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Competitive liquid–liquid extraction of metal ions with novel pyridinyl-substituted benzothioate: Experimental studies, real matrix applications and DFT insights

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Abstract

In this study, the selectivity of the compound S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate from media containing a mixture of metal ions was investigated using competitive liquid-liquid ion pair extraction, and its metal removal properties were studied in real water matrices. Extraction experiments conducted with solutions containing mixtures of Zn^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions revealed that the ligand exhibited particularly high selectivity towards the Fe^{3+} ion. The variation in extraction data was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and the best extraction efficiency was obtained for the Fe^{3+} ion (44.12%). Relative selectivity factors showed that the ligand extracted the Fe^{3+} ion more efficiently than other metal ions. Furthermore, metal removal studies were conducted on lake, stream, and tap water samples to determine the performance of the compound in real water matrices, and ion exchange was detected by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The relationship between the electronic structure of the ligand and its extraction behavior was also investigated using density functional theory (DFT) calculations. The calculated HOMO–LUMO energy gap, chemical hardness, and other spherical reactivity parameters supported the strong interactions of the ligand, particularly with Fe^{3+} ions, which have a high charge density. The results indicate that S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate can be used as a potential extraction agent for the selective removal of metal ions from environmental water samples.

Keywords: *Metal removal from water, competitive metal extraction, metal complexation, drinking water quality, DFT.*

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Yeni piridinil sübstitüe benzotiyoat ile metal iyonlarının yarışmalı sıvı-sıvı ekstraksiyonu: Deneysel çalışmalar, gerçek matriks uygulamaları ve DFT bulguları

Öz

Bu çalışmada, S,S'-di(2-piridinil)-2,2'-ditiyodibenzotiyoat bileşiğinin metal iyonlarının karışımını içeren ortamlardan yarışmalı sıvı-sıvı iyon çiftleri ekstraksiyonu ile seçiciliği ve gerçek su matrikslerindeki metal giderim özellikleri araştırılmıştır. Zn^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+} ve Cu^{2+} iyonlarının karışımını içeren çözeltilerle gerçekleştirilen ekstraksiyon deneylerinde, ligandın özellikle Fe^{3+} iyonuna karşı yüksek seçicilik gösterdiği tespit edilmiştir. Ekstraksiyon verilerinin değişimi ICP-OES ile belirlenmiş ve en iyi ekstraksiyon verimi Fe^{3+} iyonu için (%44.12) elde edilmiştir. Nispi seçimlilik faktörleri, ligandın Fe^{3+} iyonunu diğer metal iyonlarına göre daha yüksek olarak ekstrakte ettiğini göstermiştir. Ayrıca, bileşiğin gerçek su matrislerindeki performansının belirlenmesi amacıyla göl, akarsu ve musluk suyu örneklerine metal giderim çalışmaları uygulanmıştır ve iyonların değişimi ICP-MS tespit edilmiştir. Ayrıca ligandın elektronik yapısı ve ekstraksiyon davranışı arasındaki ilişki yoğunluk fonksiyoneli teorisi (DFT) hesaplamaları ile incelenmiştir. Hesaplanan HOMO–LUMO enerji aralığı, kimyasal sertlik ve diğer küresel reaktivite parametreleri, ligandın özellikle yüksek yük yoğunluğuna sahip Fe^{3+} iyonlarıyla güçlü etkileşimler oluşturduğunu desteklemiştir. Elde edilen sonuçlar, S,S'-di(2-piridinil)-2,2'-ditiyodibenzotiyoat bileşiğinin çevresel su örneklerinden metal iyonlarının seçici uzaklaştırılmasında potansiyel bir ekstraksiyon ajanı olarak kullanılabileceğini göstermektedir.

Anahtar kelimeler: *Sudan metal uzaklaştırma, yarışmalı metal ekstraksiyonu, metal kompleksleşmesi, içme suyu kalitesi, DFT.*

1. Introduction

Water is one of the indispensable and most important needs of living organisms. The fact that the percentage of potable water on Earth is around 1% highlights the need to improve the quality of water for its usability as drinking water [1–3]. Many pollutants are released as a result of human life and activities. However, the variation of pollutants across countries indicates that existing methods will become insufficient over time, and new measures will be required against new pollutants that will emerge [4]. The presence of too little or too much anion or cation also has a negative effect on organisms. Excess anions and cations, and heavy metals, can cause certain health problems if consumed in excess or insufficient amounts[5]. Examples include copper deficiency causing anemia and nervous system disorders; excess copper causing nausea, liver, and kidney damage; and consuming tap water containing arsenic pollutants causing abdominal pain, vomiting, and diarrhea. Lead poisoning, which directly affects the nervous system, can cause significant damage/death to the brain and kidneys [1,2,5–7].

Crown ethers can be classified as oxo, azo, thio, benzo, benzo-thio crown ethers, etc., due to the oxygen, sulfur, nitrogen atoms, and benzene rings they contain. Following the synthesis of benzocrown ethers by Pedersen in the 1960s, the synthesis of sulfur-

containing members began in the 1970s and 1980s [8]. The synthesis of benzo-thio crown ethers, initiated by Tanaka et al. in 1972-1973 [9,10] and Buter and Kellogg in 1981 [11], increased significantly in the 1990s. This increase is consistent with the fact that the benzene ring and sulfur donor atoms have completely different properties and are associated with completely different metal cations; the importance of compounds containing these groups together is extremely interesting [12–14]. Thiocrown ethers show high affinity for heavy metals and precious metals due to the sulfur atoms they carry [15]. Heavy metals exhibiting strong complexation with thiol (-SH) groups in enzymes and proteins have toxic effects on organisms. Modifications made to the structures of crown ethers increase their affinity for metals [1,11,16–20] Beyond traditional crown ethers, a wide variety of synthetic architectures containing mixed sulfur, nitrogen, and oxygen donor atoms have been developed to enhance metal ion coordination [21]. The complexation capabilities of these multi-donor systems with diverse metal cations are widely exploited not only in liquid-liquid ion-pair extraction and adsorption-based removal processes but also in conductometric titrations to elucidate their solution thermodynamics and binding stoichiometries [22–24].

Liquid-liquid extraction is one of the fundamental classical methods widely used in analytical chemistry for the selective separation and enrichment of target analytes in a matrix medium. However, the direct transfer of polar or ionic compounds with a permanent net charge to the organic phase is thermodynamically unfavorable, and this greatly limits the efficiency of conventional extraction methods [19,25]. To overcome this limitation, "liquid-liquid ion-pair extraction" is based on the principle that the charged analyte in the aqueous phase forms an electrically neutral and hydrophobic ion pair (association complex) with a suitable counter-ion with an opposite charge. This neutral complex is transferred to the organic solvent phase with high selectivity and efficiency thanks to the chemical potential difference between the phases [26]. This method, which is of critical importance in both pharmaceutical analysis and the determination of environmental chemicals, by optimizing experimental parameters such as pH, ionic strength, counterion type, and solvent polarity, it offers the possibility of high-sensitivity separation even in complex sample matrices [27].

The main objective of this study is to investigate in detail the complexation behavior and selectivity of an original pyridinyl-substituted benzothioate compound containing both pyridinyl and benzothioate functional groups with metal ions. Building upon previous extraction studies in the literature aimed at determining the affinity of this ligand to specific elements, the selectivity profile of the compound in competitive environments containing multiple metal ions and the stability of this selectivity in real matrices were tested. Accordingly, the contents of artificial metal ion mixture solutions subjected to liquid-liquid ion pair metal extraction and natural surface water samples were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) techniques. The extraction parameters calculated from the obtained results were discussed, supported by global reactivity parameters calculated using DFT methods.

2. Experimental studies

2.1. Material

The chemical materials used in this study were sourced from Sigma Aldrich, Carl Roth, Alfa Aesar, Isolab, and Thermo Scientific Chemicals. The salts used in this study ($Co(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$) were commercially available (Sigma Aldrich, Carlo Erba, Merck, Roth) with high purity (≥ 98.5%). Ultra-pure water with a resistance of 18.3 MΩ/cm, produced by a Human Corporation brand New Human Power I S-UV model ultra-pure water device, was used to prepare the aqueous solutions. HPLC-grade chloroform was used to prepare the solvent system (50% chloroform/water). In the experiments, a precision balance (KERN ABJ (d=0.1 mg)), automatic pipette (ErgOne and Brand), dispenser (Brand 0.5-5 mL and 1-10 mL), ultrasonic bath (Bandolin), magnetic stirrer (IKA C-MAG HS-7), shaker (Stuart/SSL1), and pH meter (Hanna HI 2211, probe HI1131) were used. Competitive liquid-liquid ion pair extraction data were obtained using a Perkin Elmer Optima 2100 model Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Data obtained from the extraction of the same cations in lake, stream, and tap water samples were obtained using a Thermo Scientific iCAP Q model Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS).

2.2. Synthesis

The benzothioate derivative used in the study and given in Figure 1 was synthesized by microwave synthesis method according to the procedures given in our previous studies [28]. The synthesized S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate compound was used in the study.

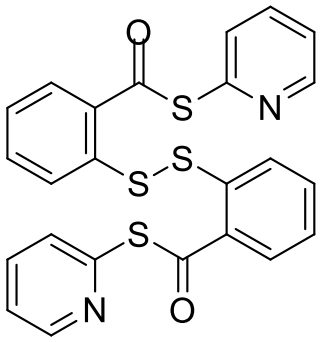

Figure 1. S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate compound.

2.3. Liquid-liquid ion pair extraction

2.3.1. Formulation

Liquid-liquid extraction is the transfer of inorganic materials to organic materials using two immiscible liquids (organic phase and inorganic phase) (Figure 2). The organic phase can be dichloromethane, diethyl ether, chloroform, benzene, etc., containing organic material. The inorganic phase is generally an aqueous metal salt solution containing cations and anions.

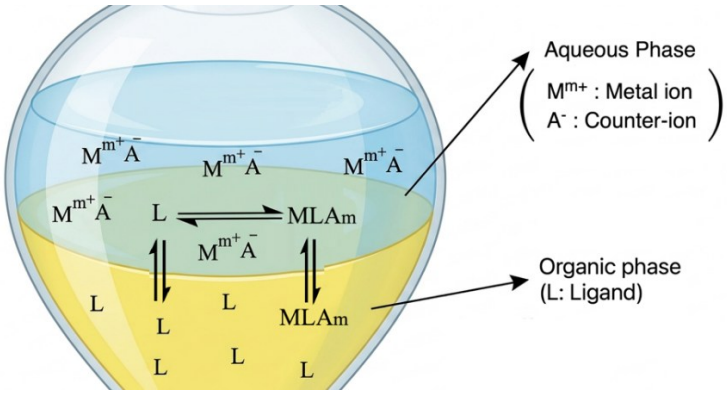

Figure 2. Schematic diagram of liquid-liquid ion pair extraction.

The formulas used in this study are as follows [29]. First, the following equation can be written for the extraction scheme given in Figure 2;

$$M^{m+}{}_{(aq.)} + mA^{-}{}_{(aq.)} + L_{(aq)} \rightleftharpoons MLA_m \quad {}_{(org.)} \tag{1}$$

According to this equation, the following formulas can be written for the extraction of liquid-liquid ion pairs:

$$K_{Ext} = \frac{[MLA_m]_{(org.)}}{M^{m+}{}_{(aq.)}\,[A^{-}]^{m}{}_{(aq.)}\,L_{(aq)}} \tag{2}$$

$$K_D = [MLA_m]_{(org.)} / M^{m+}{}_{(aq.)} \tag{3}$$

$$Ext\ \% = 100\ x\ ([MLA_m]_{(org.)} / [M_0{}^{m+}]_{(aq.)}) \tag{4}$$

$$\Delta G^{\circ}{}_{Ext} = R\ x\ T\ x\ Ln(K_{Ext}) \tag{5}$$

$$S_f = (K_D)_{M1} / (K_D)_{M2} \tag{6}$$

In these equations, $M^{m+}{}_{(aq.)}$ represents the metal ion at equilibrium, m is the anion ion coefficient, $A^{-}{}_{(aq.)}$ represents the anion ion at equilibrium, $L_{(aq)}$ represents the ligand present in the aqueous phase at equilibrium, $MLA_{m}{}_{(org.)}$ represents the complex formed in the organic phase at equilibrium, $[M_0{}^{m+}]_{(aq.)}$ represents the initial concentration of the metal ion, K_D represents the ratio of the complex formed in the organic phase to the metal ion in the aqueous phase at equilibrium, *Ext %* is the extraction efficiency/percentage, $\Delta G^{\circ}{}_{Ext}$ is the free Gibbs energy of extraction (R: 8.314 kJ mol^{-1} K^{-1} and T: 298 K), and S_f shows the relative selectivity factor.

The negative sign of the free Gibbs energy of the extraction indicates that the extraction is voluntary [18,30].

2.3.2. Determining the relative selectivity factors (S_f).

The method described in the literature was used for competitive liquid-liquid extraction [16]. A salt mixture solution prepared in 1x10^{-4} M water and a solution of S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate ligand prepared in 1x10^{-4} M chloroform were used. 10 mL of the metal mixture solution and 10 mL of the ligand solution were mixed in a 50 mL plastic-capped Falcon tube. The mixture was shaken at a constant temperature of 25 °C at 200 rpm for 2 hours. After shaking, it was allowed to stand for 30 minutes to allow

the phases to separate and the solutions to reach equilibrium. The metal ion containing solutions were taken from the aqueous phase at the top and analyzed by ICP-OES.

ICP-OES analysis parameters: Plasma Aerosol Type: Wet, Source Equiliration Delay (sec): 5, Nebuliser Start-up: Instant, Plasma (L min^{-1}): 15, Plasma Conditions: Same For All Elements, Aux (L min^{-1}): 0.2, Nebuliser (L min^{-1}): 0.80, Power: 1300 W, View Dist.: 15.0, Plasma View: Axial, Sample Flow Rate (mL min^{-1}): 1.50. Standards: 1-2.5-5-10 ppm. Wavelengths (nm): Fe 238.204, Co 228.616, Cu 327.393, Zn 206.200, Cr 267.716, Mn 257.610. Correlation coefficients (R^2): Cu 0.999438, Co 0.998807, Fe 0.999424, Zn 0.999776, Cr 0.997066, Mn 0.998447.

2.3.2. Metal ion removal studies in real matrices

Lake, river, and spring water samples were collected, and initial concentrations were analyzed. 10 mL of the prepared ligand solution was mixed with 10 mL of surface water in a 50 mL plastic-capped Falcon tube. The mixture was shaken at a constant temperature of 25 °C at 200 rpm for 2 hours. After shaking, it was allowed to stand for 30 minutes to allow the phases to separate and the solutions to reach equilibrium. The aqueous phase was taken from the supernatant and analyzed using ICP-MS.

ICP-MS analysis method parameters are given in Table 1 and Table 2.

Table 1. ICP-MS method parameters.

Isotope	Mode	Dwell time [s]	No. of channels	Spacing	Resolution
52Cr	(KED)	0.01	1	0.1	Normal
55Mn	(KED)	0.01	1	0.1	Normal
57Fe	(KED)	0.01	1	0.1	Normal
59Co	(KED)	0.01	1	0.1	Normal
63Cu	(KED)	0.01	1	0.1	Normal
66Zn	(KED)	0.01	1	0.1	Normal
115In	(STD)	0.01	1	0.1	Normal

Table 2. ICP-MS method parameters-2.

No. of sweeps	Time per sweep [s]	Time per main run [s]	Order of modes
10	0.07	0.7	KED, STD

The parameters of the calibration graphs created for determining the concentrations of lake, river, and spring water samples to evaluate the removal performance of metal ions in real matrices are given in Table 3.

Table 3. ICP-MS method parameters-3.

Analyte	Equation	Correlation coefficients (R^2)	BEC*	LoD**
Cr	f(x) = 552.4862*x + 33408.0296	0.9249	60.469 ppb	0.619 ppb
Mn	f(x) = 1747.4782*x + 4460.8086	0.9994	2.553 ppb	0.396 ppb
Fe	f(x) = 31.0680*x + 4994.3462	0.9377	160.755 ppb	30.917 ppb
Co	f(x) = 947.5329*x + 493.3449	0.9976	0.269 ppb	0.521 ppb
Cu	f(x) = 597.1653*x + 4607.5279	0.9951	7.716 ppb	1.083 ppb
Zn	f(x) = 313.9315*x + 16457.5466	0.9851	52.424 ppb	6.011 ppb

* BEC, Background Equivalent Concentration ** LOD, limit of detection yani tespit limiti

2.4. Density Functional Theory (DFT)

The frontier molecular orbitals (HOMO-LUMO) and spherical reactivity descriptors were computed within the framework of Density Functional Theory (DFT) in order to clarify the reactivity, stability, and metal extraction mechanisms of the compound S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate [26,31–33]. The general applications and calculation methods of these theoretical parameters are as follows:

Frontier molecular orbital energies (E_{HOMO} and E_{LUMO}): Used to determine the basic electronic structure and the tendency of the molecule to donate/accept electrons [34]. Many other parameters are calculated through boundary molecular orbital energies. In this study, the HOMO and LUMO energies of the compound S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate were calculated in our previous study [35].

HOMO–LUMO energy gap (ΔE): Indicates the kinetic stability and chemical reactivity of the molecule. A large ΔE gap indicates high stability, while small gaps indicate that the molecule is easily polarized and more susceptible to chemical interactions (especially metal ion extraction) [32,36–39]**.**

Ionization energy (I) and electron affinity (A): According to the Koopmans approach, these are directly related to the boundary molecular orbital energies [40,41].

Chemical hardness (η) and spherical softness (σ): According to Pearson's Hard-Soft Acid-Base (HSAB) principle, hardness is the resistance of a species to charge transfer; softness is the opposite [19,36,42–44]. Chemical hardness is calculated using HOMO and LUMO energies according to the Koopmans approach [27,41,45].

Electronegativity (χ) and electronic chemical potential (μ): These parameters, defined by Parr and Pearson, are obtained by combining ionization energy and electron affinity (or FMO energies) [40,43,46].

Spherical electrophilic index (ω) and nucleophilic (ε): The electrophilic index, introduced to the literature by Parr, is calculated using chemical hardness and chemical potential [46]. These values determine the molecule's coordination tendency with metal ions, along with its nucleophilic character [32,43,45–47].

Dipole moment (D) and single point energy (SPE): These are key electronic structure findings that quantitatively support the stability analysis and polarity of the molecule [32,38,48].

3. Results and discussion

In this study, the removal of metals from Zn^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions using liquid-liquid extraction with S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate compound (in a chloroform:water (1:1) extraction system, at natural pH and 25°C) was investigated using competitive extraction. Furthermore, the method was applied to lake, stream, and tap water samples to study the removal of metal ions in real matrices. Table 4 shows the extraction characteristics of selected ions (Zn^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, and Cu^{2+}) with S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate compound in a chloroform:water (50%) medium. The data presented in the table are KExt, KD, Ext % and ΔG°Ext values were calculated using equations (2-5) obtained from equation (1). In the general evaluation of these data, it can be said that +3 valence ions were selectively extracted in relatively higher yields.

Extraction constant (K_{Ext}) is a thermodynamic parameter that indicates the tendency of a metal ion to pass from the aqueous phase to the organic phase and the stability of the complex it forms with the ligand [27]. A high K_{Ext} value indicates that the extraction is more efficient and the metal-ligand complex is more stable [27,30]. When the extraction constant (K_{Ext}) values (Table 4) are examined, it is seen that the Fe^{3+} ion has the highest value (1.47×10^{17}). This is followed by the +3 valence Cr^{3+} ion (1.06×10^{16}). In this case, it can be said that the applied compound forms highly selective and stable complexes with Fe^{3+} and Cr^{3+} ions. The extraction constants of Zn^{2+}, Mn^{2+} and Cu^{2+} ions of the remaining ions are close to each other and considerably higher than that of the Co^{2+} ion. Thus, the Co^{2+} ion exhibits the lowest K_{Ext} value and therefore the weakest interaction with the ligand.

Coefficient of distribution (K_D) and extraction percentage (Ext %) are key parameters used to evaluate the distribution behavior of metal ions between organic and aqueous phases in liquid-liquid extraction studies. These parameters provide important information about extraction efficiency and the selectivity of the ligand towards metal ions [30,49]. The coefficient of distribution (K_D) and extraction percentage (Ext %) results also support the extraction constant (K_{Ext}) results. According to the results in Table 4, the extraction percentage is ranked as follows: $Fe^{3+} > Zn^{2+} > Mn^{2+} > Cu^{2+} > Cr^{3+} > Co^{2+}$. The highest CD value was calculated as 0.790 for Fe^{3+} ion, and a corresponding extraction efficiency of 44.12% was obtained. This result shows that Fe^{3+} ion is transported most efficiently from the aqueous phase to the organic phase. Zn^{2+} ion ranked second with 37.59% extraction efficiency, while Mn^{2+} (25.22%), Cu^{2+} (23.79%), Cr^{3+} (18.11%) and Co^{2+} (13.94%) ions showed lower extraction performance.

The positive values of the standard Gibbs free energy change ($-\Delta G°_{Ext}$) for all ions indicate that the extraction process occurs spontaneously from a thermodynamic point of view [26]. The highest $-\Delta G°_{Ext}$ values were obtained for Fe^{3+} (2.34×10^4) and Cr^{3+} (2.18×10^4) ions. This supports the idea that these ions form relatively strong, spontaneous, and stable complexes with the ligand. The fact that the Co^{2+} ion has the lowest $-\Delta G°_{Ext}$ value indicates a lower extraction tendency. Overall, it can be said that the S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate ligand shows selectivity especially towards Fe^{3+} and Cr^{3+} ions. It is thought that the nitrogen and sulfur donor atoms in the ligand structure form stronger coordination interactions with trivalent ions that have a high charge density. Furthermore, the remarkable extraction of Zn^{2+} ions may be due to favorable coordination interactions between the ligand's soft donor atoms and Zn^{2+}.

Table 4. Extraction constants (K_{Ext}, K_D, Ext %, and $\Delta G°_{Ext}$) obtained for liquid-liquid extraction of a mixture of Zn^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions with the compound S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate (in chloroform:water (1:1) extraction system, at natural pH and 25 °C).

Ion	K_{ext}	K_D	Ext %	Ln (K_{Ext})	(-)ΔG_{ext}
Co^{2+}	$5.03\text{x}10^{11}$	16.2	13.94	26.9	$1.60\text{x}10^4$
Cr^{3+}	$1.06\text{x}10^{16}$	22.1	18.11	36.9	$2.18\text{x}10^4$
Cu^{2+}	$1.45\text{x}10^{12}$	31.2	23.79	28.0	$1.66\text{x}10^4$
Fe^{3+}	$1.47\text{x}10^{17}$	79.0	44.12	39.5	$2.34\text{x}10^4$
Mn^{2+}	$3.04\text{x}10^{12}$	33.7	25.22	28.7	$1.70\text{x}10^4$
Zn^{2+}	$3.84\text{x}10^{2}$	60.2	37.59	29.0	$1.72\text{x}10^4$

When the relative selectivity factors in Table 5 are examined, it is observed that the Fe^{3+} ion has high S_f values compared to all other ions and, therefore, can be selectively removed from the solution.

The relative selectivity factor (S_f) values given in Table 5 show the relative extraction selectivity of the S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate ligand towards metal ions. An S_f value greater than 1 (one) indicates that the relevant metal ion is extracted more selectively than the other ion; a value less than 1 (one) indicates lower selectivity [29]. It can be seen in Table 5 that the Fe^{3+} ion has the highest selectivity values towards all metal ions. In particular, the values of 4.87 for Fe^{3+}/Co^{2+}, 3.57 for Fe^{3+}/Cr^{3+} and 2.53 for Fe^{3+}/Cu^{2+} reveal that the ligand shows a significant selectivity towards the Fe^{3+} ion. This indicates that the Fe^{3+} ion forms a more stable complex with the ligand and is transported more effectively into the organic phase. The Zn^{2+} ion also gave S_f values above 1 (one) against many metal ions. In particular, the Zn^{2+}/Co^{2+} (3.72) and Zn^{2+}/Cr^{3+} (2.72) values show that the Zn^{2+} ion is also significantly preferred in extraction. Although the Mn^{2+} ion showed higher selectivity compared to Co^{2+}, Cr^{3+}, and Cu^{2+} ions, it exhibited lower selectivity towards the Fe^{3+} ion. The Co^{2+} ion gave Sf values below 1 in most comparisons and is considered one of the least preferred ions by the ligand. Similarly, the Cr^{3+} ion showed lower selectivity compared to Fe^{3+} and Zn^{2+} ions. Overall, the order of selectivity of the ligand towards metal ions can be said to be $Fe^{3+} > Zn^{2+} > Mn^{2+} > Cu^{2+} > Cr^{3+} > Co^{2+}$. These results show that the nitrogen and sulfur donor atoms in the ligand structure form strong coordination interactions, especially with the Fe^{3+} ion, which has a high charge density.

Table 5. Relative selectivity factors (S_f) obtained for liquid-liquid extraction of a mixture of Zn^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions with the compound S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate (in a chloroform:water (1:1) extraction system, at natural pH and 25°C).

	Co^{2+}	**Cr^{3+}**	**Cu^{2+}**	**Fe^{3+}**	**Mn^{2+}**	**Zn^{2+}**
Co^{2+}	-	0.73	0.52	0.21	0.48	0.27
Cr^{3+}	1.37	-	0.71	0.28	0.66	0.37
Cu^{2+}	1.93	1.41	-	0.40	0.93	0.52
Fe^{3+}	**4.87**	3.57	2.53	-	2.34	1.31
Mn^{2+}	2.08	1.53	1.08	0.43	-	0.56
Zn^{2+}	3.72	2.72	1.93	0.76	1.79	-

Finally, metal removal from Zn^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, and Cu^{2+} ions in lake, stream, and tap water samples was achieved using liquid-liquid extraction with the compound S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate (Table 6). The results show that the system exhibits a variable extraction performance depending on the matrix effect. Table 6 reveals that even though the water samples contained these ions at ppb levels, the compound S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate was able to remove between 1.9% and 99.4% of them.

The high removal rate (99.4%) achieved in the lake water sample, particularly for Zn^{2+} ions, reveals that the ligand exhibits a very strong selectivity towards Zn^{2+} ions. While 25.3% removal was achieved for Fe^{3+} ions, lower but still significant extraction values were obtained for Mn^{2+} and Co^{2+}. This indicates that the ligand is more effective against Zn^{2+} and, to some extent, Fe^{3+} ions in lake water. In the stream water sample, the

extraction percentages were generally lower compared to lake water. The highest removal rates were obtained for Co^{2+} (15.0%) and Fe^{3+} (9.5%), while more limited extraction occurred for other ions. This may be due to other ionic species or organic/inorganic components present in the stream water partially suppressing complexation with the ligand. In the tap water sample, the Mn^{2+} ion showed a remarkably high removal rate (76.4%). This result reveals that the ligand can exhibit a strong affinity for the Mn^{2+} ion under certain conditions. Lower removal rates were obtained for Fe^{3+} (21.7%), Zn^{2+} (10.7%), and other ions. This difference is due to ionic equilibrium and competitive complexation processes in the tap water.

Overall, the ligand's most significant efficacy in real water matrices was observed on Zn^{2+} and Fe^{3+} ions, but significant variations in selectivity and extraction yields occurred depending on the matrix type. This indicates that the ligand is a potential extraction agent for metal removal in environmental water samples, but matrix effects should be considered.

Table 6. Metal removal of Zn^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, Cu^{2+} ions in real matrices of lake, stream and tap water using liquid-liquid extraction (in chloroform:water (1:1) extraction system, at natural pH and 25°C) with S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate compound.

ID	**Cr^{3+}**	**Mn^{2+}**	**Fe^{3+}**	**Co^{2+}**	**Cu^{2+}**	**Zn^{2+}**
Lake (First) (ppb)	0.0	1.6	1022.2	0.7	0.0	1.4
Lake (After Ext.) (ppb)	0.0	1.5	763.1	0.4	0.0	0.0
Ext %	**-**	**1.9**	**25.3**	**38.2**		**99.4**
Stream (First) (ppb)	121.4	5.4	979.4	0.8	3.1	14.0
Lake (After Ext.) (ppb)	115.9	5.1	886.3	0.7	2.9	13.0
Ext %	**4.6**	**4.1**	**9.5**	**15.0**	**5.6**	**6.9**
Tap water (First) (ppb)	154.1	22.9	1268.2	1.3	3.8	43.6
Tap water (After Ext.) (ppb)	150.5	5.4	992.6	1.1	3.6	38.9
Ext %	**2.4**	**76.4**	**21.7**	**12.3**	**4.4**	**10.7**

When the competitive extraction and surface water metal removal studies were examined, it was determined that the synthesised S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate compound can be used in the detection and removal of Zn^{2+}, Mn^{2+}, Cr^{3+}, Co^{2+}, and Cu^{2+} ions, especially Fe^{3+} ions, from aqueous environments.

There is a significant correlation between the electronic structure of the synthesised ligand and its multi-ion (competitive) extraction performance, selectivity, and behaviour in real water samples (lake, stream, tap water) in the laboratory environment. The relatively low nucleophilic value (-0.094 eV) and high chemical hardness (η = 3.402 eV) in Table 7 indicate that the ligand may exhibit a selective tendency towards hard/medium-hard metal ions. The dipole moment of the molecule (2.583 D) supports the fact that it has a polarity suitable for interphase transfer and ion-pair formation. The relative selectivity matrix in Table 5 quantitatively reveals which ion the ligand clearly prefers over the other in the competitive environment. The selectivity of the ligand towards the Fe^{3+} ion is greater than one (1) towards all other ions. Specifically, the value of 4.87 obtained for the Fe^{3+}/Co^{2+} pair shows that the ligand can bind iron with high selectivity and attract it to the organic phase, even in the presence of cobalt. This supports the idea that the charge

density coordination and hardness parameters in theoretical calculations form more stable ion-pair/complex structures with the trivalent and high charge density Fe^{3+} ion.

Table 7. Calculated molecular descriptors of S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate.

Compound	Unit	S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate
$Energy_{LUMO}$	eV	-2.390 [35]
$Energy_{HOMO}$	eV	-9.194 [35]
HOMO-LUMO gap (ΔE)	eV	6.805
Ionization energy (I)	eV	9.194
Electron affinity (A)	eV	2.390
Electronegativity (χ)	eV	5.792
Chemical potential (μ)	eV	-5.792
Chemical hardness (η)	eV	3.402
Global softness (σ)	eV^{-1}	0.294
Electrophilicity (ω)	eV	4.930
Nucleophilicity (ε)	eV	-0.094
Dipole (D)	Debye	2.583
Single Point Energy(SPE)	eh	-3663.676
Single Point Energy(SPE)	eV	-99693.753

In this study, the competitive liquid-liquid extraction capability of the newly synthesized S,S'-di(2-pyridinyl)-2,2'-dithiodibenzothioate ligand in multiple ion environments and its metal removal performance in real water matrices (lake, stream, tap water) were comprehensively demonstrated experimentally and theoretically (DFT). The high HOMO-LUMO energy gap (ΔE = 6.805 eV) and chemical hardness (η = 3.402 eV) values obtained from quantum chemical calculations show that the ligand has high kinetic stability under varying conditions in the aqueous phase; while confirming at the molecular level why this structure forms the most stable and readily complexes (highest ΔE and values) with high charge density Fe^{3+} (hard acid) and Zn^{2+} ions in the boundary region, in accordance with Pearson's Hard-Soft Acid-Base (HSAB) principle. Even in a multi-ion pool, the ligand, which can attract the ΔE ion to the organic phase with a high relative selectivity against all other ions (Fe^{3+}/Co^{2+} = 4.87), stands out with the localized charge transfer ability of its nitrogen (N) and sulfur (S) donor atoms and the phase transfer advantage provided by its optimum dipole moment of 2.583 debye. In real field applications, its ability to completely remove trace amounts (1.4 ppb) of Zn^{2+} ions from lake water with an excellent efficiency of 99.4% and achieve a removal sensitivity of 76.4% against Mn^{2+} ions in tap water demonstrates that this hydrophobic macroheterocyclic structure has a high potential for applicability as a selective chelator/extractant in industrial wastewaters as well as in natural environmental matrices; In future studies, it is suggested that this potential be transferred to continuous flow Assisted Liquid Membrane (SLM) systems or Solid Phase Extraction (SPE) cartridges to optimize the regeneration and reusability parameters of the ligand.

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