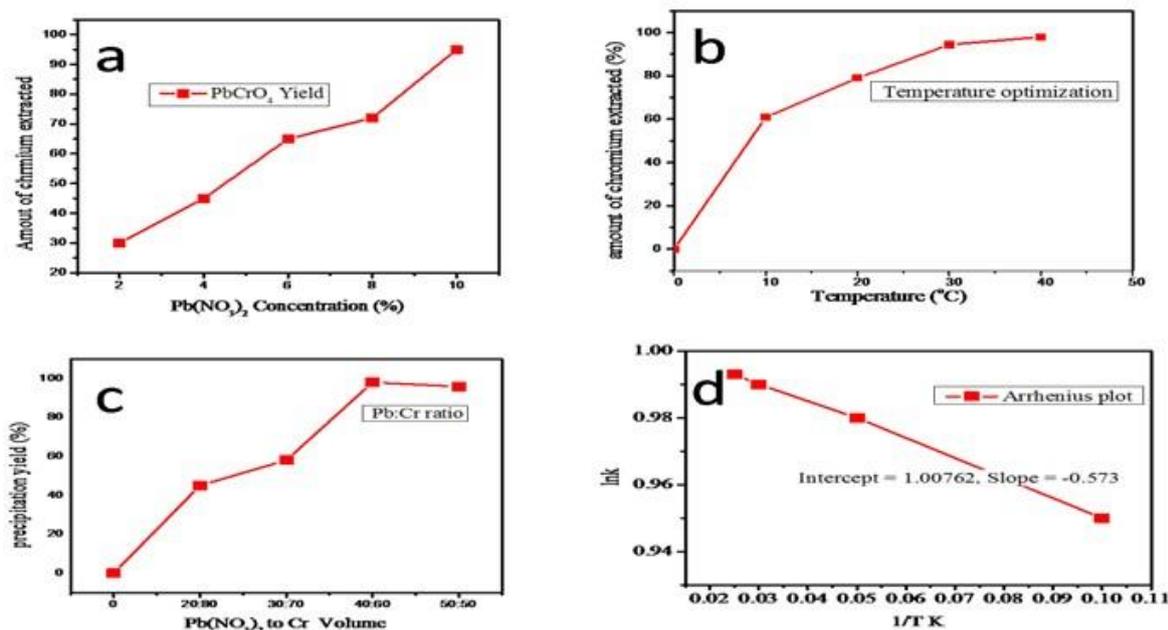


Figure 1: Optimisation profile of precipitation parameter: (a) Effect of precipitant concentration (b) Influence of system concentration (c) Leachee and precipitant flow rate (d) Arrhenius plot for activation energy calculation

As a result, an experimental design technique was utilized to explore the impacts of three parameters on the lead chromite: Pb in solution concentration, temperature, and mixing flow rate. Figure 1 depicts the optimisation data representation. The concentration of lead nitrate is critical in the chromate precipitation process. To find out how lead nitrate concentration affects lead chromate precipitation rate, experiments were conducted in precipitating solutions with varying lead nitrate concentrations (2–10%) at 30°C, 350 rpm stirring speed, and 20 ml/g L/L ratio. The results are plotted in Figure 1a. When the lead content was raised from 2% to 10%, the percentage of chromate precipitation increased considerably from 60.7% to 97.62. The chromate precipitation was studied at varying temperatures between 10 °C to 40 °C with a stirring speed of 350 rpm. Precipitation efficiency increases with increasing temperature, as illustrated in Figure 1b. After 5 minutes at 40 °C, the lead chromate production efficiency remains at 60%. However, it clearly increases

with increasing temperature during the initial and subsequent stages. When the temperature rises above 40°C, the lead chromate efficiency approaches 99%. Higher temperatures are known to modify the chemical equilibrium constant and increase the reaction rate constant. Furthermore, the higher temperature increases the solubility of the product surrounding the chromate particles, making it possible to reverse the precipitation reaction and keep the temperature at 40°C.

Furthermore, for the co-precipitation of lead chromate, a decreased liquid-to-liquid ratio of the solution leads to a decrease in Chromate efficiency. The following equation shows that for the same Pb (NO₃)₂-to-leach liquor ratio of the slurry, a higher lead nitrate concentration results in a lower liquid-to-liquid ratio.

$$R = \frac{V_p}{V_{lq}} \quad (1)$$

where R (mL/g) stands for the liquid-to-liquid ratio, V_p (mL) and V_{lq} (mL) represent the liquor volume of precipitant and , respectively.

According to Hua (2004) [16], the following

equation can be used to describe the co-precipitation macrokinetics of the ore:

$$\frac{\partial}{3D_1} + \frac{r_0}{2DS} \left[1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3} \right] + \frac{1}{Kr} \left[1 - (1 - \alpha)^{2/3} \right] = \frac{CA_0}{4\rho r_0} t \quad (2)$$

The δ denotes the liquid boundary layer thickness, D_1 denotes the mass transfer coefficient of the group from Na_2CrO_4 and $\text{Pb}(\text{NO}_3)_2$ in liquid, α denotes the lead chromate precipitating efficiency, r_0 denotes the radius of the lead chromate particle, D_s denotes the mass transfer coefficient of the group in the product layer, k_r denotes the reaction rate constant, t denotes the reaction time, C_{A_0} denotes the concentration of the group at $t = 0$, and ρ denotes the density of the lead chromate particle.

The co-precipitation of lead chromate is controlled by the diffusion of reagent in the liquid boundary layer and equation 2 is simplified as

$$\alpha = \frac{3DSct}{4\rho r_0} CA_0 \quad (3)$$

To investigate the rate-controlling step, the lead chromate precipitation efficiency versus lead nitrate concentration at 40 °C was fitted to Eqs. 3. Figure 1d represents the natural logarithm of the reaction rate ($\ln k$) versus the reciprocal of the absolute temperature (T) according to the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{R} * \frac{1}{T} \quad (4)$$

where E_a denotes the apparent activation energy, A denotes the pre-exponential factor, and R denotes the molar gas constant.

From Eq. (4) the apparent activation energy was calculated as 4.76 J/mol.K, and the rate-determining step was determined to be chemical control in the solid product layer.

Physicochemical and Powder Properties of Product

The established physicochemical properties and powder properties of the obtain product was depicted in **Table 2**. According to the physicochemical characteristics parameters shown in **Table 1**, the obtained PbCrO_4 powder is very basic with a pH value of 12.6 and a high melting point above 1400 °C. The powder solubility test revealed that the only solvent acceptable for dissolving it is 0.1M HCl. When compared to commercial lead chromate purchased from China, the engineered powder had a near range bulky density but a better hydration capacity. All of the powder qualities that have been established are in good agreement with the ASTM standard [17].

Table 2: Summary of Engineering Properties of the Obtained Lead Chromate Powder

Physicochemical properties of synthesized PbCrO_4	
Moisture Content	2.4%
pH Value	12.6
Melting point	1429 °C (1432°C)
Solubility of synthesized PbCrO_4	
0.1M NaOH	Insoluble
0.1 M HCl	Soluble
Ethanol	Partially soluble
N-hexane	Insoluble
Acetone	Insoluble
Powder property of synthesized PbCrO_4	
Tapped density	3.90
Bulk density	4.99
compressibility	32.32
Hausner Ratio	1.70
Angle of response	32.09
Stabilizer property of synthesized PbCrO_4	
Porosity	8.43
Hydration capacity	4.09 (3.98)
Swelling capacity	1.09
Moisture sorption	0.97

XRD Result of Product

For assessing the crystalline size of a synthetic lead chromate sample, X-ray diffraction is a good approach. This method is determined by carefully quantifying the peak broadening. The crystallite size of the powder sample was assessed in this study utilizing the XRD line broadening method of particle size evaluation. The XRD pattern of a prepared sample of lead chromate is shown in **Fig. 2**. As shown in figure 2, the broadening of the x-ray lines reveals the fine particle nature of the materials. The standard is confirmed by a good agreement between the studied diffraction angle and the standard diffraction angle [2] of the specimen. All interference in **Fig. 2** was listed in an index as a single phase of monoclinic lead chromate with space group $P21/n(14)$ and lattice parameters $a = 7.10$, $b = 7.46$, $c = 6.85$, and $\beta = 102.398^\circ$, which is compatible with JCPDS No. 71-2064 [18,19]. In addition, the assigned peaks showed PbO and CrO₃ as the major compound in the analyzed sample with traces of compound such as FeO, MgO as trace compounds.

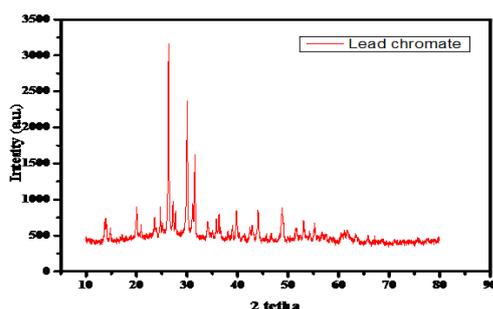


Figure 2: XRD spectra of synthesised lead chromate.

SEM Result of Product

The appearance and size of the produced lead chromate nanoparticles were examined using scanning electron microscopy. **Fig. 3** shows SEM pictures of lead chromate nanoparticles at different magnifications which indicate that they are well crystalline and have

an irregular form. **Fig. 3 (a)** shows synthesised lead chromate macrographs of polyhedral granular particles with varying particle dimensions ranging from 1 to 2 μm and a bimodal distribution devoid of agglomeration. Close grain connection and clearly visible intergranular boundaries generate a faultless compact structure throughout the sintering process at 300 $^\circ\text{C}$, as shown in **Fig. 3 (b)**.

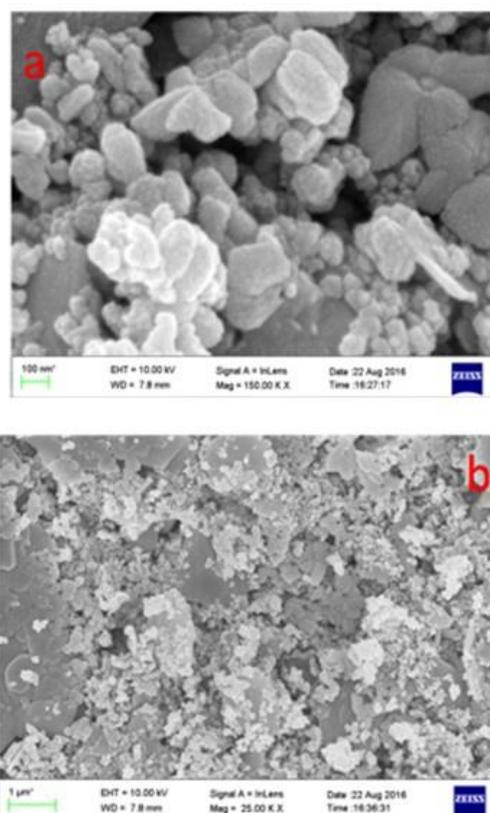


Figure 3: SEM image of synthesised monoclinic lead chromate

EDAX Result of product

The resulting lead chromate (PbCrO₄) particle was further defined by EDAX spectrum for composition and purity evaluation (**Fig. 4**). The peak in Figure 4 shows that the product is incredibly pure; it corresponds to Pb and Cr with an average atomic percentage ratio of about 60.03:15.47%. The presence of the appropriate element in stoichiometric percentage is confirmed by elemental analysis.

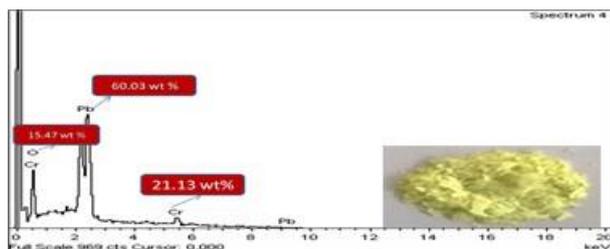


Figure 4: EDAX spectrum of synthesized pure monoclinic lead chromate

FT-IR Result of product

Fig. 5 depicts the FTIR spectrum of the lead chromate sample. The FTIR spectrum for lead chromate exhibits peaks at 3315.41cm^{-1} , 3139.9 cm^{-1} , and 3020.32 cm^{-1} , which correspond to the free O-H group [18], as well as a peak at 1191.93cm^{-1} , which indicates the presence of lead, and a peak at 855.75cm^{-1} , which reflects the Cr-O stretching mode.

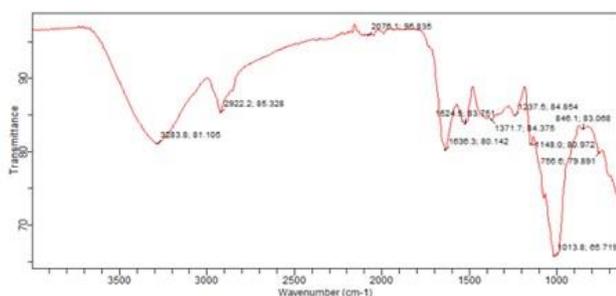


Figure 5: The FT-IR spectra of synthesized lead chromate (PbCrO_4)

Proposed Production Flow sheet

A series of hydrometallurgical processes such as roast-leaching; iron separation and pure chromate precipitation are included in this lead chromate synthesis. As a result, **Fig. 6** illustrates a straightforward and quick strategic route for the synthesis.

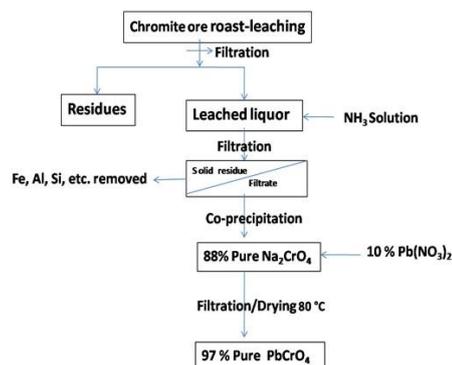


Figure 6: lead chromate (PbCrO_4) production schematic diagram

Conclusions

Lead nitrate solution was used in the leaching cum-co-precipitation process to create monoclinic lead chromate with a large surface area. The ideal parameters for this straightforward and quick method of producing lead chromate powder were: a temperature of $80\text{ }^\circ\text{C}$, a $\text{Pb}^{2+}:\text{Cr}^{6+}$ ratio of 40:60, and a 10% $\text{Pb}(\text{NO}_3)_2$ solution. The process of preparation produced powders with unique catalytic and physicochemical characteristics. The PbCrO_4 thin film's hexagonal structure as a nano-crystalline was demonstrated by the XRD data. SEM results showed that the PbCrO_4 micrograph has a compact structure composed of a single type of spherical granules with cavities and variable size. The purity of the synthesised power was affirmed by EDAX that reveals appropriate element in stoichiometric percentage and FT-IR indicates the presence of lead, and a peak at 755.75cm^{-1} , which reflects the Cr-O stretching mode. Finally, for further scaling up, the manufacturing schematic diagram was developed.

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Author's Contribution Statement

KI Ayinla: Conceptualization, Methodology,

Writing-original draft preparation, **AA Baba:** Supervision; **BC Tripathy:** Data curation, Visualization, **RK Dwari-** Validation, Formal analysis,

Conflict of Interest

The authors do not have any conflict of interest throughout this research work.

Data Availability Statement

The data supporting this study's findings are available from the corresponding authors upon reasonable request.

References

- [1] X. L. Hu. and Y. J. Zhu, Single-crystalline PbCrO_4 nanowires and their hydrothermal transformation to amorphous $\text{PbCr}_3\text{O}_{10}$ nanotubes, *Chemistry Letter*, 2004, 33, 880–881 (DOI 10.1246/cl.2004.880)
- [2] G.P. Algra, L. J. H. Erkens and D. M. Kok, Lead chromates: the state of the art in 1988. *Journal of Oil Colour Chemical Association*, 1998, 71, 71–76. (DOI: <https://trid.trb.org/View/431654>)
- [3] L. J. H., Erkens, H Hamers, R. J. M., Hermans, E. Claeys and M. Bijnens, Green synthesis of PbCrO_4 nanostructures using gum of ferula assa-foetida for enhancement of visible-light photocatalytic activity. *Surface Coatings International B*, 2001, 84, 169–176. (DOI: <https://doi.org/10.1007/BF02700395>)
- [4] K.A. Wishah, and M.M. Abdul-Gader, Green synthesis of PbCrO_4 nanostructures using gum of ferula assa-foetida for enhancement of visible-light photocatalytic activity. *Applied Physics A*, 1998, 66, 229–234, (DOI: 10.1007/s003390050660)
- [5] K. Takabasi, and K. Toda, Optical properties of calcium chromate 1D-nanorods synthesized at low temperature from secondary resources, *Optical Materials*, 1991, 2, 275–283, (DOI <https://doi.org/10.1016/j.optmat.2014.05.034>)
- [6] K. S. Knight, A high temperature structural phase transition in crocoite (PbCrO_4) at 1068 K: crystal structure refinement at 1073 K and thermal expansion tensor determination at 1000 K. *Mineralogical Magazine*, 2000, 64, 291–300, (DOI: <http://doi.org/10.1180/002646100549193>)
- [7] X. U. Hong-bin, S-L Zheng, Y. Zhang, L. Zuo-Hu, W. Zhi-Kuan, Oxidative leaching of a Vietnamese chromite ore in highly concentrated potassium hydroxide aqueous solution at 300 °C and atmospheric pressure, *Minerals Engineering*, 2005, 18, 527–535. (DOI: <https://doi.org/10.1016/j.mineng.2004.08.002>)
- [8] Y. Zhang, S-L. Zheng, H-B. Xu, D. Du, Y. Zhang, Decomposition of chromite ore by oxygen in molten NaOH-NaNO_3 , *International Journal of Mineral Processing*, 2010, 95, 10–17. (DOI: <https://doi.org/10.1016/j.minpro.2010.03.005>)
- [9] Z. Sun, Y. Zhang, S-L. Zheng, Y. Zhang, A new method of potassium chromate production from chromite and $\text{KOH-KNO}_3\text{-H}_2\text{O}$ binary submolten salt system, *AIChE Journal*, 2009, 55, 2646–2656. (DOI: <https://doi.org/10.1002/aic.11871>)
- [10] Y. Zhang, Z-H. Li, T. Qi, Z-K. Wang, S-L. Zheng, Green chemistry of chromate cleaner production, *Chinese Journal of Chemistry*, 1999, 17, 258–266. (DOI: <https://doi.org/10.1002/cjoc.19990170308>)
- [11] J. Tardio, S. Bhargava, J. Prasad, D.B. Akolekar, Catalytic wet oxidation of the sodium salts of citric, lactic, malic and tartaric acids in highly alkaline, high ionic strength solution, *Topics in Catalysis*, 2005, 33, 193–199, (DOI: <https://doi.org/10.1007/s11244-005-2527-z>)
- [12] Y. X. Hua, Introduction to Kinetics of Metallurgical Process. *Metallurgical Industry Press, Beijing, China (in Chinese)*, 2004, 12, 123–127
- [13] J. H. Xiang, S-H. Yu, and Z. L. Xu, Synthesis of silver chromate nanoparticles: Parameter optimization using Taguchi design, *Crystal Growth and Design*, 2004, 4, 1311–1315. (DOI: <https://doi.org/10.1021/cg049777k>)
- [14] J. Wang, A. Gupta, T.M. Klein, Plasma enhanced chemical vapor deposition of Cr_2O_3 thin films using chromium hexacarbonyl ($\text{Cr}(\text{CO})_6$) precursor. *Thin solid films*. 2008, 516 (21), 7366–7372. (DOI: <https://doi.org/10.1016/j.tsf.2008.02.027>)

- [15] A. A. Baba, I. K. Ayinla, B. C. Tripathy, A. S. Ibrahim, G. Sadiu, Preparation of Industrial Sodium Chromate Compound from an Indigenous Chromite Ore by Oxidative Decomposition Rare Metal Technology Rare Metal Technology, *The Minerals, Metals and Materials series*, 2021, 2, 123 – 127, (DOI: http://doi.org/10.1007/978-3-030-65489-4_24)
- [16] W. W. Wang, and Y. J. Zhu, Synthesis of PbCrO₄ and Pb₂CrO₅ Rods via a Microwave-Assisted Ionic Liquid Method. *Crystal Growth and Design*, 2005, 5, 505–507, (DOI: <https://doi.org/10.1021/cg0497546>)
- [17] J. H. Liang, and Y. D. Li, Synthesis and characterization of lead chromate uniform nanorods, *Journal of Crystal Growth*, 2004, 261, 577–580, DOI: <https://doi.org/10.1016/j.jcrysro.2003.10.002>
- [18] G. J. Zhou, M. K. Lu, F. Gu, S. F. Wang, Z. L. Xiu, and X. F. Cheng, Controlled synthesis and optical properties of PbCrO₄ nanorods and nanoparticles, *Journal of Crystal Growth*, 2004, 270, 283–289, (DOI: <https://doi.org/10.1016/j.jcrysro.2004.06.018>)
- [19] A. K. Panda, B. B. Bhowmik, A. R. Das, and S. P. Moulik, Inorganic Particle Synthesis via Macro and Micro emulsions. *Langmuir*, 2015, 17, 1811–1818, (DOI: <https://doi.org/10.1016/j.chemphyslip.2016.07.001>)