Extensive Electronic Spectroscopy Investigation of Cr(VI) Under Variable Chemical Conditions in Aqueous Media

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Abstract: The analysis of toxic chemicals in wastewater is recognized as a crucial technique for producing clean water. However, a lack of understanding of their interactions under varying chemical conditions can hinder optimal treatment. To address this issue, this research introduces the use of electronic spectroscopy (ES) to analyze Cr(VI) aqueous solutions under different chemical environments. ES is a powerful spectroscopic technique employed to study molecular interactions and dynamics within their chemical contexts. Consequently, ES was applied to Cr(VI) aqueous solutions under various chemical environments. Cr(VI) is a highly toxic, non-biodegradable, and carcinogenic oxidant, necessitating detailed spectroscopic study. This study investigates the influence of pH on the ES of Cr(VI) and determines that pH 6 (slightly acidic) is optimal for validating Beer's law. The effect of ionic strength was examined by mixing Cr(VI) solutions with varying NaCl concentrations. Increased chloride content led to greater deviations from Beer's law. Additionally, the impacts of organic solvents, specifically ethanol and DMSO, on the ES of Cr(VI) were explored.

Keywords: UV-visible spectroscopy, Cr(VI), pH impact, DMSO, Electronic spectroscopy.

1. Introduction

Electronic spectroscopy (ES) is an applied spectroscopic technique that could be investigated to study the electronic configuration, reaction mechanism, interaction between molecules, and dynamics of atoms inside their chemical environments [1]. The mechanism of ES is based on the application of photo energy like synchrotron radiation or X-rays that could excite an electron towards allowed transitions in addition to vibrational, and rotational transitions [2]. Recently, the ES technique was used to observe the fluctuation dynamics of dative bonds [3], study the excitonic structure and charge separation in the helio-bacterial reaction center [4], understand the charge separation in the photosystem reactions [5], study 1-cyanonaphthalene cation for astrochemical application [6], inspect the electronic structure of graphene nanoribbons [7], find the dye-loading of semiconductors in solar cells [8], reveal the rate of primary charge separation [9], and study the ultrafast dynamics in colloidal Au-nanorods [10]. Therefore, the ES technique is one of the most considerable techniques to investigate the dynamics of molecules and their interactions under their chemical environments. Thus, this study introduced the ES under variable chemical environments of Cr(IV) as one of the metallic pollutants in water.

Previously, "the spectroscopy of Cr(VI)" was checked to determine its concentration without extensive investigation which was studied in a work. According to the present review about Cr(VI) spectroscopy, it seems that the speciation of Cr(VI) is still a poorly understood field [11]. Investigation of the stability of Cr(VI) species was previously studied via spectroscopy technique [12]. Additionally, device integrated

with open-circuit potentialand attenuated total reflectance spectroscopy was reported to simultaneously monitor the interfacial reaction of hexavalent chromium (Cr(VI)) and oxalate and the reported data confirm that outer-sphere coordination has negative charge accumulation [13]. Vats at el., reported spectroscopy technique for analysis of airborne Cr(VI) compounds arising from arc welding fumes and the shown results identifying the Cr(VI) by the presence of Cr-O-Cr anti-symmetric as well as symmetric stretching of the tetrahedral chromate [14]. The impact of chemical environments over Cr(VI) was missed which was extensively studied in this work.

Nowadays, water pollution resulting from the discharge of toxic metals in the aquatic environment has become a great threat to human life [15]. Recently, there are a variety of chemical pollutants such as chromium [16], cadmium [17], lead [18], mercury [19], nickel [20], and copper ions [21] since they are not biodegradable and urgently needs treatment [22]. Chromium is an active metal that has many oxidation states which most stable are Cr(VI) and Cr(III) [23]. The hexavalent state is classified as carcinogenic because of its strong oxidant irritating plant [24]. Cr(VI) is extremely toxic and is regularly non-biodegradable in nature. Therefore, it resulted from several industries like leather tanning, chemical manufacturing, and electroplating [25]. Consequently, the trivalent state is considered less toxic than Cr(VI) and exists as an insoluble hydroxide that can be removed easily from water and is an essential nutrient that helps the body utilize protein, sugar, and fat [26]. The acceptable concentration of chromium is at 0.05 ppm according to the World Health Organization. Recently, there are several methods were suggested to remove or decrease Cr(VI) such as ion exchange [27], electrochemical reduction or

electrocoagulation [28], solvent extraction [29], chemical precipitation [30], and chemical adsorption [31]. The first step in any problem management is how to detect or define the problem. So, in this study, understanding the influence of different chemical effects was investigated to correctly check the existence of Cr(VI) in aqueous solutions. ES by UV-visible photoenergy has been studied for Cr(VI) after applying different chemical conditions such as pH medium, ionic strength (effect of salt existence), and the existence of organic solvents including ethanol or dimethylsulfoxide (DMSO). These solutions were scanned in the range of 300–700 nm and the used photo energy source is direct UV–vis spectrometry.

2. Materials and methods

The used chemicals as potassium dichromate, H_3PO_4 , NaOH and NaCl were from AR grade. The used solvents Ethanol (EtOH) and dimethyl sulfoxide (DMSO) were from Aldrich.

Firstly, UV-visible spectroscopy in this study was conducted via Perkin Elmer Lambda 35 spectrophotometer with a CE 836 cell and wavelength program controller). Potassium Cr(VI) solution (88 ppm) in 100 ml H_2O was prepared using distilled water as a stock solution and then was diluted to other concentrations from 163 µM till reached 27.20 µM including 108.80 µM, 54.40 µM, 48.69 µM, 43.50 µM, 38.01 µM, and 32.64 µM. Additionally, all these Cr(VI) contents were scanned by ES UV-visible spectroscopy. After that, various concentrations of NaCl salt from (0.05 M to 0.4 M) as ionic strength with different Cr(VI) aqueous solutions were measured. The pH medium was studied via NaOH (0.1 N) and H_3PO_4 (0.1 N) and different volumes from them to prepare assumed buffer solutions from NaH_2PO_4 and Na_2HPO_4 followed by the addition of variable contents from Cr(VI). The pH medium was studied between pH 3 up to pH 11 after measuring it via an instrumental pH meter followed by ES measurements using Perkin Elmer Lambda 35 spectrophotometer. Additionally, DMSO in the range of 10 % to 40 % aqueous solution was used as another chemical environment followed by preparing different Cr(VI) concentrations and measuring the ES analysis of them. Moreover, to monitor the effect of ethyl alcohol, different ethanolic aqueous solutions were used (5 % to 40 %) and accomplish the spectrophotometric analysis.

3. Results & Discussion

3.1. Spectroscopic investigation:

In this work, the UV-visible spectroscopy measurements were recorded for different concentrations of Cr(VI) aqueous solution at fixed pH (pH =6) and (pH =11) as an acidic and alkaline media, respectively as shown in Fig. 1A and Fig. 1B. Clearly, the high Cr(VI) concentration has a higher absorbance value except the transfer from 48.69 µM to 54.4 µM. At 163 µM of Cr(VI) which is the highest investigated concentration that was applied to this work, the clear band at 372.4 nm with absorbance around 1.73 was observed. As reported, In aqueous solutions orange dichromate, $[Cr_2O_7]^{2-}$ and yellow chromate, $[CrO_4]^{2-}$ exists in an equilibrium [32]. $Cr_2O_7^{2-}+H_2O$ dichromate ion aqueous solution (orange-red) could be in equilibrium with $HCrO_4^-+H^+$ chromate ion aqueous solution (yellow) which could interpreted as the majority of chromate in alkaline media

[33]. So, in alkaline media, the equilibrium could be shifted forward, and the solution becomes yellow (chromate ions). As expected, when the concentration reduced from 163 µM to 27.2 µM, the absorbance value descended from 1.73 to 0.38. Despite this, there was an interaction between one of the two concentrations having up normal behavior (54.4 µM and 48.69 µM), which led to an increase in absorbance value instead of a decrease. The observation that the absorbance of dichromate at a concentration of 48.69 µM is higher than at 54.4 µM at pH 11 is unusual and indicates that factors other than concentration are influencing the absorbance. At pH 11, the equilibrium between dichromate and chromate shifts towards chromate. However, the amount of chromate formed is insufficient to cause a clear shift in λ_{max}. This small amount of chromate affects the absorbance-concentration relationship, especially at near concentrations like 48.69 µM and 54.4 µM. The Beer-Lambert Law, which states that absorbance is directly proportional to concentration, assumes ideal environment. However, the chromate species exhibit non-ideal behavior, making their spectroscopic study particularly interesting. This unusual property of chromate species was reported by Daszkiewicz in "Coordination Chemistry Reviews," where it was concluded that "the speciation of Cr(VI) is still a poorly understood field, and we are at the beginning of the process of uncovering its significance" [11]. This anomalous behavior was not observed at pH 6 because the formation of chromate is negligible under these conditions. Additionally, this phenomenon was not detected at other concentrations due to the larger differences between those concentrations. Following up, the UV-visible spectroscopy results were analyzed at a wide range of Cr(VI) absorptions at pH 6 as displayed in Fig. 1A. In this situation, the medium of solution was slightly acidic. According to the previously mentioned chemical equation, decreasing pH causes the equilibrium to move left, and confirmed by the change of color to orange. Furthermore, as concentration went down, the absorbance fell. Fig. 2A showed the ES data of different pH media at 22.7 µM of Cr(VI). There are two peaks around 375 nm and 270 nm and the first one could be applied to determine the concentration of Cr(VI). Additionally, there is another clear spectroscopic peak at lower wavelengths (at 272, 273, 273, 262, and 255 nm for pH values of 11, 9, 6, 4.5, and 3, respectively). This peak of dichromate could be due to ligand-to-metal charge transfer (LMCT) transitions [34, 35]. In dichromate ions, the LMCT transitions involve the transfer of electrons from the oxygen ligands to the central chromium atoms, which typically occur in the UV region. The shift in this peak to lower wavelengths with decreasing pH could be attributed to the increasing protonation of the solution, which alters the electronic environment and the energy levels of the chromium species. This results in a blue shift (movement to shorter wavelengths) of the absorption peak. These additional peaks provide further insights into the electronic structure and behavior of chromium species under different pH conditions, complementing the main absorption peak in the visible region used for quantifying Cr(VI) concentrations. This comprehensive spectral analysis enhances the understanding of the speciation and electronic transitions of Cr(VI) in varying pH environments. In the case of the basic medium, the predominant content is one Cr(VI) species which leads to negligible difference in the

absorption values. After that, the absorbance decreases when pH is reduced. Interestingly, the maximum wavelength at pH 6 is near to pH 11 which could be interpreted via the previous study by Michel et al. [36]. This study carefully examined the Raman spectra of chromate and dichromate species and found that the protonated form of chromate $HCrO_4^-$, does not exist in aqueous solutions of Cr(VI) compounds. According to the equilibrium, an increase of the hydro chromate concentration should be significant with dilution. The Raman spectra of the diluted solutions did not confirm the existence of any protonated form of the Cr(V1) oxo anions. Instead, the authors proposed a simple equilibrium existing in the pH range between 1 and 11. Examining Raman lines under dilution, the authors showed that at pH = 11, the Cr(V1) ion was 100% present in the form of the CrO_4^- ion whereas at pH = 1.2, it was 100% as the $Cr_2O_7^-$ ion. Therefore, to see the clear shift in maximum wavelength, the pH should be studied at 1 and 11 and the shown figure had pH 6 and 11. Even though the equilibrium shifts with pH, if the concentration of the absorbing species (either dichromate or chromate) remains high enough in both pH conditions, the λ_{max} would not shift noticeably because the overall absorption profile remains dominated by one of the species (high contents from dichromate if compared with the produced chromate). Cr(VI) displays charge transfer absorption bands, which vary in acid and alkaline mediums. Fig. 2A presents the electronic spectroscopy data of Cr(VI) at 22.7 μM across different pH levels. The spectra from pH 6 to 11 show nearly identical λ_{max} at 373 nm, with absorbance values of 0.3789 at pH 9 and 0.3622 at pH 6. A noticeable shift begins at pH 4.5 (λ_{max} at 367 nm and absorbance 0.2201), and a significant shift is observed at pH 3 (λ_{max} at 348 nm and absorbance 0.1714). These experimental results confirm that the λ_{max} and absorbance changes correlate with the observed color change. The color change from orange to yellow between alkaline and acidic media, despite no shift in the absorption peak in the pH range of 6-11, could be explained by the equilibrium and concentration effects of chromate and dichromate ions. Both ions have electronic transitions that absorb in the UV-visible region, contributing to their characteristic colors. The main absorption peak remains unchanged because the energy levels of the electronic transitions in both species are similar. Although the λ_{max} does not shift, the relative contributions of chromate and dichromate to the overall absorption spectrum change with pH. Dichromate has a broad absorption band responsible for its orange color, while chromate absorbs in the region that gives a yellow color. Therefore, the perceived color changes due to variations in the relative intensities of these species. In summary, a shift in λ_{max} is observed only when the pH changes from 11 (or 9 or 6) to 4.5, with a clear shift at pH 3. Fig. 2B illustrates the relation between the absorbance values at λ_{max}, which expresses the effect of pH at different mediums from pH 11 to pH 3 on varied concentrations. The molar absorptivity could be determined from this slope according to the traditional relation: A= εbc [37]. The best pH to verify the traditional beer's law is pH 6 (slightly acidic) and the estimated molar absorptivity was found at 9163 $M^{-1}cm^{-1}$ and the equation of absorbance concentration is Abs. = 9163 C (M) ± 0.114. The R-square values decreased after increasing or decreasing the pH away from pH 6. This behavior could be due to the equilibrium between two different Cr(VI)

species (dichromate and chromate). Therefore, it is clear from this graph that the best chemical condition is pH 6 so it is preferable to study the Cr (VI) contents in aqueous solution samples.
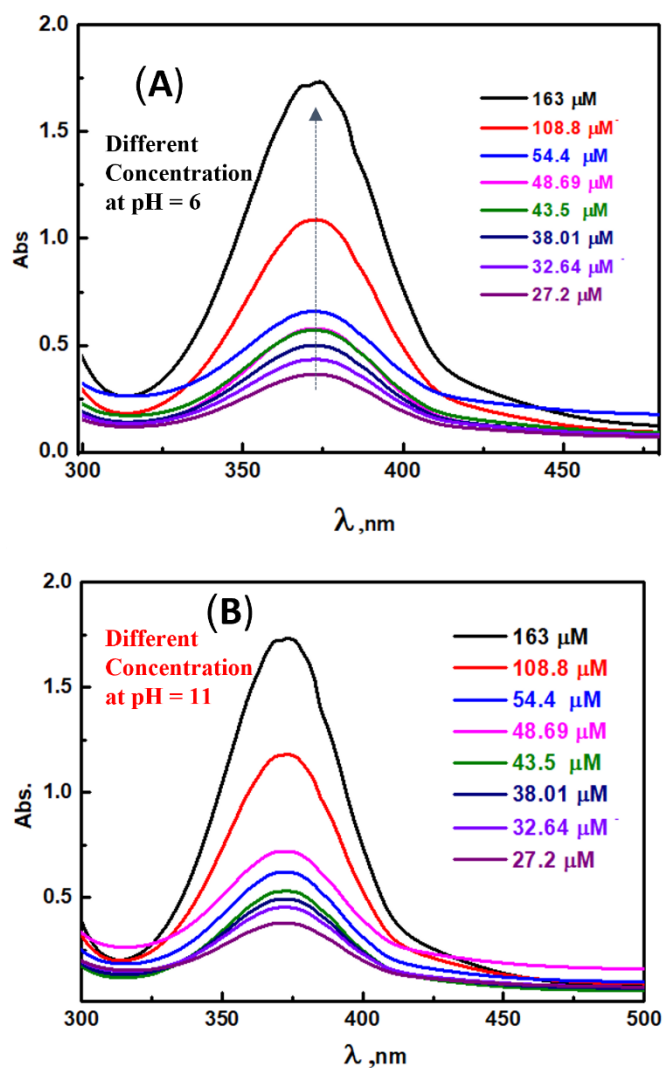

Figure 1. *Electronic spectra of different concentrations from Cr(VI) aqueous solution at pH 6; (A), and pH 11; (B).*

3.2. Effect of ionic strength

In continuation of some factors that were applied to study the effect of the chemical environment on the chemistry of Cr (VI), the effect of ionic strength was investigated by the addition of different concentrations of NaCl salt as the source of ionic strength which is considered one of the major characteristics of solution ionic strength. By applying 0.1 M of the utilized salt at 163 μM of Cr(VI), the absorbance was found at 0.95 which expresses the highest value. As expected, the absorbance value went down with lower concentrations. As shown, in the case of 54.4 μM of Cr(VI) the absorbance became 0.40 which indicates the Cr(VI) could be interacted and its amount went down in solution. Furthermore, the lowest concentrations from 32.64 μM to 27.2 μM have the same characteristics peak. As seen, as the concentration of reactants increases, By increasing the reaction rate the ionic strength increases [38]. At low Cr(VI)

concentrations, there is a deviation from Beer's law could be found because the Cr(VI) concentration increased from 27.20 μM to 32.64 μM and no clear change in ES could be found which indicates that the high ionic strength could deviate the Beer's law at a low concentration from the active species (Cr(VI) in this work) [39].
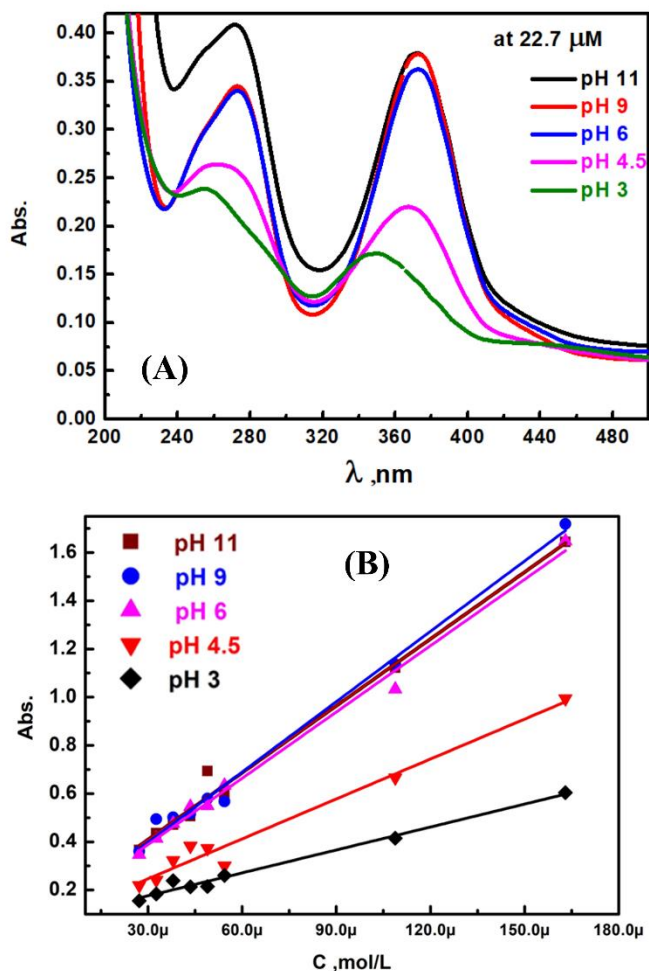

Figure 2. Electronic spectra of aqueous solution of Cr(VI)(22.7 μM) at different pHs*; (A), and verification of beer's law at different pH aqueous solutions ; (B).*

By applying another value of ionic strength on varying contents of Cr(VI) aqueous solution to determine the spectroscopic influence of Cr(VI), the found conclusion in the previously applied value could be affirmed. The checked ionic strength is 0.3 M of NaCl on the Cr(VI) molar concentrations of 163.0 μM, 108.80 μM, 54.40 μM, 48.69 μM, 43.50 μM, 38.01 μM, 32.64 μM, and 27.20 μM. At 163μM of Cr(VI), the clear band at 365 nm with absorbance around 0.290 compared this value with 0.1 M of NaCl which was used at the same concentration that was the highest this means that the greater amount of ionic strength, the lower absorption value, which indicates the interaction of small contents from Cr(VI) with the anions of NaCl in aqueous solution [40]. As known, the ionic strength illustrates the number of anions in solution. So, higher NaCl contents could decrease the active Cr(VI) in ES. Other properties could be modified result of this effect such as the dissociation constant or solubility [41]. Additionally, any interaction between the used
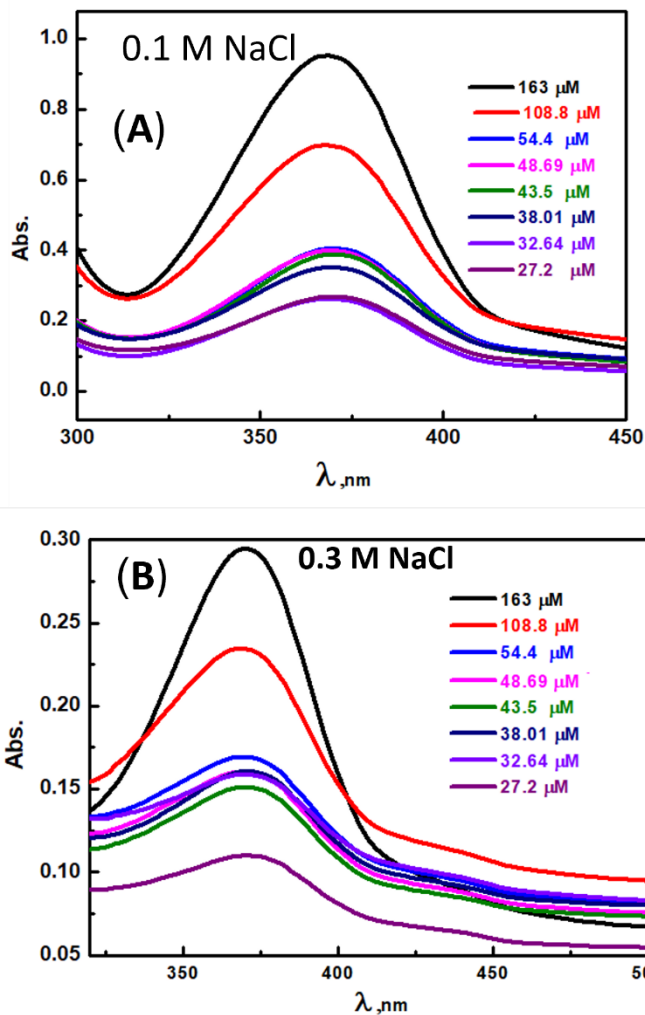
concentration of Cr(VI) and the chemical environment could lead to a decrease in the absorbance value. At 0.3 M NaCl, the data of ES show that three concentrations have the same absorbance value at similar wavelengths from 48.69 μM to 32.64 μM. The higher chloride contents lead to faster interaction between Cr(VI) and salt anions so, the deviation from Beer's law was found at lower contents (48.69 μM Cr(VI) in the case of 0.3 M NaCl and 27.20 μM Cr(VI) in the case of 0.1 M NaCl).

Figure 3. Electronic spectra of different [Cr(VI)] aqueous solutions in the presence of ionic strength = 0.1 M (A) and 0.3 M (B).

After that, the effect of ionic strength at three Cr (VI) concentrations was compared in terms of ES. As seen, the higher the ionic strength has lower visible absorbance values. It was clear that the absorbance value went down from 1.03 to 0.11 when the concentration of ionic strength increased from 0.05 M to 0.3 M. Consequently, the ionic strength of the solution is directly proportionally to the concentration of ionized species which could be due to the interaction between Cr(VI) and Cl⁻ anion. This interaction changed the chemistry behavior of Cr(VI). Finally, by applying Bear's law to obtain the molar absorptivity (Fig. 4B). The figure explained that 0.3 M of ionic strength has the lowest value of absorbance and its R-square

0.94161 which confirms the chemical interaction and Beer's law deviation. At 0.05 M and 0.1 M have better R-square values at 0.98203 and 0.99035, respectively. Thus, the low ionic strength is preferred during the application of Beer's law of Cr(VI) in aqueous solution.
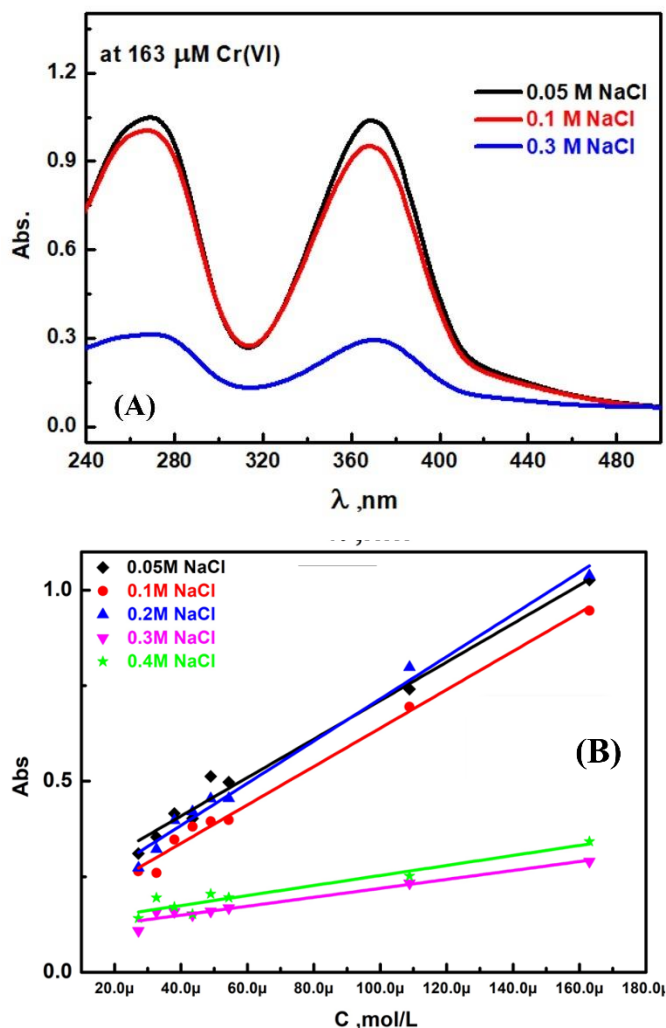

Figure 4. (A) ES of Cr(VI) = *163 µM solution at different ionic strength, (B) the variation of absorbance of different [Cr(VI)] at ionic strength from 0.05 M to 0.4 M.*

3.3. Effect of organic solvents

Fig. 5A. illustrated the effect of organic solvent on the varying concentrations of Cr(VI) which could be helpful to understand the interaction between the Cr(VI) species and organic solvents. As seen, applying 10 % EtOH showed that the optical density value went down from 0.96 at 163 µM to 0.81 at 108.8 µM. As reported, Cr(VI) is an oxidizing agent that could oxidize organics such as ethyl alcohol to acetaldehyde [42]. This could be occurred in this investigation because of two reasons. The first one is the decrease of hydronium ion dissolvation after introducing organic solvent and the second one is the utilized concentration which is low so, the oxidation reaction rate would be low. At high concentrations (163 µM, 108 µM, and 54 µM), the measured absorbance is directly proportional to the Cr(VI) concentration. After that, the found spectrum doesn't follow this

relation and deviates away from Beer's law. The ES of 54 µM and 48 µM were found at the same absorbance and the lower one had higher absorbance at the region near UV range. This trend was found again at the lowest used concentration (27.2 µM) which could be attributed to the higher relative concentration of ethanol if compared with Cr(VI) content. Besides, the spectrophotometric measurements were studied in the presence of 20% EtOH as shown in Fig. 5B and were performed using the same earlier procedure as Fig. 5A. The same conclusion could be obtained where the higher concentration of Cr(VI) has a higher absorbance value except at a low concentration of Cr(VI) as discussed before in the case of 10 % EtOH. After that, Fig. 6A displayed the varying contents of applied organic solvent on one of the Cr(VI) concentrations which was measured by UV-visible spectrophotometry at 22.7 µM of Cr(VI). As examined, at 5% EtOH there was a characteristic peak of Cr(VI) at an optical density equal to 0.29. Whenever the amount of organic solvent increased, no characteristic peak could be seen. This is evidence that the species of Cr(VI) in the solution interacted with the organic solvent. Conclusively, Fig. 6B presented the relation between absorbance and Cr(VI) concentration. The relation was seen as unexpected, and the absorbance decreased as Cr(VI) increased because of the high relative concentration of EtOH if compared to Cr(VI) (EtOH/Cr(VI)) which could lead to strong chemical interaction and followed by an oxidation reaction and could be confirmed via the observed turbidity as shown in Fig. 7. Additionally, the high contents of Cr(VI) have the highest absorbance value because of increasing the metal contents and so, Beer's law could be applied only at high-ethanol content with high expected error which was indicated from the R-square values. The interaction between Cr(VI) and ethanol, which leads to observed turbidity, indicates a chemical reaction likely resulting in the reduction of Cr(VI). This reaction changes the chromium species present in the solution and can lead to the disappearance of the characteristic Cr(VI) color according to the following chemical equation:

$$Cr_2O_7^{2-}+3C_2H_5OH+8H^+\rightarrow2Cr^{3+}+3CH_3CHO+7H_2O$$
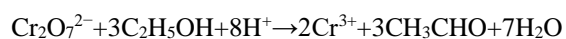
In this reaction, Cr(VI) is reduced to Cr(III), and ethanol is oxidized to acetaldehyde [43, 44]. Cr(III) is typically green or violet in color, but if it has low-concentration, the solution could appear turbid, and the color could be less intense or even disappear completely. This disappearance means that Cr(VI) cannot be measured at the same wavelength (typically 370 nm for dichromate) because the Cr(VI) species is no longer exist in the solution.

Eventually, the last influence that has been studied in this work by ES is the different contents of dimethyl sulfoxide (DMSO) as an organic solvent as shown in Fig. 8A and 8B. As expected, the absorbance values were seen at high values as Cr(VI) content increased in both 10 % and 30 % DMSO. These data showed that concentrations of 10% and 30% of DMSO at 365 nm has absorbance values around 1.03 and 0.74 respectively by applying 163 µM of Cr(VI). Therefore, as the prepared concentrations decreased, the optical density decreased. Fig. 9A and Fig. 9B illustrated the change occurring by different concentrations of the used DMSO at two Cr(VI) concentrations; 163 µM and 22.7 µM. It was found that at 10%, 20%, 30%, and

40 % each of them has a different value of absorbance which were found at 0.25, 0.18, 0.19, and 0.17 respectively. Therefore, the low contents of DMSO have higher absorbance after 20% DMSO, the absorbance is nearly constant. According to the previous literature, there is no direct interaction between DMSO and Cr(VI) [45]. As known, DMSO has higher polarizability than traditional aqueous solution [46], which could form a weak interaction between the formed mixture (DMSO and water) and Cr(VI). This interaction was confirmed by the slight change in λmax and the corresponding absorbance when the contents of DMSO changed. After 20 %, the influence of interaction is stable compared to the Cr(VI) concentration. Moreover, at the highest concentrations requires a large amount of solvent to interact. Fig. 9C showed the verification of beer's low and obtained molar absorption factor and R-square at 5% was 0.9596 and 4746.02987 for R-square and molar absorptivity, respectively. Solvent-solvent interaction is the devious force in dilute solutions where ion–ion interaction is minimum, and this information could affect on Cr(VI) and DMSO interaction.
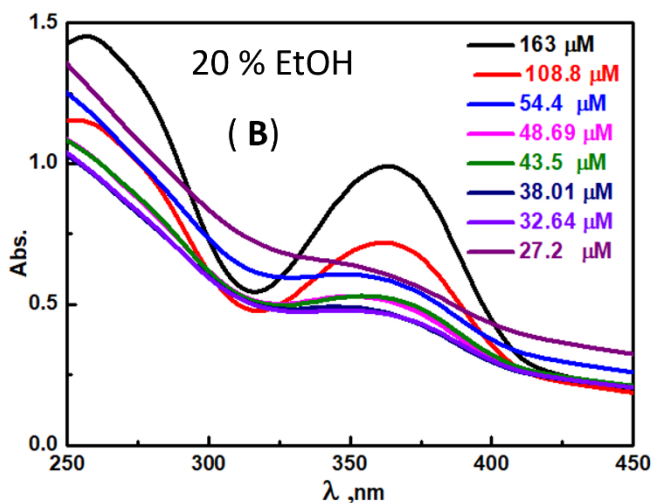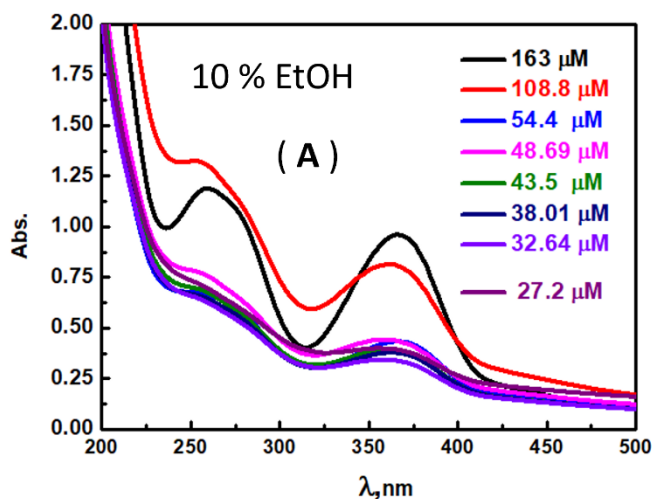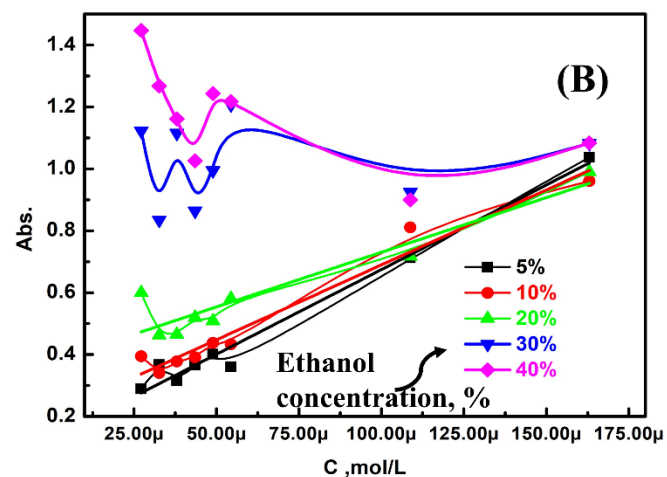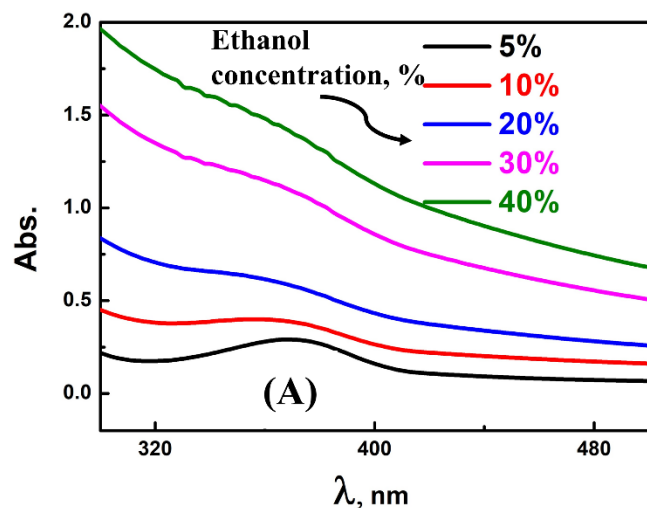

Figure 6. *Electronic spectra of Cr(VI) = [22.70 M] at different EtOH%; (A), and the relation between [Cr(VI)] and absorbance at different EtOH%; (B).*

Figure 5. *Electronic spectra of different concentrations from Cr(VI) at 10 % EtOH; (A), and 20 % EtOH; (B).*

Figure 7. *The observed turbidity between Cr(VI) and ethanol at [Cr(VI)] = 88 PPm, and EtOH% = 30 %.*

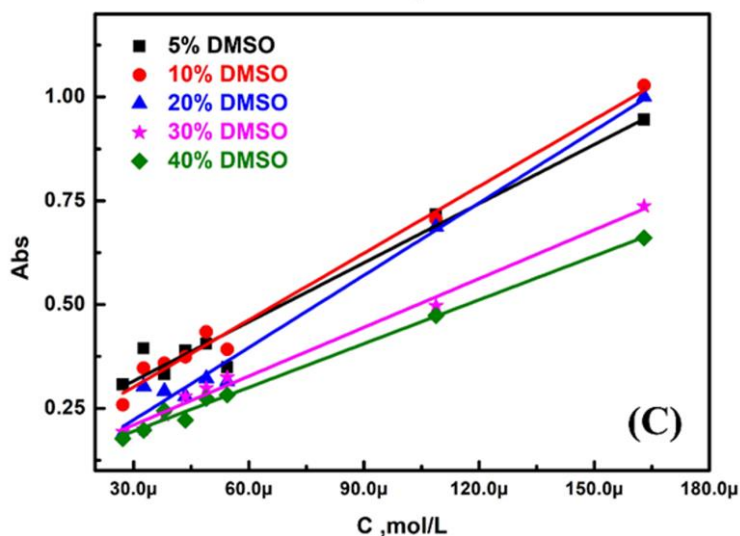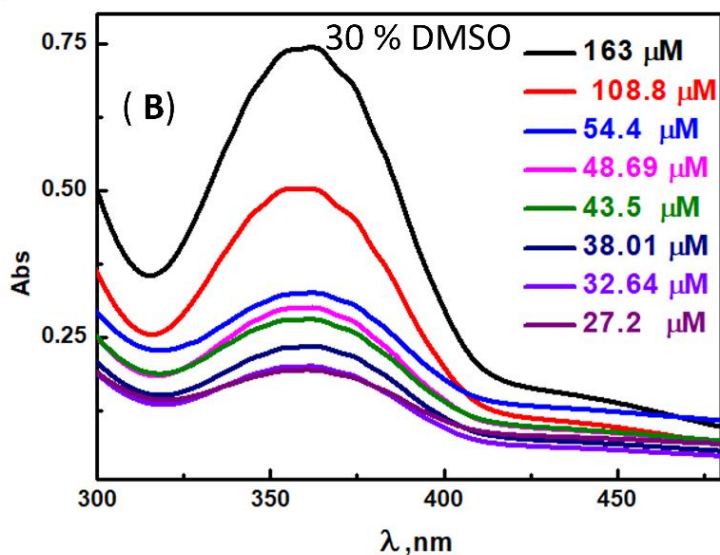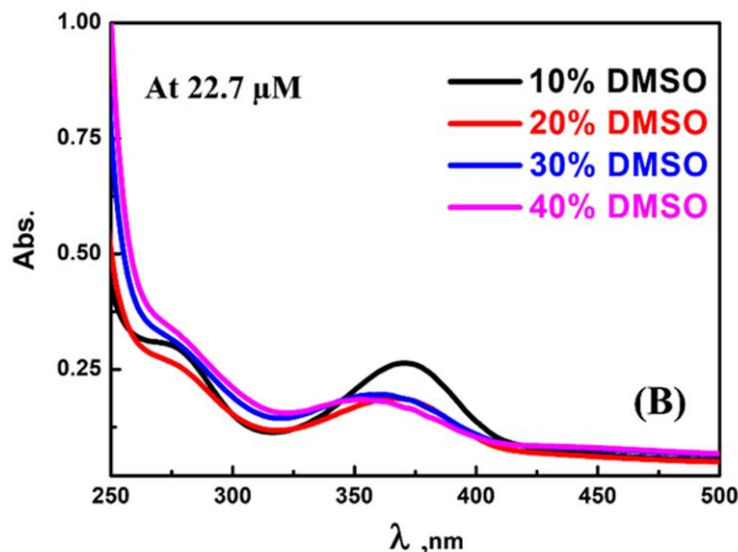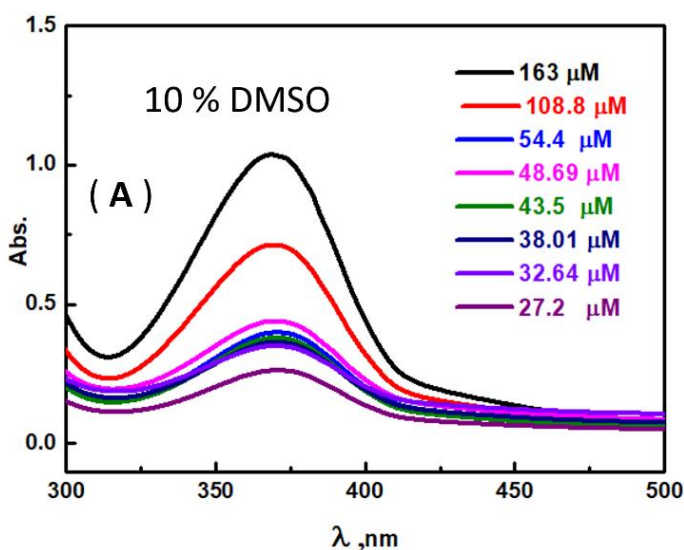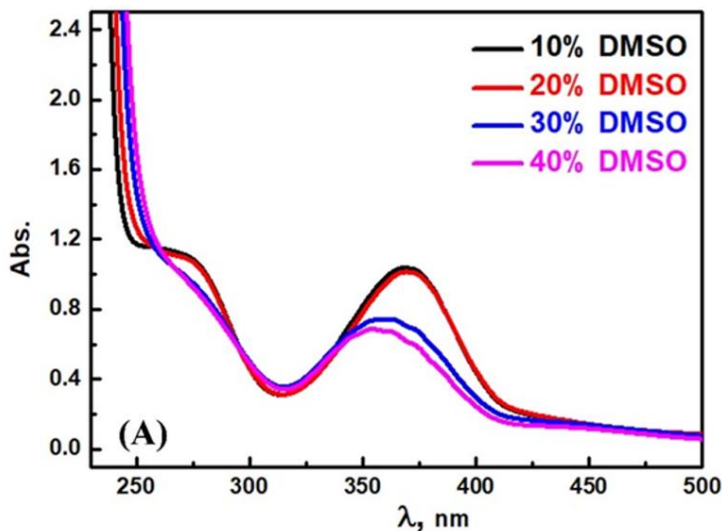**Figure 8.** *Electronic spectra of different concentrations from Cr(VI) at 10 % DMSO; (A), and 30 % DMSO; (B).*

Figure 9. (A) Electronic spectra of Cr(VI) = 163 µM at different DMSO%, (B) Electronic spectra of Cr(VI) = 22.7 µM at different DMSO%, (C) The variation of the absorbance of different [Cr(VI)] at variable DMSO%.

4. Conclusion

Studying spectroscopic studies of Cr(VI) in aqueous solution is helpful to simply understand its possible interactions and its fast detection. Electronic spectroscopy (ES) is the utilized spectroscopic technique that could be investigated to study Cr(VI) behavior under different chemical environments starting from pH effect, ionic strength, ethanol, and DMSO impact. The best-found pH to verify the traditional beer's law is pH 6 (slightly acidic) and the estimated molar absorptivity was found at 9163 M⁻¹cm⁻¹ and the equation of absorbance concentration is Abs. = 9163 C (M) ± 0.114. The R-square values decreased after increasing or decreasing the pH away from pH 6. This behavior could be due to the equilibrium between two different Cr(VI) species (dichromate and chromate). The effect of ionic strength was studied via the preparation of different Cr(VI) concentrations in different NaCl concentrations. As the chloride contents increased, more deviation from Beer's law was

detected. 0.3 M of ionic strength has Beer's law R-square around 0.94161 which confirms the Beer's law deviation and chemical interaction between chloride anions and Cr(VI). At 0.05 M and 0.1 M have better R-square values at 0.98203 and 0.99035, respectively. Thus, the low ionic strength is preferred during the application of Beer's law of Cr(VI) in aqueous solution. For the ethanol effect, the relation was seen as an unexpected behavior, and the absorbance decreased as Cr(VI) increased because of the high relative concentration of EtOH if compared to Cr(VI) (EtOH/Cr(VI)) which could lead to strong chemical interaction and followed by an oxidation reaction and could be confirmed via the observed turbidity. In contrast, DMSO has a weak interaction with Cr(VI) which could be used in the case of organic aqueous solutions.

CRediT authorship contribution statement:

Conceptualization, I.M.A.M and G.H.; methodology, G.H.; software, L.A.E.N, A.M.S.; validation, L.A.E.N, G.H., A.M.S. and I.M.A.M.; formal analysis, L.A.E.N., G.H.; investigation, G.H., I.M.A.M.; resources, L.A.E.N., A.M.S.; data curation, G.H.; writing—original draft preparation, L.A.E.N., G.H., and I.M.A.M.; writing—review and editing, L.A.E.N., G.H., and I.M.A.M.; visualization, L.A.E.N., A.M.S.; supervision, L.A.E.N., A.M.S., and I.M.A.M. project administration, L.A.E.N., A.M.S., and I.M.A.M.; funding acquisition, L.A.E.N., A.M.S., and I.M.A.M. All authors have read and agreed to the published version of the manuscript.

Data availability statement

The data used to support the findings of this study are available from the corresponding author upon request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

References

1. L. Turi and P.J. Rossky, *Chemical reviews*, 112 (2012). 5641-5674.
2. V. Barone, S. Alessandrini, M. Biczysko, J.R. Cheeseman, D.C. Clary, A.B. McCoy, R.J. DiRisio, F. Neese, M. Melosso, and C. Puzzarini, *Nature Reviews Methods Primers*, 1 (2021). 38.
3. T.N. Do, J.H.N. Sim, H.L. Nguyen, Y. Lu, and H.-S. Tan, *The Journal of Physical Chemistry Letters*, 12 (2020). 165-170.
4. Y. Song, R. Sechrist, H.H. Nguyen, W. Johnson, D. Abramavicius, K.E. Redding, and J.P. Ogilvie, *Nature communications*, 12 (2021). 2801.
5. H.H. Nguyen, Y. Song, E.L. Maret, Y. Silori, R. Willow, C.F. Yocum, and J.P. Ogilvie, *Science Advances*, 9 (2023). eade7190.
6. F.C. Daly, J. Palotás, U. Jacovella, and E.K. Campbell, *Astronomy & Astrophysics*, 677 (2023). A128.
7. T. Nagahara, F.V. Camargo, F. Xu, L. Ganzer, M. Russo, P. Zhang, A. Perri, G. de la Cruz Valbuena, I.A. Heisler, and C. D'Andrea, *Nano Letters*, (2024).
8. I.M.A. Mohamed, V.-D. Dao, N.A.M. Barakat, A.S. Yasin, A. Yousef, and H.-S. Choi, *Journal of Colloid and Interface Science*, 476 (2016). 9-19.
9. P. Akhtar, I. Caspy, P.J. Nowakowski, T. Malavath, N. Nelson, H.-S. Tan, and P.H. Lambrev, *Journal of the American Chemical Society*, 143 (2021). 14601-14612.
10. F. Toffoletti and E. Collini, *The Journal of Physical Chemistry Letters*, 15 (2024). 339-348.
11. M. Cieślak-Golonka and M. Daszkiewicz, *Coordination Chemistry Reviews*, 249 (2005). 2391-2407.
12. R. Steinberger, J. Duchoslav, T. Greunz, M. Arndt, and D. Stifter, *Corrosion Science*, 90 (2015). 562-571.
13. S. Cao, N. Chen, M. Li, K. Wei, G. Zhan, F. Guo, T. Gao, F. Jia, and L. Zhang, *Environmental Science & Technology*, 57 (2023). 16532-16540.
14. V. Vats, G. Melton, M. Islam, and V.V. Krishnan, *Journal of Hazardous Materials*, 448 (2023). 130862.
15. M. Mokarram, A. Saber, and V. Sheykhi, *Journal of Cleaner Production*, 277 (2020). 123380.
16. S.M.I. Mohamed, M. Yılmaz, E.K. Güner, and A. El Nemr, *Scientific Reports*, 14 (2024). 1241.
17. Z. Gou, C. Liu, M. Qi, W. Zhao, Y. Sun, Y. Qu, and J. Ma, *Journal of Hazardous Materials*, 463 (2024). 132910.
18. M. Ebrahimi, N. Khalili, S. Razi, M. Keshavarz-Fathi, N. Khalili, and N. Rezaei, *Journal of Environmental Health Science and Engineering*, 18 (2020). 335-343.
19. K.G. Pavithra, P. SundarRajan, P.S. Kumar, and G. Rangasamy, *Chemosphere*, 312 (2023). 137314.
20. A. Yazidi, L. Sellaoui, M. Badawi, G.L. Dotto, A. Bonilla-Petriciolet, A.B. Lamine, and A. Erto, *International journal of biological macromolecules*, 158 (2020). 595-604.
21. F. Kordbacheh and G. Heidari, *Materials Chemistry Horizons*, 2 (2023). 139-153.
22. J.G. Paithankar, S. Saini, S. Dwivedi, A. Sharma, and D.K. Chowdhuri, *Chemosphere*, 262 (2021). 128350.
23. J. Liang, X. Huang, J. Yan, Y. Li, Z. Zhao, Y. Liu, J. Ye, and Y. Wei, *Science of The Total Environment*, 774 (2021). 145762.
24. S. Bassaid, M. Chaib, S. Omeiri, A. Bouguelia, and M. Trari, *Journal of Photochemistry and Photobiology A: Chemistry*, 201 (2009). 62-68.
25. A. Saravanan, P.S. Kumar, S. Jeevanantham, S. Karishma, B. Tajsabreen, P. Yaashikaa, and B. Reshma, *Chemosphere*, 280 (2021). 130595.
26. S.-S. Chen, B.-C. Hsu, and L.-W. Hung, *Journal of hazardous materials*, 152 (2008). 1092-1097.
27. H. Wang, X. Song, H. Zhang, P. Tan, and F. Kong, *Journal of hazardous materials*, 384 (2020). 121459.
28. H. Peng and J. Guo, *Environmental Chemistry Letters*, 18 (2020). 2055-2068.
29. Z. Ying, X. Ren, J. Li, G. Wu, and Q. Wei, *Hydrometallurgy*, 196 (2020). 105440.
30. B. Verma and C. Balomajumder, *Bulletin of the Chemical Society of Ethiopia*, 34 (2020). 67-74.
31. M.E. González-López, C.M. Laureano-Anzaldo, A.A. Pérez-Fonseca, M. Arellano, and J.R. Robledo-Ortíz, *Separation & Purification Reviews*, 50 (2021). 333-362.
32. F. Brito, J. Ascanio, S. Mateo, C. Hernandez, L. Araujo, P. Gili, P. Martín-Zarza, S. Dominguez, and A. Mederos, *Polyhedron*, 16 (1997). 3835-3846.
33. G. Grampp, S. Landgraf, T. Wesierski, B. Jankowska, E. Kalisz, D.-M. Sabou, and B. Mladenova, *Monatshefte für Chemie/Chemical Monthly*, 133 (2002). 1363-1372.
34. G. Zhang, G. Kim, and W. Choi, *Energy & Environmental Science*, 7 (2014). 954-966.
35. A.M. May and J.L. Dempsey, *Chemical Science*, 15 (2024). 6661-6678.
36. G. Michel and R. Cahay, *Journal of Raman spectroscopy*, 17 (1986). 79-82.
37. A. Sanchez-Hachair and A. Hofmann, *Comptes Rendus Chimie*, 21 (2018). 890-896.
38. E. Aranda-García, L. Morales-Barrera, G. Pineda-Camacho, and E. Cristiani-Urbina, *Environmental monitoring and assessment*, 186 (2014). 6207-6221.
39. F. Gharib, F. Soleimani, A. Farajtabar, and H. Aghaei, *Journal of Chemical & Engineering Data*, 54 (2009). 2060-2066.

40. Y. Dai, G. Qian, Y. Cao, Y. Chi, Y. Xu, J. Zhou, Q. Liu, Z.P. Xu, and S. Qiao, *Journal of Hazardous Materials*, 170 (2009). 1086-1092.
41. K. Divan, *Improved Separation and Detection of Inorganic Ions by Capillary Electrophoresis*, in *Progress in Ion Exchange*. 1997, Elsevier. p. 176-186.
42. H.-B. Seo, H.-J. Kim, O.-K. Lee, J.-H. Ha, H.-Y. Lee, and K.-H. Jung, *Journal of industrial Microbiology and Biotechnology*, 36 (2009). 285-292.
43. C. Zhu, X. Huang, T. Li, Q. Wang, and G. Yang, *Journal of Colloid and Interface Science*, 603 (2021). 37-47.
44. P. Bandara, J. Peña-Bahamonde, and D. Rodrigues, *Scientific reports*, 10 (2020). 9237.
45. R. Kalal and D. Panday, *Journal of the Indian Chemical Society*, 98 (2021). 100009.
46. T. Poblete, D. Millán, and M.C. Rezende, *Journal of Molecular Liquids*, 391 (2023). 123227.