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SCIENTIFIC PAPER

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APPLYING DENSITY FUNCTIONAL THEORY TO PREDICT THE REDUCTION POTENTIAL IN THE INDIGO DYEING PROCESS

Highlights

- Experimental results were assessed using redox potential and color strength.
- E_{HOMO} values showed iron(II) gluconate had the highest electron-donating power.
- Complexation energy calculations matched well with experimental dyeing results.
- DFT efficiently predicted the reducing power of organic iron(II) salts.

Abstract

This study employs density functional theory (DFT) to quantify the electron donor-acceptor properties and polarizability of organic iron(II) salts as reducing agents in indigo dyeing processes. The potential of some iron(II) salts to serve as environmentally friendly alternatives to the ecologically harmful sodium dithionite in the indigo dyeing process was investigated. A comparative analysis assessed the redox potential of reduced indigo and the color strength of dyed fabrics. Experimental results identified iron(II) gluconate as the most efficient, yielding superior color intensity. Theoretical calculations using B3LYP/LANL2DZ confirmed the superior electron-donating ability of iron(II) gluconate compared to the other iron(II) salts. The indigo reduction ability with the iron(II) salts was evaluated on the basis of complexation energies. The theoretical thermodynamic study reveals that the indigo-iron(II) gluconate complex is the most thermodynamically stable, requiring less energy input for its formation compared to the other complexes. Iron(II) salts-to-indigo electron donations in the complexes studied have been revealed by Mulliken charge analysis. These findings highlight the efficiency of DFT-based approaches in accurately predicting the reducing capacity of iron(II) salts and their suitability as eco-friendly alternatives in indigo dyeing applications.

Keywords: Indigo dyeing; iron(II) salts; DFT calculations; experimental results, complexation energy.

INTRODUCTION

Indigo dyeing is a widely used process in the textile industry, known for its distinctive blue color and durability. In this process, the initially insoluble dye needs to be reduced into its leuco-soluble form, which exhibits an affinity for cellulosic fibers. Once indigo penetrates the fiber, it is fixed by regenerating its initial insoluble form, typically through oxidation with air. Currently, the majority of indigo dyeing processes rely on sodium dithionite as a reducing agent [1]. However, this chemical compound poses several challenges. Sodium dithionite is highly flammable, demanding special storage precautions, and exhibits poor stability [2]. Furthermore, its oxidation results in the production of sulfates, sulfites, thiosulfates, and toxic sulfides, all of which have detrimental toxic effects on the environment and corrosive impacts on waste lines. The decomposition of sodium dithionite also affects aerobic processes during wastewater treatment [3]. Consequently, there is an urgent need to identify eco-friendly alternatives that maintain or improve the efficiency of the dyeing process while reducing environmental impact.

Numerous environmentally friendly reducing agents were explored as alternatives to sodium dithionite, such as sodium borohydride [4,5] and α-hydroxycarbonyls (e.g., glucose, hydroxyacetone) [6]. While these compounds align with environmental standards, they fall short in terms of dyeing performance compared to sodium dithionite.

Iron(II) complexes were extensively employed for the chemical reduction of indigo [7,8]. A recent consideration

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involves the use of ecological enzymes in combination with iron(II) sulfate as a reducing agent for indigo dyeing. The efficiency of several enzymes, such as alkaline catalase and alkaline protease combined with iron(II) sulfate in the indigo reduction and solubilization was also studied [9]. Dyeing performance with this approach demonstrated comparability with that achieved using sodium dithionite [10].

Density functional theory (DFT) has become one of the most powerful computational tools for understanding and predicting the electronic properties and chemical reactivity of molecules. In particular, DFT is highly effective in studying systems where electron transfer and donor-acceptor interactions are fundamental [11]. These interactions are important in various chemical and biological processes, such as charge transport in organic semiconductors, redox reactions in electrochemistry [12], and energy transfer in photovoltaic materials [13]. A thorough survey of the literature reveals a significant gap in studies utilizing DFT to explain the reduction mechanism of indigo. While extensive research has been conducted on the dyeing properties, redox behavior, and reduction of indigo using conventional chemical and electrochemical methods, there is a notable absence of computational investigations that employ DFT to elucidate the electronic and molecular factors governing its reduction process.

This paper presents a novel and unique feature in indigo dyeing processes by combining experimental reduction and dyeing experiments with DFT. The capacity of iron(II) gluconate (E 574), iron(II) lactate (E 585), and iron(II) fumarate to reduce indigo was studied and compared to that of conventional sodium dithionite. These ferrous compounds, commonly used as food additives and dietary supplements, are notable for their low toxicity and biocompatibility. The organic iron(II) salts used are considered environmentally friendly as they undergo oxidation to ferric compounds during the dyeing process. These ferric compounds can act as flocculants, promoting the aggregation and subsequent removal of suspended solids and dye residues during wastewater treatment. This dual role as reducing agents and facilitators of effluent purification makes them attractive, sustainable alternatives to the conventional sodium dithionite reducing agent. Their use supports cleaner production practices and aligns with circular economy principles in textile manufacturing. DFT was used to quantify the electron donor-acceptor character and the polarizability of organic iron(II) salts. In order to quantify the reducing power of iron(II) salts and their efficiency in the dyeing process, the complexation energies between the reducing agents and indigo molecules were calculated. The effectiveness of DFT was evaluated by comparing the predicted interaction energy values with the obtained redox potential values and the color strength of the dyed samples.

EXPERIMENTAL

Chemicals and Materials

The chemicals used were: Sodium hydroxide (NaOH ≥ 99%, Loba Chemie, Germany), iron(II) gluconate dihydrate ($C_{12}H_{22}FeO_{14}$, Sigma-Aldrich, USA), iron(II) lactate ($C_6H_{10}FeO_6$ ≥ 98%, Sigma-Aldrich, Spain), iron(II) fumarate ($C_4H_3FeO_4$ ≥ 95%, Sigma-Aldrich, Spain).

Dyeing experiments using indigo powder ($C_{16}H_{10}N_2O_2$, Benzema, Switzerland) were performed on 100% bleached cotton fabric with the following specifications: plain weave structure, a fabric weight of 173 g·m^{-2}, warp count of 25 yarns cm^{-1}, and weft count of 31 yarns cm^{-1}.

Indigo Reduction process

The reduction of indigo by organic iron(II) salts was conducted using 2 g·L^{-1} of indigo, 15 g·L^{-1} of sodium hydroxide, and a reducing agent concentration of 0.02 mol·L^{-1} at 75 °C for 120 min. The dye bath was prepared and subsequently placed in an AHIBA dyeing autoclave. Once the reduction temperature reached 75° C, the reducing agent was introduced to the dye bath. After 120 min, the redox potential was measured using a pH meter (pHM210) equipped with a platinum electrode and a reference electrode (Ag/AgCl, 3KCl). The reduced dye bath was then utilized for dyeing experiments following the 6-dip-6-nip method.

To compare the dyeing results achieved with iron(II) salts with those of conventional methods, a series of tests employing sodium dithionite as a reducing agent were conducted. These tests adhered to the guidelines of the traditional process used at an industrial scale. Typically, the dye bath contains 2 g·L^{-1} of indigo, 4 g·L^{-1} of sodium hydroxide, and 4 g·L^{-1} of sodium dithionite, maintained at a temperature of 50 °C [14].

Dyeing process

Cotton samples were dyed using the 6-dip/6-nip impregnation process. Each cycle (1 dip-1 nip) consisted of immersing the fabric in the dye bath for 1 minute, followed by aeration for approximately 2 minutes. This process was repeated six times. After dyeing, the samples were thoroughly washed with tap water and dried at room temperature.

Color strength measurement

Dyed samples were estimated by measuring the color strength (*K/S*) at 660 nm using a Spectraflash 600+ spectrophotometer (Datacolor International, USA, illuminant: D65, geometry: d/10°). The presented results were calculated as the mean of three values. The color strength value (*K/S*) was calculated following the Kubelka-Munk equation [15]:

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0} \qquad (1)$$

where K is the absorption coefficient, S is the scattering coefficient, R_0 is the reflectance value of undyed fabric, and R is the reflectance of the dyed fabric.

DFT calculations

The optimized structures of the ferrous salts molecules, sodium dithionite and indigo, were determined using the Gaussian16 program package, based on the B3LYP level of theory in conjunction with the LANL2DZ basis set, accompanied by Grimme's D3BJ correction [16,17] and CPCM model for water solvation. Molecular orbitals were visualized by GaussView 6, while the VMD

1.9.4 program was used for Electrostatic potential (ESP) visualization [18]. The multifunctional wavefunction analyzer, Multiwfn, was employed to analyze electron density distributions [19]. The ESP evaluation code based on the LIBRETA library is being used.

To better understand the reduction mechanism of indigo with iron(II) salts and sodium dithionite, key quantum chemical descriptors of the reducing agents were analyzed based on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy values. The HOMO corresponds to the highest energy level occupied by electrons, reflecting a molecule's ability to donate electrons. In contrast, the LUMO represents the lowest available energy level, indicating the molecule's capacity to accept electrons. The energy gap (E_{Gap}), defined as the difference between HOMO and LUMO energy levels, serves as a parameter for assessing the molecule's stability and reactivity [20].

The overall reactivity descriptors using Koopman's theorem [21] are expressed by the following equations:

Electronegativity $\chi = \frac{(IP+E\quad)}{2}$ *(2)*

Chemical potential $\mu = \frac{-(IP+\qquad)}{2}$ *(3)*

Hardness $\eta = \frac{(IP-\qquad)}{2}$ *(4)*

Electrophilicity index $\omega = \frac{\mu^2}{2\eta}$ *(5)*

Energy gap $\Delta E = E_{LUMO} - E_{HOMO}$ *(6)*

where E_{HOMO} is the highest occupied molecular orbital energy, E_{LUMO} is the lowest unoccupied molecular orbital energy, $IP = -E_{HOMO}$ is the ionization potential, and $EA = -E_{LUMO}$ is the electron affinity. Absolute electronegativity (χ), expressed in electron volts (eV), is a chemical descriptor that quantifies a system's (atom, molecule, ion, or radical) ability to attract electrons when forming chemical bonds, making it a useful tool for predicting chemical reactivity and behavior in various interactions. Softness is a characteristic attributed to molecules that denotes the capacity of an atom or group of atoms to accept electrons [22]. Hardness (η) characterizes the resistance of the molecular electron cloud to deformation under small perturbations. The electrophilicity index (ω) is a parameter that measures the energy reduction resulting from the maximum electron flow between donor and acceptor in a reaction, as defined by Eq. (5) [23]. Molecules can exhibit either electrophilic behavior, characterized by a higher electrophilic index, or nucleophilic behavior, associated with a lower electrophilic index, during reactions [24].

RESULTS AND DISCUSSION

Assessment of the Reducing Ability of Iron(II) Salts and Their Impact on Dyeing Performance

The influence of reducing agents concentration on the evolution of redox potential was examined in the presence of 2 g·L^{-1} of indigo and 15 g·L^{-1} of sodium hydroxide. To compare the reduction capacities of iron(II) salts with those of the conventional process, reductions were performed with different concentrations of sodium dithionite using 4 g·L^{-1} of caustic soda at a temperature of 50 °C.

The results are presented in Figure 1(a). This figure demonstrates that sodium dithionite generates the most negative redox potential values, below -700 mV, from a concentration of 0.01 M, highlighting its high efficiency as a reducing agent for indigo. Besides, it can be observed that exceeding a concentration of 0.036 M 16 g·L^{-1}, iron(II) gluconate gives a redox potential of about -732 mV. Iron(II) fumarate gives its minimum redox potential of -520 mV for a concentration of 0.047 mol·L^{-1}. This value decreases to -532 mV at a concentration of 0.043 mol·L^{-1} for iron(II) lactate. These findings indicate that iron(II) lactate and iron(II) fumarate are less effective as reducing agents and cannot achieve complete reduction of indigo.

Following the reduction of indigo with various reducing agents, the resulting dye baths were used for dyeing experiments. The dyeing performance was evaluated by measuring the color strength (K/S) at 660 nm. Figure 1(b) illustrates the variation in color strength of the dyed samples as a function of reducing agent concentration. The results indicate that iron(II) gluconate exhibits significantly superior dyeing performance compared to the other iron(II) salts, achieving a K/S value of 19 at a concentration of 0.04 mol·L^{-1} (18 g·L^{-1}). This value exceeds the color strength (K/S) of 17 obtained from reference dyeings using sodium dithionite. Beyond this concentration, a slight decline in color strength is observed. Similarly, iron(II) fumarate shows an increase in color strength from 0.07 mol·L^{-1} (12 g·L^{-1}), peaking at K/S= 5 at 0.095 mol·L^{-1} (16 g·L^{-1}), after which the color strength stabilizes. For iron(II) lactate, the color strength begins to increase from a concentration of 0.04 mol·L^{-1}and reaches a maximum K/S value of 11 at 0.085 mol·L^{-1} (20 g·L^{-1}), suggesting that a large quantity of this reducing agent is required to effectively reduce indigo. These findings indicate that, in addition to generating the necessary redox potential, iron(II) gluconate achieves the highest color strength, confirming its superior efficiency as a reducing agent in indigo dyeing.

DFT study of the investigated iron(II) salts as reducing agents for indigo

Global reactivity descriptors of indigo and iron(II) salts

Geometries of indigo and the reducing agents were first optimized using the B3LYP level of theory with the LANL2DZ basis set. The HOMO and LUMO energies were determined. From these two parameters, the molecular properties and global reactivity descriptors of the iron(II) salts, reducing agents, and indigo were calculated and tabulated in Table 1.

To evaluate the electron-donating capabilities of various iron(II) salts, their HOMO energy levels (E_{HOMO}) were analyzed and compared to that of sodium dithionite. E_{HOMO} is a key quantum chemical descriptor associated with a molecule's ability to donate electrons; a higher (less negative) HOMO value generally reflects stronger electron-donating potential [25,26]. As shown in Table 1, iron(II) gluconate has the least negative HOMO value (-6.19 eV) among the studied salts, indicating the highest electron-donating ability in this group. In comparison, sodium dithionite exhibits a much higher HOMO energy (-3.50 eV), highlighting its superior reducing power.

Furthermore, iron(II) gluconate shows the largest HOMO-LUMO gap (4.45 eV) and highest chemical hardness (η = 2.23 eV), suggesting greater electronic stability and lower polarizability features typically associated with kinetically stable but less reactive species. Conversely, sodium dithionite, with its minimal energy gap (0.41 eV) and extremely low hardness (η = 0.21 eV), exhibits a highly reactive nature, consistent with its well-known effectiveness as a reducing agent.

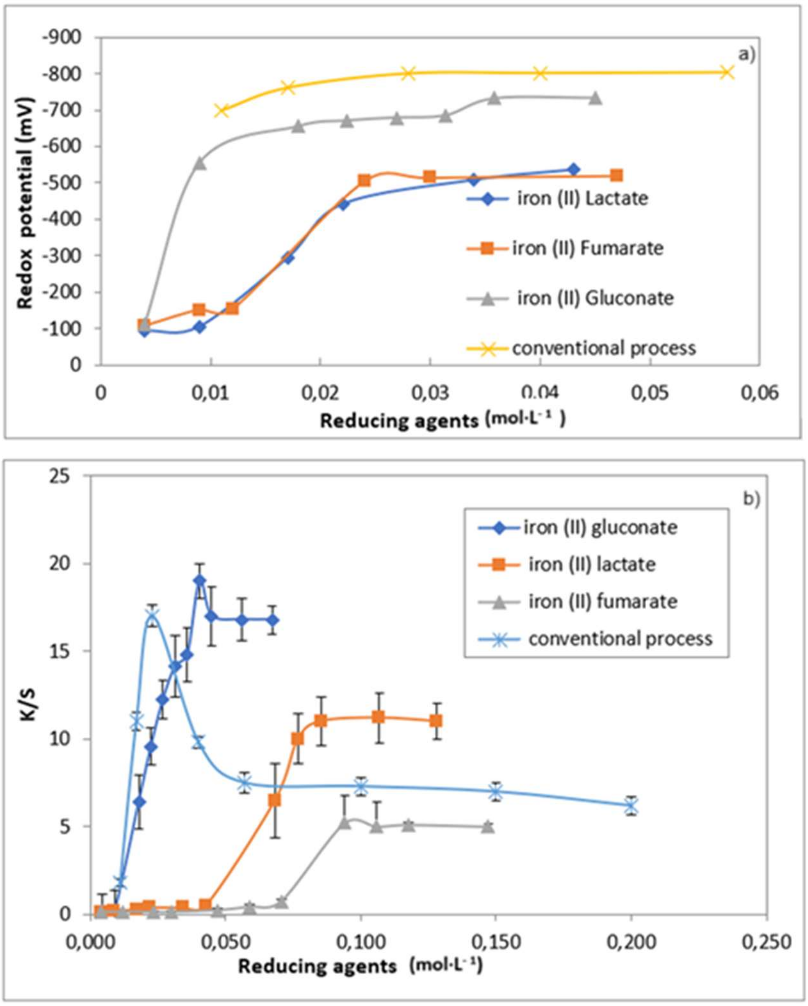

Figure 1. The evolution of (a) redox potential and (b) color strength (K/S) of the dyed samples as a function of the reducing agent concentrations.

Table 1. The optimized calculations of global reactivity descriptors for iron(II) salts.

Molecule	HOMO (eV)	LUMO (eV)	GAP (eV)	μ (eV)	η (eV)	ω (eV)
Indigo	-5.52	-3.21	2.31	4.37	1.16	8.25
Sodium dithionite	-3.50	-3.09	0.41	3.30	0.21	26.48
Iron(II) fumarate	-7.54	-4.30	3.24	5.92	1.62	10.83
Iron(II) lactate	-6.51	-2.21	4.30	4.36	2.15	4.43
Iron(II) gluconate	-6.19	-1.73	4.45	3.96	2.23	3.52

Notably, sodium dithionite displays an exceptionally high softness value (S = 4.76 eV), in contrast to iron(II) fumarate (0.617 eV), iron(II) lactate (0.465 eV), and iron(II) gluconate (0.448 eV). This high softness reflects its strong polarizability and electronic flexibility, both of which contribute to its rapid electron-transfer capacity in redox systems.

Regarding the electrophilicity index (ω), the trend among the iron(II) salts follows: iron(II) fumarate (10.83 eV) > iron(II) lactate (4.43 eV) > iron(II) gluconate (3.52 eV).

This descending order indicates that iron(II) gluconate is the least electrophilic and therefore the most nucleophilic, suggesting a greater ability to donate an electron pair during electron-transfer processes. Although sodium dithionite has an unusually high electrophilicity index (ω = 26.48 eV), a result of its high chemical potential and low hardness, this descriptor primarily reflects its overall reactivity. In aqueous solution, dithionite behaves as a strong reducing agent due to favorable thermodynamics and its capacity to deliver electrons to suitable oxidants.

Overall, the quantum chemical descriptors calculated for the studied compounds align well with the experimental dyeing results. In particular, the performance of iron(II) gluconate, which combines a relatively negative HOMO energy with moderate softness and low electrophilicity, supports its potential as an efficient and sustainable alternative to conventional reducing agents in textile applications.

Analysis of Electrostatic Potential (ESP)of the reducing agents and indigo

The Electrostatic Potential (ESP) maps provide a visual representation of the charge distribution within a molecule, allowing for the identification of electrophilic (electron-deficient) and nucleophilic (electron-rich) regions, which are critical for understanding molecular reactivity and non-covalent interactions [27-29]. In the ESP maps shown in Figure 2, red regions correspond to areas of high electron density (negative potential), indicating nucleophilic sites, while blue regions represent low electron density (positive potential), characteristic of electrophilic centers. Intermediate colors, such as light blue, yellow, and green, reflect areas of slight electron deficiency, slight electron richness, and neutrality, respectively.

The ESP surfaces of the iron(II) salts, gluconate, fumarate, and lactate, clearly show that the regions surrounding the Fe(II) centers are predominantly blue, indicating significant electron deficiency and supporting their role as electrophilic centers. In contrast, the ligands coordinating to Fe (II), particularly oxygen-containing groups, display red regions consistent with their nucleophilic nature. Notably, the ESP map of indigo reveals strong red zones around the carbonyl oxygen atoms, confirming them as the most nucleophilic sites within the molecule. This polarity pattern suggests favorable electrostatic interactions between the electrophilic iron(II) centers and the nucleophilic carbonyl oxygens of indigo, thereby supporting potential complexation pathways. These findings are in excellent agreement with experimental expectations and provide valuable insight into the electronic complementarity driving iron-indigo interactions. In addition, the ESP map of sodium dithionite reveals pronounced blue regions around the sodium atoms and the S-S bond, indicating areas of positive electrostatic potential, while red regions near the -SO_2 groups reflect high electron density. These nucleophilic zones make sodium dithionite an effective reducing agent, capable of donating electrons to electron-deficient (electrophilic) regions of indigo, thereby facilitating its reduction.

Reduction Mechanisms and Complexation Energies of [Iron(II) Salts -Indigo] Dimers

Visualization of complexation sites

The visualization of non-covalent interactions (NCIs) between indigo and iron(II) salts was utilized to identify complexation sites and gain deeper insights into the reactivity of the complexes. The NCI plots of indigo-iron(II) gluconate, indigo-iron(II) lactate, and indigo-iron(II) fumarate are presented in Figure 3. Based on this figure, it can be noted that in both Indigo-iron(II) fumarate and indigo-iron(II) gluconate complexes, the interaction primarily occurs between the oxygen of the carbonyl group in indigo and the iron(II) ion. Additionally, a hydrogen bond, represented by the blue isosurface, is observed between the N-H group of indigo and the oxygen atoms of iron(II) fumarate and iron(II) gluconate. In the indigo-iron(II) lactate complex, the carbon of the carbonyl (C=O) group in indigo appears to play a key role in the interaction with Fe(II), rather than the oxygen. Additionally, a coordination interaction is observed between the nitrogen of indigo and the Fe(II) ion.

To better understand the interaction sites between iron(II) salts and indigo, indigo Fukui indices used to identify nucleophilic attack sites were calculated. The nucleophilic sites correspond to regions where electron density increases upon electron addition, providing insight into potential interaction points within the complex.

The Fukui indices of the indigo molecule have been determined and presented in Table 2. The Fukui function f+ Measures a site's susceptibility to nucleophilic attack, indicating where an electron-rich species would most likely donate electrons. The atoms most reactive toward electrophilic attack have been identified by ranking the f+ values in descending order. According to the data, the following trend is observed: f+(O1, O2) = 0.1 > f+(C9, C11) = 0.08 > f+(C18, C20) = 0.07 > f+(C5, C8) = 0.04. These results show that the most nucleophilic sites in the indigo molecule are O1, O2, C9, C11, C18, and C20.

These atoms are the most favorable for electrophilic attack, suggesting their potential involvement in coordination with iron(II) centers. Figure 4 further visualizes the f+ indices for each atom in the indigo molecule, calculated using the B3LYP/6-311G (d,p) level of theory combined with LANL2DZ for iron(II). The corresponding molecular structure highlights the reactive centers identified by the Fukui analysis. The high f+ values at the carbonyl oxygens (O1 and O2) support their coordination with iron(II) in the indigo-iron(II) fumarate and indigo-iron(II) gluconate complexes. Similarly, the elevated f+ values at the adjacent carbon atoms (C9 and C11) are consistent with their interaction with iron(II) in the Indigo-iron(II) lactate complex.

Evaluation of the interaction energy between indigo and the reducing agents

In this section, the reducing capacity of the studied iron(II) salts was determined through the complexation energies between indigo and the different iron(II) salts using the DFT, as mentioned by the following equation:

$$E(complexation) = E(dimer) - [E(indigo) + E(reducing\ agent)] \qquad (7)$$

The interaction energy values, calculated using Eq. (7), were corrected using the counterpoise method to account for the basis set superposition error (BSSE). This correction improves the accuracy of the calculated interaction energy, ensuring it better reflects the true physical value, particularly in systems dominated by weak interactions such as hydrogen bonding and *Van der Waals* forces.

The complexation energy calculations presented in Table 3 indicate that the [indigo-iron(II)-gluconate] complex exhibits the highest complexation energy (-1078 kJ·mol^{-1}), signifying greater stability. This suggests stronger intermolecular forces, including charge transfer between Fe(II) and indigo, hydrogen bonding, and electrostatic and *van der Waals* interactions.

Following this, the [indigo-iron(II)-lactate] complex with an interaction energy of (-996 kJ·mol^{-1}) demonstrates comparatively lower stability. Meanwhile, the [indigo-iron(II)-fumarate] complex has the lowest interaction energy (-844 kJ·mol^{-1}), indicating the weakest stability. As a result, Fe(II) in this complex is more subjected to oxidation, making it the least effective reducing agent for indigo. These interaction energy calculations align with experimental observations, confirming that iron(II) gluconate enhances indigo reduction by stabilizing Fe(II) in its reduced state.

Thermodynamic properties of the (indigo-reducing agents) complexes

To investigate the thermodynamic properties of the reduction reactions, thermodynamic calculations were performed using the DFT approach at 298.15 K. To assess the overall stability of the (indigo-iron(II) salts) complexes, the thermodynamic parameters: Gibbs free energy (ΔG°), entropy (ΔS°), and enthalpy (ΔH°) of formation were determined using the following equations and presented in Table 4.

$$\Delta G° = \Delta G°_{complex} - (\Delta G°_{indigo} + \Delta G°_{reducing\ agent}) \qquad (8)$$

$$\Delta H° = \Delta H°_{complex} - (\Delta H°_{indigo} + \Delta H°_{reducing\ agent}) \qquad (9)$$

$$\Delta S° = \Delta S°_{complex} - (\Delta S°_{indigo} + \Delta S°_{reducing\ agent}) \qquad (10)$$

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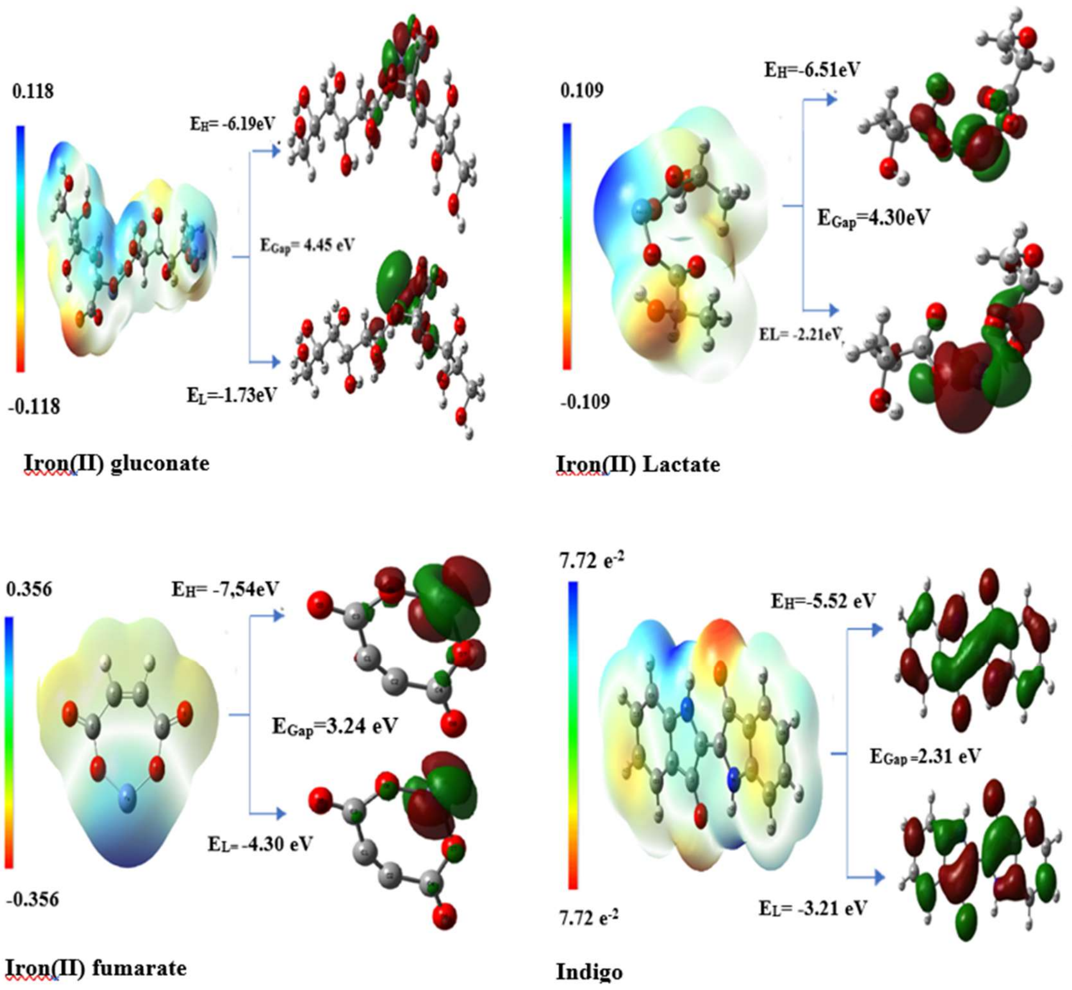
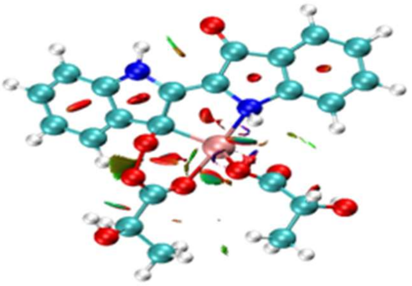
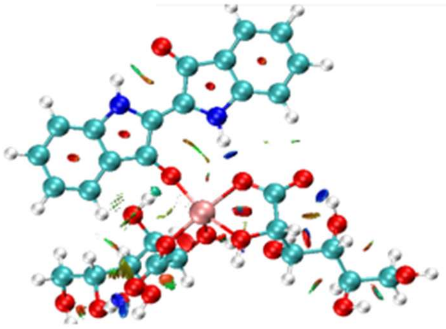


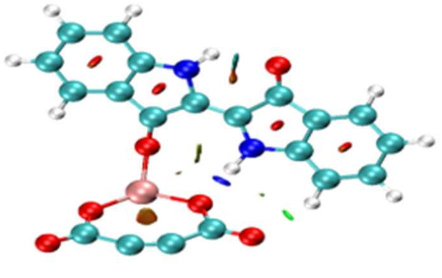
Fig 2. Electrostatic potential (ESP) and HOMO/LUMO orbital distributions with energy levels for indigo and the reducing agents, showing regions of electron density and potential reactivity.



Indigo-Iron(II) lactate



Indigo-Iron(II) gluconate



Indigo-Iron(II) fumarate

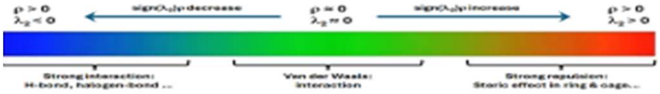


Fig 3. NCI plots of indigo-iron(II) gluconate, indigo-iron(II) lactate, and indigo-iron(II) fumarate complexes.

Gibbs free energy (ΔG) is a key indicator of reaction feasibility, with lower values indicating a more thermodynamically favorable reaction. According to Gaussian calculations, the positive ΔG values suggest that complex formation in the studied state is not spontaneous and requires external energy input. This finding supports the experimental condition of a reduction temperature of 75 °C.

Furthermore, these positive values can be attributed to the presence of a polar solvent such as water, which stabilizes ions in solution and alters the reaction dynamics. Among the investigated iron(II) salts, the indigo-iron(II) gluconate complex exhibits the lowest Gibbs free energy, indicating that it is the most thermodynamically stable complex. Additionally, this complex has the lowest enthalpy ($\Delta H° = 1338$ kJ·mol^{-1}), suggesting that its formation requires less energy input compared to the other complexes. Moreover, all complexes exhibit negative entropy values ($\Delta S° < 0$), implying increased structural order upon complexation.

Mulliken Charge Analysis

To investigate the reduction of indigo by ferrous salts, Mulliken charges of the reducing agents and indigo before and after complex formation were calculated. Figures S1 and S2 (Supplementary Materials) illustrate the Mulliken charge distribution in the individual iron(II) salts, indigo, and their respective complexes. The initial charge on Fe(II) in iron(II) gluconate, lactate, and fumarate was 0.887, 0.999, and 2.663, respectively. After complexation with indigo, these values decreased to 0.603, 0.357, and 0.776, respectively, suggesting partial electron transfer from Fe^{2+} to indigo.

Table 4. Mulliken charges of indigo at B3LYP/6-311G(d,p) with LANL2DZ for iron(II).

	Indigo		
	$f^{-}\cdot10^2$	$f^{+}\cdot10^2$	$f^{0}\cdot10^2$
O1	7.45	10.39	8.92
O2	7.45	10.39	8.92
N3	11.01	0. 15	5.58
N4	11.01	0. 15	5.58
C5	3.62	4.92	4.27
C6	2.27	-0.98	0.65
C7	-2.35	2.28	0.04
C8	3.62	4.92	4.27
C9	0.83	8.51	4.67
C10	2.27	-0.98	0.65
C11	0.83	8.51	4.67
C12	-2.35	2.28	0.04
C13	2.48	4.62	3.55
C14	5.43	0.93	3.18
C15	2.48	4.62	3.55
C16	5.43	0.93	3.18
C17	6.97	2.24	4.61
C18	1.86	7.04	4.45
C19	6.97	2.24	4.61
C20	1.86	7.04	4.45

Table 5. Complexation energies for (indigo-iron(II) salts) dimers.

Dimers	Complexation Energy (corrected) (kJ·mol $^{-1}$)
Indigo-iron(II) gluconate	- 1078
Indigo-iron(II) lactate	- 996
Indigo-iron(II) fumarate	- 844

Concurrently, the charge on the oxygen of the indigo carbonyl group (C=O) shifted from -0.344 to -0.477 and -0.527 for iron(II) gluconate and iron(II) fumarate complexes, respectively, supporting increased electron density on indigo and its reduction.

For indigo-iron(II) lactate complex, upon complexation, the charge on the carbonyl carbon decreased from +0.272

to -0.187, while the charge on the nitrogen of indigo shifted from -0.522 to -0.606. These changes indicate an increase in electron density at the reactive sites of indigo, suggesting significant electron transfer and stabilization within the complex.

Table 4. Thermodynamic parameters of [indigo-iron(II) salts] complexes in kcal.mol-1 at B3LYP with LANL2DZ.

Complexes	$\Delta H°$ (kJ·mol $^{-1}$)	$\Delta G°$ (kJ·mol $^{-1}$)	$\Delta S°$ (kJ mol^{-1}·K^{-1})
Indigo-iron(II) gluconate	1338	1417	-0.159
Indigo-iron(II) lactate	1612	1925	-0.347
Indigo-iron(II) fumarate	4489	4546	-0.184

Although the indigo-fumarate complex exhibited the highest theoretical charge transfer from Fe(II), experimental findings indicate that iron(II) gluconate achieves superior reduction efficiency. This divergence may be attributed to differences in solubility, complex stability, and electron transfer kinetics.

CONCLUSIONS

DFT was used to predict the reducing capacity of iron(II) gluconate, iron(II) lactate, and iron(II) fumarate, as possible alternatives to sodium dithionite in indigo dyeing processes. Experimental results revealed that iron(II) gluconate demonstrated superior reducing efficiency and color strength in dyeing applications. The chemical descriptors calculations using DFT indicated that iron(II) gluconate has a stronger electron-donating capability and higher nucleophilicity, which may contribute to its superior performance in indigo reduction. For the complexes studied, all complexation reactions were found to be thermodynamically unfeasible at 25 °C and require an external energy input. Mulliken charge analysis showed the possibility of iron(II) salts in the indigo charge transfer.

Beyond complexation energy calculations, additional evidence confirmed that iron(II) gluconate promotes indigo reduction by stabilizing Fe(II) in its reduced form.

As a result of the above outcomes, it can be stated that the combination of theoretical and experimental studies is very efficient in evaluating the reducing power of ferrous salts.

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NAUČNI RAD

PRIMENA TEORIJE FUNKCIONALA GUSTINE ZA PREDVIĐANJE REDUKCIJIONOG POTENCIJALA U PROCESU BOJENJA INDIGOM

U ovom radu je korišćena teorija funkcionalne gustine za kvantifikaciju svojstava donora i akceptora elektrona i polarizabilnosti organskih soli gvožđa(II) kao redukcionih agenasa u procesima bojenja indigom. Istražen je potencijal nekih soli gvožđa(II) kao ekološki prihvatljive alternative ekološki štetnom natrijum-ditionitu u procesu bojenja indigom. Komparativnom analizom je procenjen redoks potencijal redukovanog indiga i jačina boje obojenih tkanina. Eksperimentalni rezultati identifikovali su gvožđe(II)-glukonat kao najefikasniji, koji daje superiorni intenzitet boje. Teorijski proračuni korišćenjem B3LYP/LANL2DZ potvrdili su superiornu sposobnost gvožđe(II)-glukonata kao donora elektrona u poređenju sa drugim solima gvožđa(II). Sposobnost redukcije indiga sa solima gvožđa(II) procenjena je na osnovu energija kompleksacije. Teorijska termodinamička studija otkriva da je kompleks indigo-gvožđe(II)-glukonat termodinamički najstabilniji, tako da zahteva manje ulaganja energije za njegovo formiranje u poređenju sa drugim kompleksima. Donacije elektrona od soli gvožđa(II) do indiga u proučavanim kompleksima otkrivene su Mulikenovom analizom naelektrisanja. Ovi nalazi ističu efikasnost pristupa zasnovanih na teoriji funkcionalne gustine u preciznom predviđanju redukcionog kapaciteta soli gvožđa(II) i njihovu pogodnost kao ekološki prihvatljivih alternativa u primenama bojenja indigom.

Ključne reči: Bojenje indigom; soli gvožđa(II); proračuni na bazi teorije funkcionalne gustine; eksperimentalni rezultati, energija kompleksacije.