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Research Article

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Dynamic protonation of nickel, manganese & cobalt (NMC) and its effect on
simultaneous estimation and chelation potential of polyphenolic ligand(s)

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Abstract:

Quantitative simultaneous estimation and chelation of transition-metal cations such as Ni, Co, and Mn (NCM) associated with Li-ion cathodes is challenging because of their overlapping physicochemical properties. Lithium-ion recycling is currently performed by conventional pyrometallurgical and hydrometallurgical processes, which are costlier, energy-intensive, and low-resolution techniques. A systematic approach was adopted for simultaneous estimation and high-throughput chelation of NCM by polyphenolic natural ligands using Plackett-Burman screening design, followed by physicochemical analysis by FTIR, SEM-EDX, & ICP-OES and validation using density functional theory (DFT). The simultaneous estimation of Ni, Co, & Mn and their equimolar mixture (NCM) was fitted and analyzed based on Pearson's r and adjusted R^2 value. PB design analysis of the simultaneous chelation study conferred curcumin with the highest standardized effect and expected half-normal probability values of 9.22 and 1.6, respectively. The single-point energy (E_h) derived from density functional theory (DFT) was used to compute the binding energy (ΔE) between the chelating ligand & NCM in protonated and deprotonated states, providing quantitative relative intermolecular stability along with the corresponding HOMO-LUMO energy gap (ΔE_{gap}). FTIR profile confirms the role of keto and enol functional groups of curcumin in simultaneous chelation of NCM; further SEM-EDX of the co-coordination complex and ICP-OES elemental analysis of NCM confirm the significance of protonation on transitional NCM chelation by polyphenolic natural ligands.

Keywords: transitional metal cations, oxidation reduction potential (ORP), density function theory (DFT), ICP-OES, binding energy,

1. Introduction

The lithium-ion recycling process constitutes a critical strategy within sustainable energy resource management. This approach supports the circular economy, reinforces the supply chain, and promotes long-term environmental sustainability [1]. In spent lithium-ion batteries, the cathode terminus serves as a primary source for the recovery of monovalent lithium ions (Li: 2-7%), which are distributed along with transitional elements such as manganese (Mn): 2-5%, nickel (Ni): 5-10%, and cobalt (Co): 5-20% [2].

Currently, lithium-ion enrichment is performed from spent sources primarily by pyrometallurgical and hydrometallurgical processes [3]. Pyrometallurgical processes typically include high-temperature smelting of spent sources followed by phase separation. In the hydrometallurgical enrichment method, lithium ions are recycled by acid leaching followed by sequential precipitation and extraction by solvent extraction or ion exchange chromatography. These recovery methods are not economical, as they are energy-driven processes, have poor resolution for lithium-ion recovery, and are associated with environmental concerns due to the release of carbon dioxide as an effluent gas and other toxic byproducts. These limitations highlight the need for a green solution for lithium-ion recycling [4].

Polyphenolic phyto ligands possess electron-donating functional groups ($-\text{OH}$, $\text{C}=\text{O}$, $-\text{COOH}$) that enable the formation of stable bidentate or multidentate coordination complexes with transitional transition metal ions, including manganese (Mn), nickel (Ni), and cobalt (Co) [5]. The interaction between these ligands and transitional ions leads to the formation of insoluble coordination complexes and induces distinct changes in redox potential. Oxidation-reduction potential (ORP) measurement is a non-destructive electrochemical technique for detecting signals generated by redox reactions[6]. The binding of metal ions to ligands alters the electrochemical properties of the free metal ions, resulting in measurable shifts in ORP that can be detected without the need for complex standard operating procedures (SOPs).

Simultaneous estimation is widely used in analytical chemistry to analyze analytes with overlapping physicochemical properties. Analytical methods such as ultraviolet (UV)

spectroscopy, HPLC, and LC-MS, among others, are commonly used for the quantitative simultaneous estimation of analytes in combination, which facilitates rapid estimation by addressing the issues related to the resolution of overlapping spectra [7]. However, simultaneous estimation has some practical limitations, as it has poor resolution for analytes that tend to precipitate or form a non-opaque solution[8]. Its applicability may be limited for transitional ions, which often tend to form insoluble coordination complexes with polyphenolic ligands.

The present study aimed to simultaneously estimate multi-transitional cathodic metals (Manganese, Nickel, and Cobalt; NMC) at equimolar concentrations by measuring the oxidation-reduction potential (ORP). The efficiency of this estimation model was assessed using a screened phytoligand in protonated and deprotonated states at pH 4, 7, and 9. The outcomes were further analyzed and validated by single-point energy calculations of the metal(s)-ligand coordination complex (ΔE) using density functional theory (DFT). The resolution of the interaction between NMC and curcumin was analyzed using FT-IR, SEM-EDX, and ICP-OES. These findings provide a strategic scientific basis for the effective recycling of monovalent lithium ions via specific chelation with transitional metal ions in both protonated and deprotonated states.

2. Materials and methods

2.1. Materials

All chemicals and reagents used in the present study were of HPLC-grade and analytical-grade quality. Phytoligands such as curcumin were obtained from SRL Chemicals, Mumbai, India. Quercetin, rutin, naringin, and phytic acid were obtained from Sigma-Aldrich, Germany. Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) was obtained from Nice Chemicals Pvt. Ltd. (Cochin, India). Cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) was obtained from Mumbai, India. Manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) was obtained from Central Drug House, Pvt Ltd. (New Delhi, India). Ethanol was obtained from RCP Distilleries Pvt Ltd, India. All reagents and standard stock solutions were prepared in deionized Milli-Q grade water.

2.2. *Simultaneous estimation of Mn, Co, and Ni at varying pH by ORP method*

1M of standard stock solutions of manganese (M), cobalt (C), and nickel (N) were prepared in deionized Milli-Q-grade water. 1M mixed stock of MNC was prepared by combining equal volumes of 0.33 mM each standard stock of manganese, nickel, and cobalt. Working stock solutions ranging from 10 to 120 mM were subsequently prepared from the mixed stock. After reaching equilibrium, the oxidation-reduction potential (ORP) of the mixed working stock was measured at $25\pm 2^{\circ}\text{C}$ at pH values of 4, 7, and 9 using an ORP meter (Wellon, OPP meter-169E, Taiwan). ORP profiles were analyzed using descriptive statistics, including Pearson's r and adjusted R^2 .

2.3. *Screening of Phyto ligands by ORP method: Placket–Burman (fold-over design)*

A Plackett–Burman (PB) fold-over design, a key principle of design of experiments (DoE), was used to screen potential phytoligands capable of chelating multivalent metal ions in NMC based on ORP. NMC was mixed with curcumin, quercetin, rutin, naringenin, and phytic acid in a 1:1 ratio at specified concentration levels for each experimental trial run. The ORP values for the corresponding trials are shown in **Table No. 1**. The interaction between Phyto ligand(s) and NMC produced distinct redox signals, which were measured by an ORP meter. These redox signals were due to the interaction of multi-valent ions with the keto-enol functional group of phytoligand(s). The PB screening design was analyzed using a Pareto chart of standardized effects, ANOVA, and a half-normal probability plot.

Table. No. 1: Plackett Burman (PB)- fold-over design matrix for screening of phytoligand based on observed ORP value

Run NO	Curcumin	Quercetin	Rutin	Naringin	Erro1	Phytic acid	Error2	ORP (mV)
1	1	1	1	10	10	10	1	128
2	10	1	1	1	1	10	10	168.5
3	1	10	1	1	10	1	10	128.5
4	10	10	1	10	1	1	1	179.5
5	1	1	10	10	1	1	10	186.5
6	10	1	10	1	10	1	1	208.5
7	1	10	10	1	1	10	1	145
8	10	10	10	10	10	10	10	189.5
9	10	10	10	1	1	1	10	217.5
10	1	10	10	10	10	1	1	159.5
11	10	1	10	10	1	10	1	199.5
12	1	1	10	1	10	10	10	130.5
13	10	10	1	1	10	10	1	168.5
14	1	10	1	10	1	10	10	135.5
15	10	1	1	10	10	1	10	204.5
16	1	1	1	1	1	1	1	133.5

2.4. Analytical profiling: Simultaneous estimation and chelation

The simultaneous estimation profile and chelation of multi-transitional metal ions in NMC with the screened phytoligand, i.e., curcumin, in protonated and deprotonated states was systematically investigated by spectroscopic studies. The screened phytoligand (curcumin) was mixed with NMC at a 1:1 ratio at pH 4, 7, and 9 and allowed to reach equilibrium at room temperature. The contents were centrifuged at 10,000 rpm for 10 minutes. The precipitated coordination complex of curcumin-NMC was subjected to FTIR and SEM-EDX. The raffinate (supernatant) was subjected to ICP-OES analysis. The elemental composition in the coordination complex and in the raffinate

was correlated to infer the effect of protonation or deprotonation on simultaneous estimation and chelation **studies**.

The FTIR profile of the coordination complex of curcumin with MCDMI-NCM was recorded using a Thermo Fisher Scientific Nicolet iS50 equipped with a Mid-IR (KBr) beamsplitter with DTGS-KBr covering a spectral range of 4000–400 cm^{-1} . The Instrument provides a spectral resolution of 4, an optical velocity of 0.4747, wavelength repeatability of $\pm 0.02 \text{ cm}^{-1}$, and an accuracy of $\pm 0.1 \text{ cm}^{-1}$ at 1600 cm^{-1} . Samples were analyzed using the FTIR-ATR technique.

The microstructural features of the curcumin-NMC coordination complex were analyzed using SEM ZEISS ULTRA®55 (Carl Zeiss NTS GmbH, Oberkochen, Germany), which was equipped with integrated energy and angle-selective backscattered electron (EsB) and an Everhart–Thornley SE detector. The filtering grid was maintained at 0–1500 V to improve image quality and enable auto-adjustment during *image acquisition*. *The grid was* sensitive to edge contrast & charging effects. The samples were subjected to sputtering prior to SEM analysis. A quantity sufficient (q.s) of sample was placed onto the sample holder using double-sided carbon conductive adhesive tape (Agar Scientific, Stansted, UK). The curcumin-NMC coordination complex was subsequently analyzed using SEM coupled with energy-dispersive X-ray spectroscopy (EDX).

Sputtered samples were subjected to accelerating X-rays at 20kV at a distance of 10mm to record EDX profiles. The elemental profile was recorded in different areas of interest to evaluate uniformity or homogeneity of elemental composition within the coordination complex. The free elemental profile present in the supernatant left after curcumin-NMC complex formation was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (iCAP 6000, Thermo Fisher Scientific, Cambridge, United Kingdom). The supernatant was digested with 4% nitric acid and filtered through a $0.22 \mu\text{m}$ membrane filter. The ICP-OES were calibrated with acidified standard solutions of cobalt, manganese, and nickel at concentrations of 1 to 15 ppm at their absorption maxima, and the samples were scanned at 229nm, 258nm, and 232nm, respectively.

2.5. Validation of simultaneous estimation and chelation by DFT analysis

The Density Functional Theory (DFT) study was employed to assess electronic interactions and the stability of the metal(s) and their coordination complex with the screened phytoligand. In the

AVOGADRO platform, the three-dimensional (.SDF) files of metal ions, curcumin, and their corresponding coordination complexes with NMC were subjected to geometry optimization using the 3D XYZ coordinates in the corresponding input files. Further, the ORCA output file(.inp) was generated by defining the single-point energy function in AVAGDRO under the defined BLYP functional conditions. The charge and multiplicity were varied to correlate the protonated or deprotonated states of the ligand-metal complex at varying pH of 4, 7, and 9, respectively, as shown in the **Table. No.2**. The command prompt was used to transform the ORCA input file (.inp) into the output file (.output). From this output .txt file, total single-point energy, binding energy, and HOMO-LUMO gap energy were calculated using the following expression (Eq.1) [9].

$$\Delta E = E_{\text{complex}} - (E_{\text{ligand}} + E_{\text{metal}}) \quad \text{Eq.1.}$$

Where ΔE : Binding energy of the co-ordination complex; E_{complex} : Single point energy of the complex; $E_{\text{ligand}} + E_{\text{substrate}}$: Summation of single point energy of the ligand and metal

The molecular orbital energy gap (between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) is used to calculate molecular dynamics parameters related to the molecular stability of the screened phytoligand curcumin-NMC and to assess overall electron-transfer capabilities using the following expression (Eq.2).

$$\Delta E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad \text{Eq.2.}$$

Table No.2: DFT analysis of curcumin and transitional metal ion coordination complex at varying change and multiplicity attributing protonated and deprotonated state

Metal-ligand complex	pH	Charge	Multiplicity
Curcumin-Nickel	4	2	3
	7	-2	3
	9	0	3
Curcumin-Manganese	4	+2	6
	7	-2	6
	9	0	6
Curcumin- Cobalt	4	2	4
	7	-2	4
	9	0	4

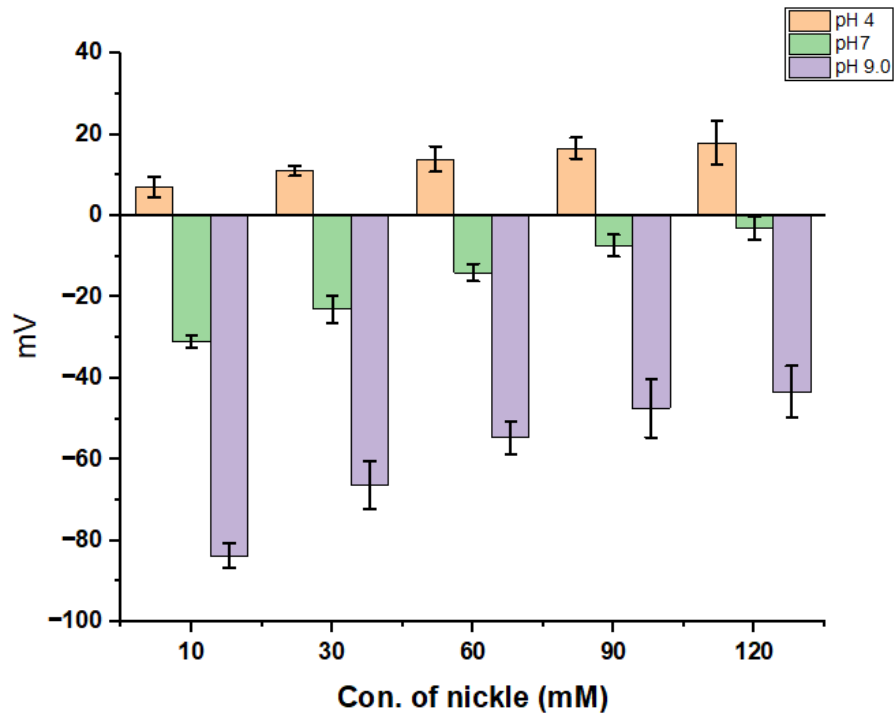
3. Results and Discussion:

3.1. Oxidation reduction potential: Transitional metal ions and its combination

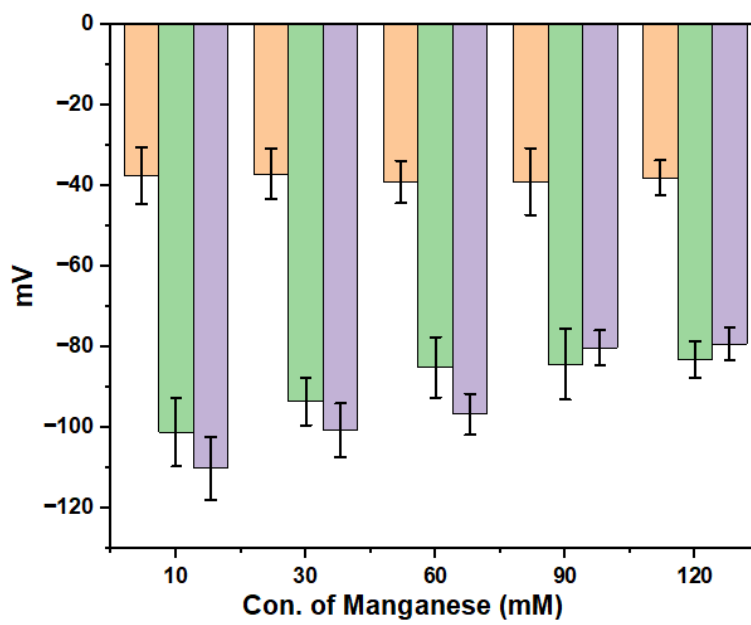
As shown in Fig. No. 1, the oxidation-reduction potential (ORP) profile of nickel (N), manganese (M), and cobalt (C), as well as the stoichiometric ratio of the NMC combination at pH 4, 7, and 9. Integrating descriptive statistics parameters with an ORP-based standardization study helped establish a statistical basis for drawing inferences and conclusions. Pearson's r , or correlation coefficient, provides a quantitative and statistical basis to determine the strength and direction of the relationship. In contrast, the adjusted R^2 value indicated the proportion of the response explained by the model.

At pH 7 and 9, the selected transitional metal ions demonstrate consistent and dose-dependent changes in redox potential, with acceptable Pearson's r (correlation coefficient) and adjusted R^2 values, as shown in **Table No. 3**. At acidic pH, the protonation of transitional metal ions leads to a gradual increase in ORP value, referring to dose dependent build-up of reduction equilibrium, whereas, at pH 7 and 9, the deprotonation state favours a gradual, dose-dependent decrease in ORP value for selected transitional metal ions and their combination due to gradual oxidation equilibrium, as shown in **Fig. No.1 (a-c)**. At pH 4, manganese and cobalt exhibit poor stability in the protonated state, which was reflected by low Pearson's r and adjusted R^2 values, as shown in the **Table.No.1**

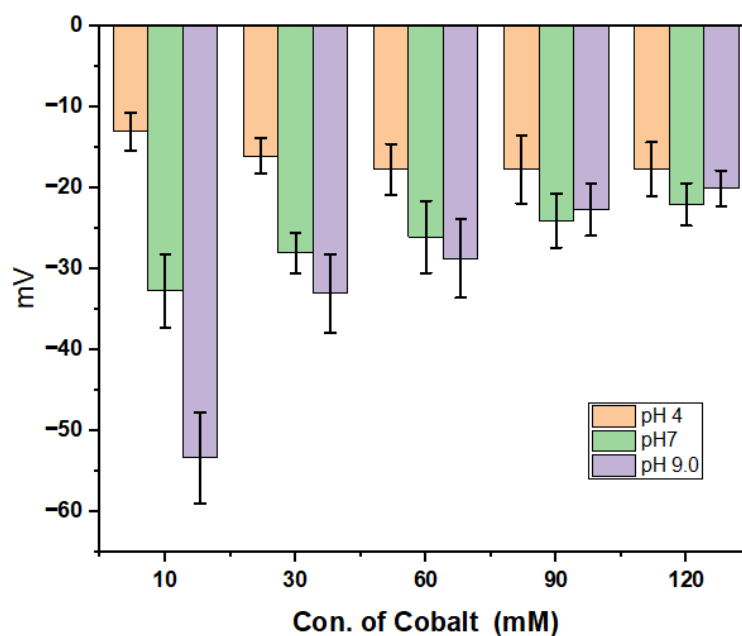
Interestingly, the mixture of transitional metal ions in the combination at acid pH (protonated state) exhibits relatively strong negative Pearson's correlation with an acceptable adjusted R^2 value. Simultaneous estimation of NMC in an equimolar stoichiometric combination provided more consistent ORP values than individual counterparts. This may be due to simultaneous electrochemical potential speciation equilibrium of transitional metal ions, especially for metals such as manganese and cobalt, which are poorly stable in the protonated state [10].



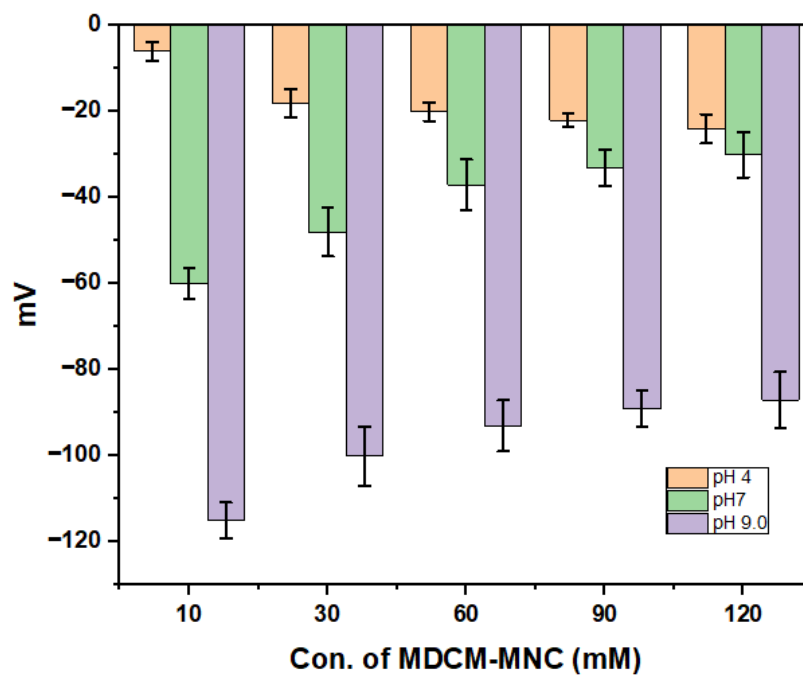
(a)



(b)



(c)



(d)

Fig.No.1(a-d): Comparative ORP profile of transitional metal ions and their combination (a) nickel (N), (b) manganese(M), (c) cobalt (C) and (d) Equimolar stoichiometric combination (NMC) in protonated and deprotonated condition.

Table 3: The comparative ORP value of transitional metal ions nickle (N), manganese (M) and cobalt (C) and their 1:1 :1 stoichiometric ratios of MNC and related descriptive statistics

Ligand	pH	Regression equation	Perarson' r	Adjusted R ²
Nickle (N)	4	$Y=0.101x + 7.54$	0.96	0.91
	7	$Y=0.27x - 32.63$	0.98	0.96
	9	$Y=0.40x - 84.61$	0.95	0.88
Manganese (M)	4	$Y= 0.0025x -38.62$	0.56	0.09
	7	$Y= 0.13x - 97.82$	0.91	0.77
	9	$Y= 0.028x -110.61$	0.94	0.86
Co (C)	4	$Y=-0.041x -13.82$	-0.81	0.56
	7	$Y= 0.007x -31.12$	0.96	0.90
	9	$Y= 0.22x -45.06$	0.90	0.75
NMC	4	$Y=-0.16x- 7.78$	-0.90	0.75
	7	$Y=0.28x - 60.25$	0.96	0.89
	9	$Y=0.27x - 114.32$	0.94	0.84

The Plackett–Burman fold-over design was used for screening of potential phytoligands that chelate mixed transitional metal ions NCM with curcumin, rutin, phytic acid, naringenin, and quercetin in a 1:1 ratio based on the ORP method, as shown in **Table No. 1**. The interaction between phytoligand(s) and corresponding transitional ions has resulted in the formation of distinct redox reactions due to the keto-enol form of the phytoligands [11]. The design was analyzed using ANOVA, a Pareto chart of standardized effects, and a probability plot.

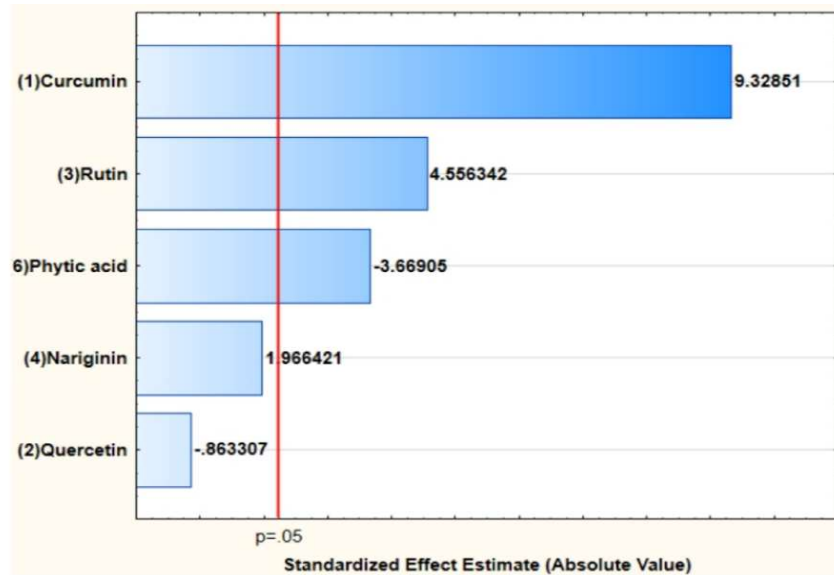
Based on the analysis of observed ORP values from the PB design, the Pareto chart of standardized effects of the selected independent variables ranked the mean effects according to their level of significance. In the Pareto chart, a vertical line indicates the statistical significance ($p = 0.05$); any selected independent variable standardized effect represented by a horizontal bar that crosses the vertical line, referring to the standardized effect ($p=0.5$), is regarded as a significant criterion.

The Pareto chart results (**Fig. 2a**) indicate that nutraceuticals such as curcumin, rutin, and phytic acid have standardized effects (absolute values) of 9.32, 4.55, and 3.66, respectively, and are statistically significant.

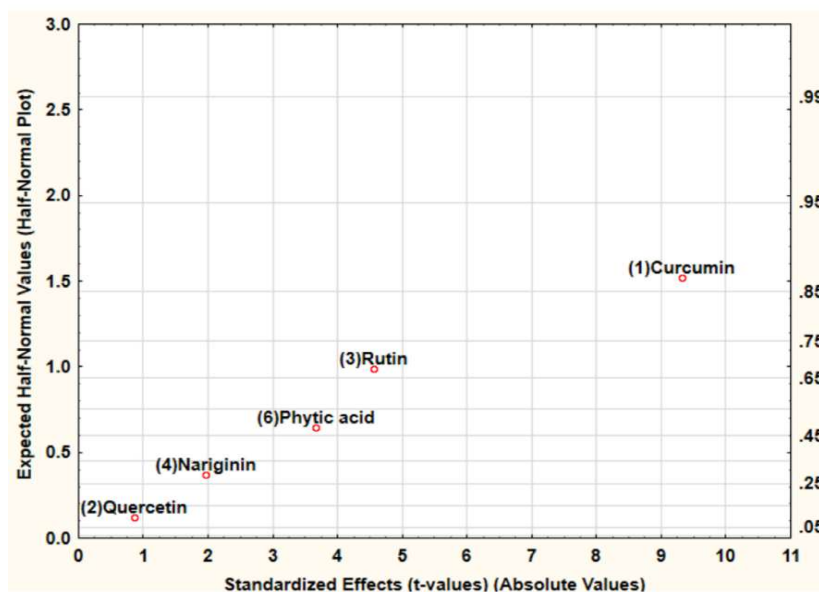
The Pareto chart outcomes were verified by ANOVA. The lowest observed p-value (0.000013) and highest F value (89.24) were observed with curcumin, followed by rutin and phytic acid. The half-normal probability was used to separate random noise from the screening design and help identify the ‘real effects’ based on their distribution profile, as shown in **Fig. 2(b)**. Among the selected independent variables, curcumin was identified as an outlier with a higher factor level. The half-normal distribution matrix (half-normal PB model predicted solutions are obtained by the following polynomial regression equations (Eq.3)

$$Y = 132.31 + 5.40x_1 - 0.5x_2 + 2.63x_3 + 1.13x_4 - 2.12x_5 \quad \text{Eq.3.}$$

Where x_1 , x_2 , x_3 , x_4 , and x_5 corresponds to curcumin, quercetin, rutin, naringenin and phytic acid respectively.



(a)



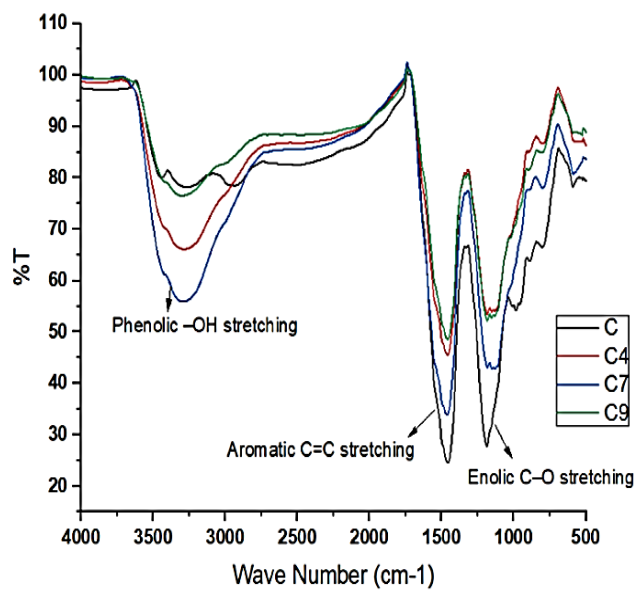
(b)

Fig.2(a, b): Screening of phytoligands based their relative interaction with NMC measured as ORP: (a) Pareto-chart of standardized effect; (b) Half-normal probability plot value

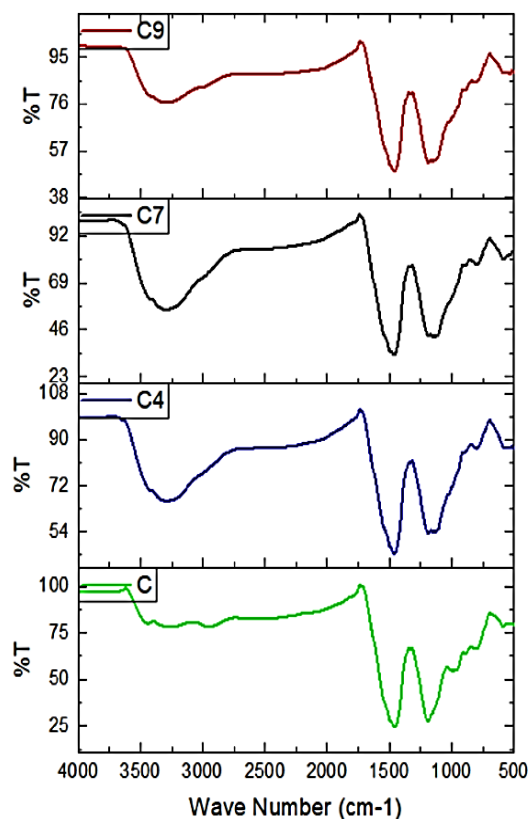
The native curcumin without chelation exhibits distinct functional groups such as phenolic –OH, aromatic C=C stretching, and enolic C–O stretching between 3648 cm^{-1} – 2835 cm^{-1} , 1600 cm^{-1} – 1366 cm^{-1} and 1240 cm^{-1} – 1056 cm^{-1} as shown in **Fig.3(a-b)**.

The chelation of cathodic transitional metal ions (NCM) with curcumin in a 1:1 ratio result in distinct variation and peak broadening in the phenolic –OH stretching region with decreased %T. At pH 7, the interaction between NCM and curcumin resulted in a decline in %T from 80% to 55. This deformation and %T in transmittance attributed coordination bond formation between NCM and curcumin at pH 7. Interestingly, at pH 9, the increased % T of the FTIR bands at 1600 cm^{-1} – 1366 cm^{-1} and 1240 cm^{-1} – 1056 cm^{-1} indicates greater rigidity of the aromatic C=C stretching region due to increased electronic delocalization.

The interaction between curcumin and NCM mainly takes place through the keto-enol moiety (C–O). The % Intensity changes in the C–O–C functional group between 1240 cm^{-1} and 1056 cm^{-1} may be due to redistributed electronic density. The deformation and change in %T of the aromatic C=C bond, though not a direct metal coordination site, are indirect indicators of changes in electronic structure due to curcumin-NCM interactions at equilibrium.



(a)



(b)

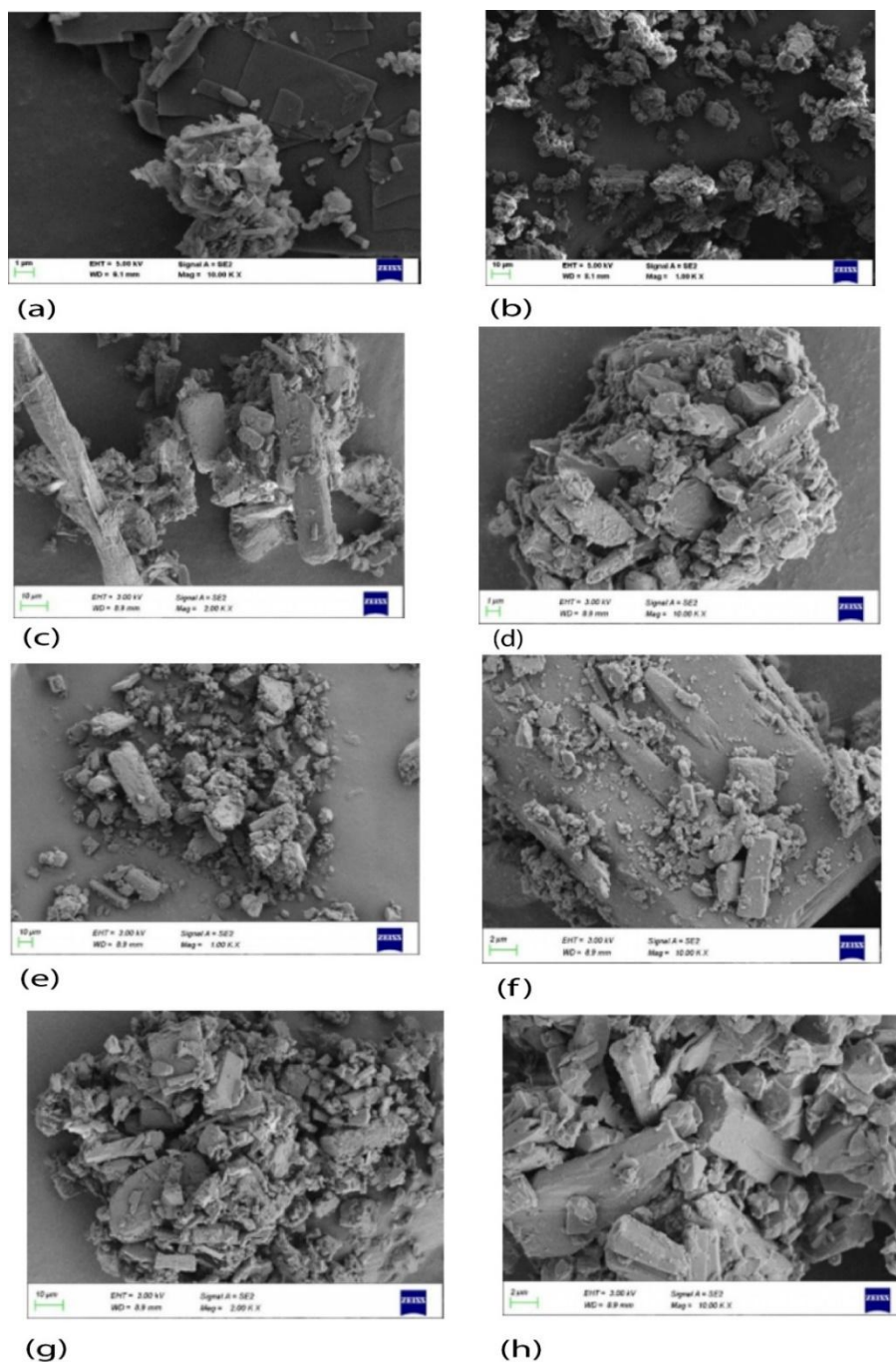
291

292 **Fig.3(a, b):** FTIR profile of curcumin and curcumin-NMC at varying pH of 4, 7 and 9; (a)
 293 Overlay form; (b) stacked form.

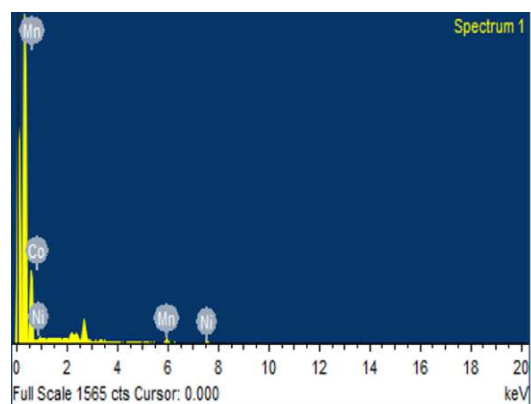
294

295 The interaction between curcumin and NCM at an equal stoichiometric ratio, and the analysis of
 296 the complex by SEM-DEX, provided critical input on the elemental balance of the interaction or
 297 complexation. As shown in **Fig. No. 4(a-h)**, the interaction between the ligand and metals has
 298 resulted in changes in the structural and topographical surface features. The SEM integrated EDX
 299 profile was also recorded, the average element weight % of corresponding element is as shown in
 300 **Fig.No.5(a-c)**. The coordination complex between curcumin and NCM at pH values of 4, 7, and 9
 301 showed varying elemental weight percentages of, Ni, Co, and Mn.. **At pH 4**, the ligand chelated a
 302 significant amount of elemental Mn compared to pH of 7 and 9. Co and Ni were chelated
 303 significantly at pH of 7 and 9 compared to pH of 4. The observed % weight of the EDX profile

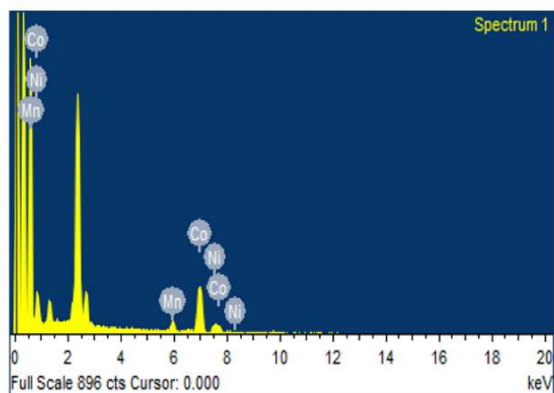
304 averaged across 3 profiling regions varied, as indicated by a pronounced SD among the observed
 305 values. This demands a more sensitive method for elemental analysis.



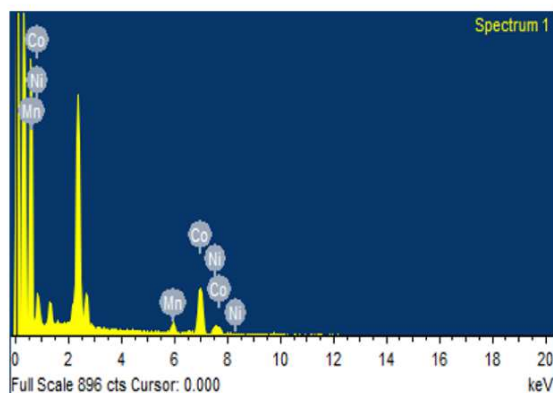
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 307 **Fig.4(a-h):** SEM based structural analysis of NCM and its interaction with curcumin in a
 308 protonated and deprotonated state by varying pH of 4, 7 & 9.



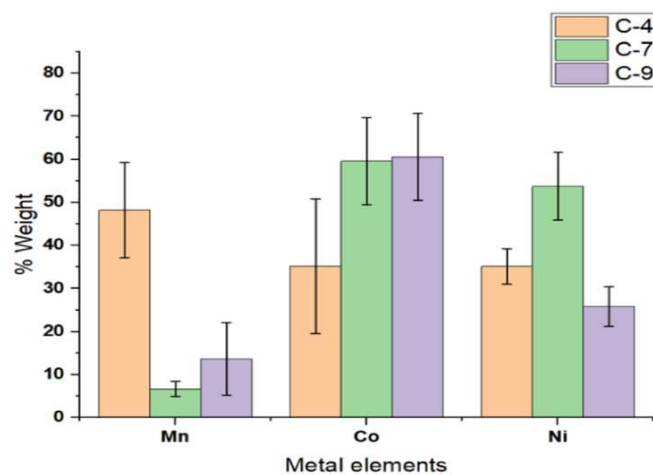
(a)



(b)



(c)



(d)

Fig.5(a-c): Energy dispersive X-ray spectroscopy based elemental profile in curcumin-NMC in a protonated and deprotonated state

The interaction between curcumin and transitional ions NCM in an equal stoichiometric ratio, and the residual elements in the supernatant by ICP-OES, provide critical input on the elemental balance of the interaction. As shown in **Fig. No. 6(a)** at a pH of 9, cobalt and nickel are significantly reduced in the raffinate as compared to pH 4 and 7. The elemental nickel was significantly reduced (p value of < 0,001) at pH 7. Overall, the datasets have shown consistent results with minimal standard deviations, highlighting the advantage of ICP-OES over elemental analysis by SEM-EDX, which exhibits higher standard deviations. As compared to the blank the % chelation study of curcumin with NCM has exhibited the significant chelation at pH of 7 and 9 for cobalt, manganese and nickel elements, as shown in **Fig. No 6(b)**. Moreover, the standard deviation among the elemental analysis was found to be minimal as compared to EDX profile, which marks the selectivity and sensitivity of ICP-OES method in the elemental analysis [12] .

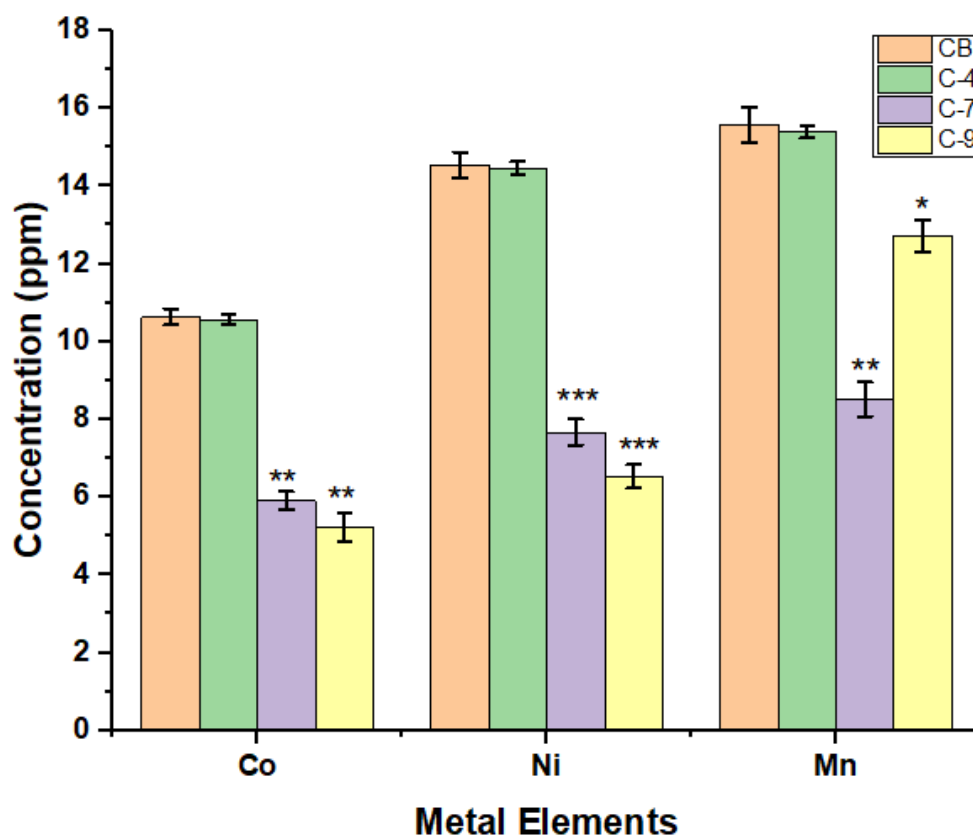


Fig.6(a): ICP-OES analysis elemental concentration in a raffinate of curcumin-NMC in a protonated and deprotonated state. Turkey's multi-comparison ANOVA test used to determine the level of significance.

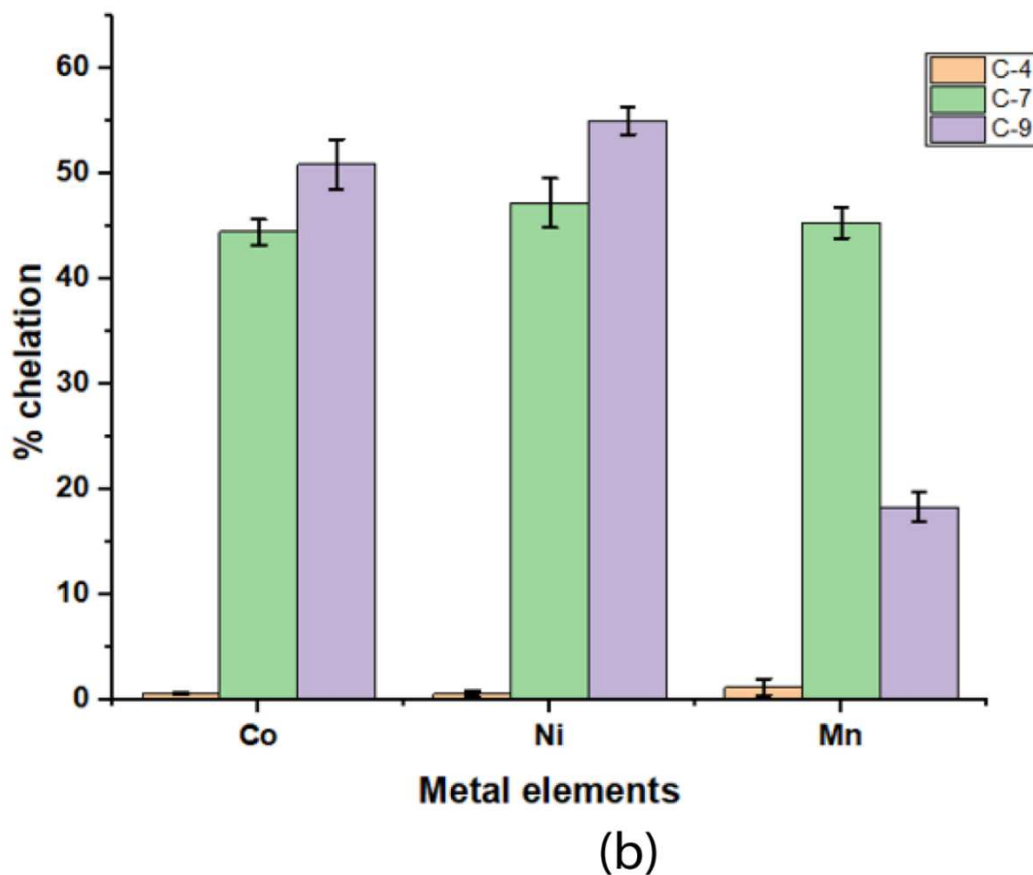


Fig.5(b): ICP-OES analysis based % chelation study raffinate of curcumin-NMC in a protonated and deprotonated state

DFT- results

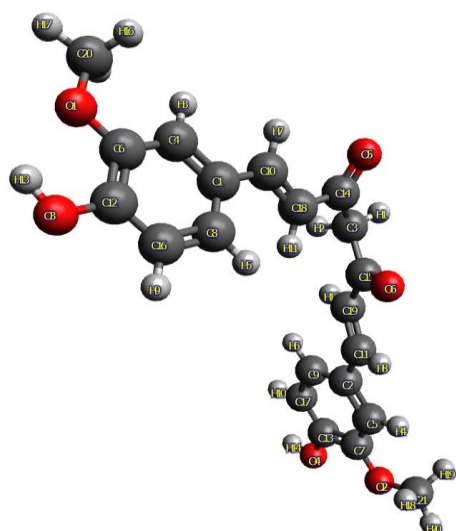
The DFT-based single-point energy (Eh) of the metal, ligand, and metal-ligand coordination complexes as shown in **Fig.No.7**, and their corresponding binding energy (ΔE) and HOMO-LUMO energy gap, are presented in **Table No.4**. The computed ΔE , derived from the single-point energy (Eh) of metal, ligand, and their metal-ligand coordination complexes, was calculated based on **Eq.1**. The ΔE values exhibited a distinct trend with respect to the binding energy (ΔE) of curcumin and its respective coordination complex with transitional ions, i.e., Mn, Ni, and Co. Notably, the protonation and deprotonation of curcumin at pH 4, 7, and 9 resulted in improved ΔE values, suggesting improved molecular stability during chelation of transitional metal ions.

For the curcumin-cobalt coordination complex, the binding energy ΔE at pH 4, 7, and 9 was 0.56, 0.09, and 0.03, respectively. Similarly, for the curcumin-manganese coordination complex, ΔE values in this pH range were 0.44, -0.02, and -0.07, respectively. Whereas for the curcumin-nickel coordination complex, ΔE values were 0.059, 0.12, and 0.07, respectively, these observations demonstrate that varying pH influences the protonation and deprotonation state of the polyphenolic ligand. Thereby affecting its transitional metal chelation properties. The coordination complexes possess relatively greater stability in the deprotonated state as compared to the protonated ligand-metal counterparts.

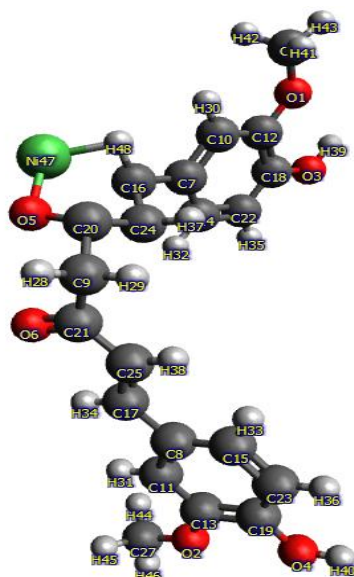
The smaller HOMO-LUMO energy gap (ΔE_{gap}) in the metal-ligand coordination complex indicates increased electronic redistribution and flexibility, thereby promoting the formation of metal-ligand coordination complexes, as shown in the table. The variation in pH results in protonated and deprotonated states that adversely affect the binding energy of ligand-metal coordination complex formation, potentially causing the precipitation of transitional metal ions. Curcumin with a polyphenolic functional group undergoes deprotonation across a pH range of 4, 7, and 9. This phenomenon can influence curcumin's ability to chelate transitional metal ions across a varying pH range, with a corresponding effect on binding HOMO-LUMO gap energies.

Table No-4: Transitional metal ions, Binding energy (ΔE) and HUMO-LUMO energy gap of transitional metal ions, curcumin-transitional metal coordination complexes in the protonated and deprotonated state

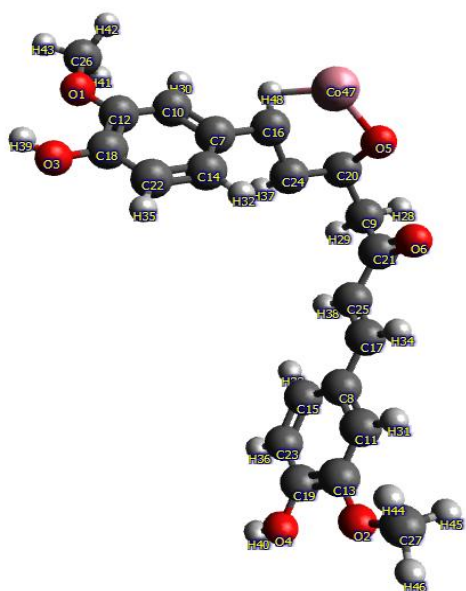
Metal/ligand/metal-ligand	FINAL SINGLE POINT ENERGY (Eh)	$E_{Complex}$	$E_{Metal} + E_{ligand}$	$\Delta E = E_{Complex} - (E_{Metal} + E_{ligand})$	HOMO-LUMO gap
Cobalt	-1382.58				-0.010
Manganese	-1150.71				0.001
Nickel	-1508.12				0.004
Curcumin	-1262.19				0.069
Curcumin-cobalt 4	-2644.21	-2644.21	-2644.77	0.56	0.031
Curcumin-cobalt 7	-2644.68	-2644.68	-2644.77	0.09	0.009
Curcumin-cobalt 9	-2644.74	-2644.74	-2644.77	0.03	-0.001
Curcumin-Manganese 4	-2412.46	-2412.46	-2412.9	0.44	0.034
Curcumin-Manganese 7	-2412.92	-2412.92	-2412.9	-0.02	-0.303
Curcumin-Manganese 9	-2412.97	-2412.97	-2412.9	-0.07	0.019
Curcumin-Nickel 4	-2769.72	-2769.72	-2770.31	0.59	-0.178
Curcumin-Nickel 7	-2770.19	-2770.19	-2770.31	0.12	0.011
Curcumin-Nickel 9	-2770.24	-2770.24	-2770.31	0.07	-0.030



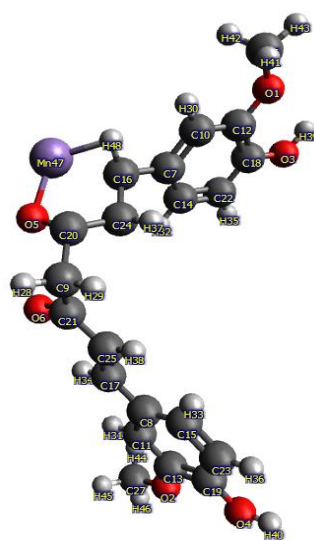
(a)



(b)



(c)



(d)

Fig No. 7: DFT based geometry optimization and 3D pose in Avogadro (a) Phytoligand: curcumin(C); (b) C-Ni; (c) C-Co; and (d) C-Mn

Conclusion

Simultaneous estimation is routinely used as a rapid profiling method for multi-ingredient compositions with overlapping physicochemical properties. This approach is justified in the lithium-ion enrichment process from spent cathode electrodes, where manganese (Mn), nickel (Ni), and cobalt (Co) tend to act as interfering transition-metal cations. These ions tend to precipitate at varying operational conditions such as acid digestion, among others. These conditions typically do not favour the simultaneous estimation of the mentioned transitional metal ions by conventional UV spectroscopic and other related spectroscopic techniques. The summary of critical observations of the present investigation is as follows:

- i. The present investigation aimed to standardize the simultaneous estimation and chelation method for transitional metal cations: NCM using screened polyphenolic nutraceuticals based on oxidation-reduction potential (ORP). This indirect approach may favour effective recycling of lithium ions by strategically removing NCM.
- ii. The NCM produced consistent and statistically reliable ORP signals in the dynamic protonated and deprotonated states, compared with the individual counterparts of selected transitional metal cations.
- iii. The polyphenolic ligand curcumin was found to be effective in simultaneous chelation of NCM in a deprotonated state as compared to the protonated state.
- iv. The single-point energy-based binding energy (ΔE) validated the ORP outcomes for relative chemical stability of chelation in the protonated state.
- v. The relative chemical fingerprints of the screened phytoligand and NCM coordination complex in varying protonated and deprotonated states resulted in altered % T in the stretching frequencies of non-keto-enol functional groups, conferring redistribution of electronic density. Whereas EDX and ICP-OES provided direct or indirect quantitative validation datasets for phytoligand-mediated simultaneous NCM chelation in protonated and deprotonated states.

The present standardization of simultaneous estimation and chelation of multi-transitional NCM by the ORP method provides an important lead and basis for selecting a phytoligand, along with the dynamic deprotonated state by varying pH, for effective NCM removal. This strategy may indirectly support better lithium-ion enrichment by alternative methods.

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402
403 **Data availability**

404 The datasets generated during and/or analysed during the current study are available from the
405 corresponding author on request.

406 **Declarations**

407 **Ethics approval**

408 Not applicable. This article does not contain any studies involving human participants or animals
409 performed by any of the authors.

410 **Consent to participate**

411 Not applicable. This article does not contain any studies involving human participants or animals
412 performed by any of the authors.

413 **Consent for publication**

414 Not applicable. All authors have reviewed the manuscript and agreed to its publication.

415 **Competing interests**

416 The authors declare no competing interests.

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