The following ***"research literature-based assessment"*** is based on the publication: "*Practical and Environment-Friendly Indirect Electrochemical Reduction of Indigo and Dyeing*" by Yi, C. *et al.,* Nature Chemical Biology – *Sci Rep* **10,** 4927 (2020). (https://doi.org/10.1038/s41598-020-61795-5)

1. Analyze the structures of *insoluble, blue-indigo molecule* and the *soluble, colorless, leuco-indigo* molecule in Figure**-**1. Why is **leuco-indigo more soluble** then **blue indigo**? *(Give a 1-2 sentence answer)*

2. After the dying process, what form of indigo is present in the final product of the dyed fabric? What is the necessity of creating the **leuco-indigo intermediate** during the dying process?
(1-2 sentences short answer)

3. Conversion blue-indigo to leuco-indigo is also an organic chemistry transformation reaction from a ***ketone*** to a ***secondary alcohol***. Draw both molecules, and **circle** and **label** the ketone and secondary alcohol functional groups on the respective indigo molecules:

blue-indigo leuco-indigo

4. If the oxidation number of a carbon atom in the carbonyl group of a ketone is **+2**, and the oxidation number of a carbon atom of a secondary alcohol is **zero**, then **write the half reaction** that converts the blue-indigo to leuco-indigo. Make sure to **balance** the half reaction in proper medium. Pay attention to overall charge balance. Is it an **oxidation** or **reduction half reaction**?

*The half reaction you wrote in **(4)** must occur with another reaction to complete electron flow and form a redox pair. Historically, indigo dying has always been done with sodium dithionite, but this paper proposes an original, previously un-tested technique.*
Let's analyze them and have the correct electron count with the balanced equations:

5. Historical industry-standard for indigo dying is explained in Figure-1b. It uses sodium dithionite ($Na_2S_2O_4$) "insurance powder" that yields harmful "sulfur wastes" as by-product. Note that the process done in **excess NaOH**. Let's assume that all sulfur wastes are in **SO_3^{2-} (sulfite)** form. Using this information, **show the balanced half reaction in proper medium**. You may want to review the methods we learned in our lectures. **Underline each atom** that is undergoing redox, and label them with their **proper oxidation numbers**.

6. How would you write the balanced half reaction if $S_2O_4^{2-}$ produced **both the sulfite** and the **sulfide (S^{2-})** in the same half reaction. Show your work, and once again **underline each atom** that is undergoing redox, and **label them with their proper oxidation numbers**.

7. Couple the reactions in **(5)** and **(4),** not **(6)**, to write the overall redox reaction with proper stoichiometric coefficients.

*The **newly proposed electrocatalytic method** uses **Fe-TEOA-Ca** as the mediator. You can assume TEOA-Ca as a **"molecular cage"** to hold onto Fe–ions in solution.*

8. With a quick search of your textbooks or a reliable resource online (such as another research article, not a random webpage such as course-help) to **draw the structures** of **triethanolamine** and **calcium gluconate**.

Triethanolamine

Calcium gluconate

Creative Bonus: Triethanolamine and calcium gluconate are the components for the molecular cage and they could potentially be in a large complex. The exact structure of this complex is not yet determined, so we do not know how it holds onto the Fe cations, but as a bonus, propose how it could be **solvating** and **stabilizing** this metal.

*For the rest of this assessment, we will consider the triethanolamine and calcium gluconate complex as one, and use the symbol **L**, as **a ligand** to Fe ions. So, **L = 'TEOA-Ca'** and it will be shown as **$Fe^{2+}L$** or **$Fe^{3+}L$** when it binds to iron ions.*

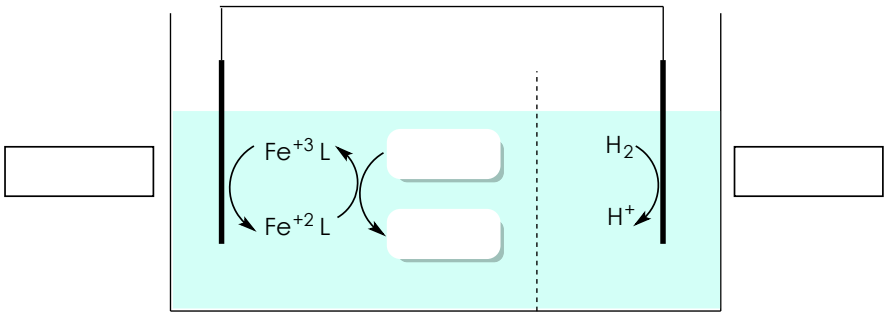
*The paper proposes an indirect processing of indigo via two repeated single electron oxidations that is helped **by $Fe^{2+}L$** and **hydrogen.***

9. Write the **half reaction** to convert **$Fe^{2+}L$** to **$Fe^{3+}L$**. Is it an **oxidation** or **reduction** half reaction?

10. Using the half reactions in **(9)** and **(4)** write an overall redox reaction happening in the solution.

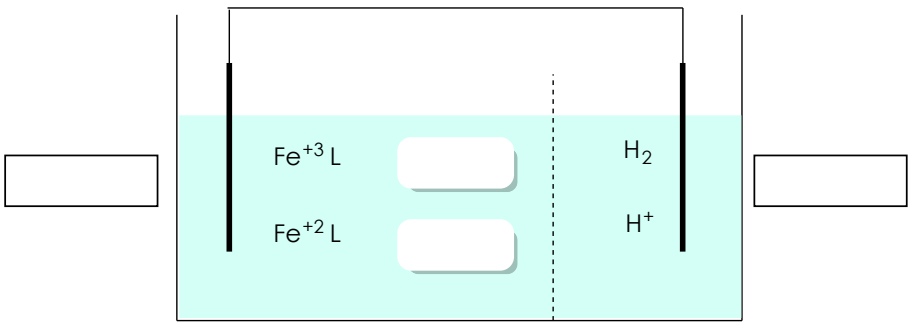
11. *Let's make sense of **Figure-1c**. Authors chose a simpler way to show the complete process all-in-one, but it can accidentally be misinterpreted. Here are some tips for you. Think of this process in **two-steps**:*

a. In Step-1, **indirect reduction of indigo** is being conducted via **$Fe^{2+}L$ / $Fe^{3+}L$** pair. At this step, the direction of the anode reaction should be opposite to what is shown in Figure1c, and should go from H_2 to H^+. In the **cell drawn below,** only show **Step-1** as we described above. Clearly show the direction of electron flow on the wire and label the electrodes.



------- membrane, only permeable to H^+

b. In Step-2, all the indigo is already converted to **leucoindigo**, and the fabric is dipped into the solution. Now it needs to be converted back, so the electron flow needs to be reversed. Using the $Fe^{2+}L$ /$Fe^{3+}L$ couple, show the conversion of leucoindigo back to indigo **by correctly placing the arrows for electron** donation between the molecules. Note that the electrodes have to switch roles and H_2 is produced.



------- membrane, only permeable to H^+

c. How do you convince yourself that H^+ production is helpful for obtaining leucoindigo in **Step-1**? *(Hint: Get help from Q#4, explain in only one sentence.)*

d. What is the source of the H^+ ions during **Step-2**? (*only one sentence)*

Let's see how all these reactions are run in large scale. Figure-2 shows a practical Electrochemical Dyeing Device that can be used as a prototype. This is designed to ***achieve both the proposed redox reactions and the dying process in a single device****, at the same time.*

12. Is this a voltaic or electrolytic cell?

13. Using the *Results section labeled "****Concept and design of electrochemical dyeing device****" and Figure* 2**, list and explain** all the materials that the paper is using and put them into their right compartments (a-m). Make sure to **explain the purpose/role** of the materials used in these compartments for the electrochemical cell:

a.

b.

c.

d.

e.

f.

g.

h.

i.

j.

k.

l.

m.

14. Time to step back and **look at the big picture**. How does this new proposed method **differ** from the already existing ones? You are expected to give a summary with a few sentences to conclude **if** this is a **better/safer dying method** and **how electrochemistry makes it possible**. *(Explain in 4-5 sentences)*

15. Many other dyes function by forming **chemical linkages** with cloth fibers. Does the indigo-dying method use a chemical bond to fibers to produce the permanent color on denim? *(Explain in 3-4 sentences)*

*At the end of the dyeing process, researchers use **oxalic acid** treatment to wash **iron hydroxide** from the fabric surface. It is not easy to extract iron hydroxide from the fabric in aqueous solutions because of its solubility problem.*

16. a. Exactly how insoluble is iron hydroxide? Use your textbook to find its ***Ksp***. Write the solubility reaction, comment on the value of Ksp. Then calculate the solubility of the iron hydroxide.
*(For this question, and for practical purposes, let's use the **ferric hydroxide** instead of ferrous)*

b. During the oxalate-washing step, iron-oxalate formation must be driving the reaction for cleaning up the iron hydroxide. Using your textbook again, find the formation constant, ***Kf,*** between iron and oxalate. **Draw its proposed structure**. Write the **balanced complex formation** reaction. *(Again, be careful to use **ferric oxalate** instead of ferrous)*

c. Write the **two reactions in 19(a) and (b)**, and sum up these two reactions to show the conversion from **iron hydroxide** to **iron oxalate**. Do not forget to **balance**. What do you find as an **overall equilibrium constant**? Is it **enough** to make the iron **soluble enough** to wash-off?
(Explain in 3-4 sentences)

d. Since the washing step is used as an efficient technique, what do you think is **driving the** conversion reaction from **iron hydroxide** to **iron oxalate** during washing? *(Explain in 3-4 sentences)*