



Removal of Cadmium From its Aqueous Solution by Benzoyl Thiourea Compounds as an Extractant

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Abstract

Benzoyl thiourea compounds (PBTU, MBTU) were used to remove the cadmium ion from its aqueous solution. The effect of benzoyl thiourea concentration and the initial concentration of cadmium ions on the removal process was examined at varied contact times, and temperatures ranging from 25 to 50 °C. Cadmium ions concentration was measured using an atomic absorption instrument. The distribution coefficients (KD), loading coefficients (Z), and extraction efficiency were determined using the experimental extraction findings (E %). The results showed that at 60 min, and 25 °C, the percentage of cadmium ion removal increased with the increase in the concentration of benzoyl thiourea compounds. The optimum efficiencies of MBTU and PBTU substances were 92.86 % and 98.21 % respectively. Density function theory (DFT) was used to study the interaction of cadmium ions with benzoyl thiourea compounds. Computational studies have shown that the donor atoms of the benzoyl thiourea are the oxygen and the sulfur atom.

Keywords: Heavy Metal, Cadmium, Benzoyl Thiourea, Liquid-Liquid Extraction, Distribution Coefficients (KD), Loading Coefficients (Z), Extraction Efficiency (%E).

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1. Introduction

The problem of environmental pollution is not a new or urgent problem for the earth, but what is new in it is the increase in the intensity of pollution in terms of quantity and quality in our present time. Heavy metal is any metallic element with a high relative density exceeding (5 g/cm^3). The World Health Organization (WHO) has placed cadmium, lead, mercury, and arsenic among the ten most dangerous substances for health in 2018, as they enter our bodies through drinking water and air. These metals are toxic and among the most dangerous pollutants of the aquatic environment as they can move through aquatic systems, either through physical processes or as a result of human activities such as industrial waste, electric power, and agricultural and household wastewater [1, 2]. These metals are considered among the most dangerous pollutants, as most of them have an accumulation characteristic, as they accumulate in the bodies of aquatic animals such as birds and reach humans by eating these foods [3]. Despite the presence of heavy metals in low concentrations, the concentrations of some of them may reach dangerous and toxic levels for living organisms in many environmental systems [1, 4].

So scientists have tried to find ways to purify the water and the environment from these heavy elements. There are many physical and chemical methods used to treat mine and industrial effluents containing heavy metals. These methods can be broadly divided into the following categories: chemical methods, ion exchange, solvent extraction, and adsorption techniques [5]. Liquid-liquid extraction is one of the most important of these techniques due to its high efficiency in this field, the simplicity of the technology used for this purpose compared to other methods, as well as its lower economic cost. Recently, many researchers tended to develop newly extracted materials. Liquid /liquid extraction from an aqueous medium is also applied using specific extractors to separate cadmium [5]. Reddy and colleagues [6] were able to use different solvents such as TOPS 99, Cyanex 923, Cyanex 272, Cyanex 302, and Cyanex 301, which are diluted in kerosene to remove cadmium from sulfate solutions. The extraction of cadmium and zinc from solutions of thiocyanate with diethyl hexyl sulfoxide in benzene has also been studied [7, 5]. Carboxylic acids have also been used to remove cadmium [5, 8]. In the case of solvent extraction, the contact time of the organic and aqueous phases is only a few minutes and this separation technique is further controlled by the efficient combined distribution of the effective separation. The high cost of solvents combined with solvent losses during continuous operations remains a costly issue, especially for water treatment.

The benzoyl thiourea can be considered as one of the important classes of substituted thiourea, where the benzoyl group is attached to one of the thioamide nitrogen atoms as in Figure 1 [9]. Interest in thiourea and its derivatives, in addition to its mineral complexes, can be explained by their wide applications [10, 11]. Each of its associated mineral complexes confers a wide range of biological activity, including antibacterial and antifungal properties [12-15], anti-tuberculosis [12], antithyroid [16], insecticidal [17],

and nematocidal activity [18]. The ligands of benzoyl thiourea and their mineral groups have been tested for antimalarial activity [19], anticancer agents [20, 21], heavy metal determination [22-24], and antioxidant activity [25].

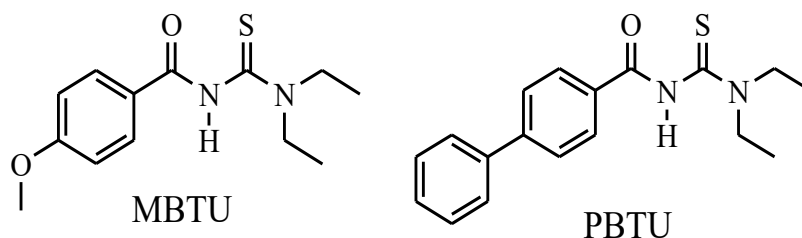


Figure 1: Chemical structure of used benzoyl thiourea compounds for cadmium extraction

Based on the properties of benzoyl thiourea compounds that made it among the most promising extracted materials in the field of water purification from heavy metals, this research aims to study the possibility of using benzoyl thiourea compounds, PBTU and MBTU, as an extracting material for removing cadmium from aqueous solutions, identifying the ideal conditions for this process (the change in the initial concentration of benzoyl thiourea and cadmium ion, as well as, studying the effect of time, and temperature on the extraction.

2. Theoretical Part

liquid-liquid Extraction is a chemical separation method that aims to remove or separate a certain substance from another substance that has been mixed [26]. It is described as the process of using a liquid solvent to remove a chemical from a mixture. This method, which depends on the solubility of materials in two immiscible solutions as water and organic nonpolar solvent, has shown to be particularly effective in recovering compounds from mixtures of materials. The distribution of components between two immiscible liquids is a factor that affects the extraction principle [15]. The extraction of cadmium ion with benzoyl thiourea (HL) can be described by the following reaction:



The distribution coefficient, (K_D), is the ratio between the concentration of a substance distributed between two immiscible solvents.

$$K_D = \frac{[\text{Cd}^{2+}]_{org}}{[\text{Cd}^{2+}]_{aq}} \quad (1)$$

Where $[\text{Cd}^{2+}]_{org}$ is the metal ion concentration in the organic layer and $[\text{Cd}^{2+}]_{aq}$ is the metal ion concentration in the aqueous layer. Removal percentage, ($E\%$), is the percentage of solute that moves from

one phase to another at equilibrium. It is expressed as the removal efficiency or removal percentage ($E\%$) as in the following equation:

$$E\% = \left(1 - \frac{[Cd^{2+}]_{aq}}{[Cd^{2+}]_{0,aq}} \right) \times 100 \quad (2)$$

Where $[Cd^{2+}]_{0,aq}$ is the initial concentration of cadmium ion in the aqueous layer.

Load capacity, (Z), is defined as the maximum concentration of solute that a solvent can be loading under specified conditions. The load capacity (Z) can be expressed by the equation next:

$$Z = \frac{[Cd^{2+}]_{org}}{[BTU]_0} \quad (3)$$

where $[BTU]_0$ is the primary concentration of benzoyl thiourea in the organic phase.

3. Methodology

3.1 Materials Used

The chemicals used are all of a high degree of purity, produced by well-known companies: Cadmium Chloride (100 % Laboratory Reagent), Toluene (99 %, PARK), N-diethyl amine (99 %, Merck), Ammonium Thiocyanate (99 %, R. Dehaen), 4-methoxybenzoyl chloride (99, Aldrich), Biphenyl-4-carbonyl chloride (97%, Aldrich), Acetone (99.8%, Carlo Erba), Methanol (99.8%, CARLO ERBA).

3.2 Instrumentation

Atomic absorption spectroscopy (Thermo Elemental). UV/V spectra were collected with a Shimadzu UV2450 spectrometer, FT-IR (Bruker model tensor 27, made in Borken, Germany), and recorded over the range of 400–4000 cm^{-1} .

3.3 Synthesis of Benzoyl Thiourea Compounds

The benzoyl thiourea compounds were prepared according to the method of Alabbassi [27-36]. The method of preparing the studied compounds is presented in Figure 2.

I) Synthesis of *1,1-diethyl-3-(4-methoxybenzoyl)thiourea* (MBTU): Yield 90%; mp 135°C; FT-IR (KBr, cm^{-1}): 1634 (C=O), 3300 (N-H). UV (DCM, λ_{max} (nm), $\epsilon \times 10^3$ (L mole $^{-1}$ cm^{-1}):251(21.666).

II) Synthesis of *1,1-diethyl-3-(4-phenylbenzoyl)thiourea* (PBTU); Yield (80%); mp 146°C, FT-IR (KBr, cm^{-1}): 1651 (C=O), 3266, 3229 (N-H). UV (DCM, λ_{max} (nm), $\epsilon \times 10^3$ (L mole $^{-1}$ cm^{-1}):281(14794).

3.4 Preparation of Standard Solutions

A solution of concentration (10 ppm) of cadmium chloride was prepared as a mother solution, by weight (0.005 g) and placed in a 500 ml standard flask, and completed the volume with deionized distilled water. A series of concentrations of (1, 2, 4, and 8 ppm) were prepared. The stock solution at a concentration of

1 mM of PBTU and MBTU was prepared by taking 0.0312g and 0.0266g, respectively, placing them in a 100 ml standard flask, and completing the volume with toluene up to the mark. The concentrations of 0.01, 0.02, 0.03 and 0.04 mM were prepared in 50 ml standard flasks.

3.5 Procedures for Removing Cadmium Ions from its Aqueous Solution

In tightly capped bottles, two equal volumes of the previously prepared organic and aqueous layers are taken in a 1:1 ratio. The organic layer (Org) consists of MBTU or PBTU solutions dissolved in toluene. The aqueous layer (aq) consists of aqueous solutions of cadmium ions with different concentrations. The bottles with the mixture are placed in a shaking water bath at a certain temperature. The bottles are shaken for the desired time, then the aqueous layer is separated from the organic layer using a separating funnel. They are placed in sealed bottles until the cadmium ion concentration in the aqueous layer is measured by an atomic absorption device (AA). To obtain the best conditions for the removal process, the effect of the initial concentration of cadmium ion and the initial concentration of benzoyl thiourea compounds, as well as the effect of temperature and time, were studied.

3.6 Computational Study of The Interaction Between Cadmium and Benzoyl Thiourea Compounds

The main objective of this work is to gain a better understanding of the molecular properties that determine the nature of the binding as well as the energies of the HOMO and non-LUMO bonding orbitals of the complexes using the theoretical density function DFT applied to the DMol3 program, where the molecular geometry, orbitals, and the total electronic structure of the complexes were calculated by performing partial structure optimization calculations using the BLYP (Becker-Lee-Yang-Parr) approximation (GGA) function with double-digit base plus polarization DNP.

4. Result and Discussion

4.1 Preparation and Characterization of Benzoyl Thiourea Compounds

Benzoyl thiourea compounds can be prepared through condensation reactions of benzoyl chloride (or its derivatives) with ammonium thiocyanate (first step). The product of benzoyl thiocyanate (or its derivatives) is condensed with secondary amine (second step). The reaction mechanism in the first step involves a nucleophilic attack on the carbonyl atom of benzoyl chloride by the electron pair of the nitrogen atom in the thiocyanate ion, while the second step involves a nucleophilic attack on the carbon atom of the isothiocyanate molecule by the secondary amine as in [Figure 2](#).

4.2 Cadmium Removal by Thiourea Compounds

The removal of cadmium from its aqueous solution by solvent extraction (liquid/liquid) has been studied. The cadmium was extracted using benzoyl thiourea compounds dissolved in the toluene solvent as an

extracting material. The effects of the initial concentration of cadmium ion as an extracting material, the effect of the concentration of benzoyl thiourea (MBTU and PBTU) compounds as an extractive material, the effect of temperature and the effect of contact time between the organic and aqueous layers during shaking were studied. These results were collected in [Table 1](#) for the two compounds MBTU and PBTU, respectively.

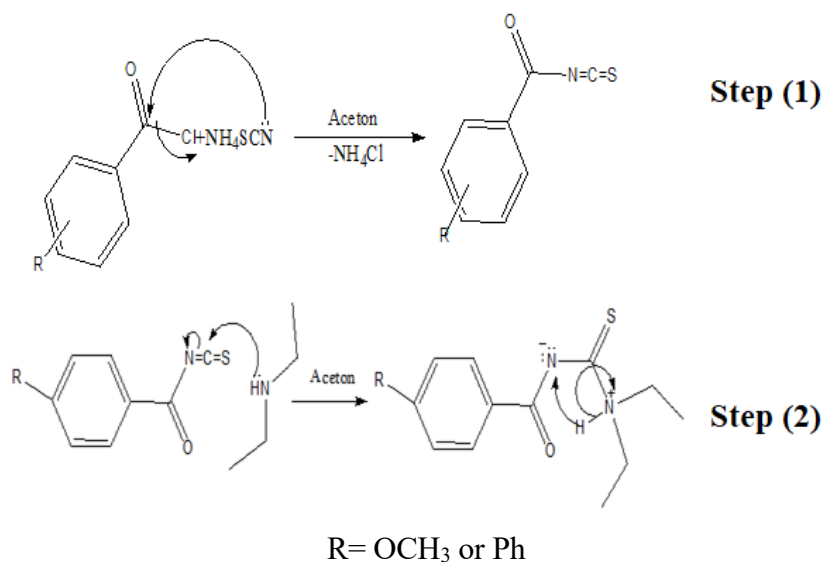


Figure 2: Reaction mechanism of the formation of the benzoyl thiourea compounds

The effect of MBTU and PBTU on the removal of cadmium from an aqueous solution was studied. In general, the results showed the effectiveness of these compounds in removing cadmium ions from their aqueous solution, as a good removal efficiency was obtained for the two substances, noting that (PBTU) gives better efficiency than (MBTU) as shown in [Figure 3](#) and [Table 1](#). The obtained results showed that the high E% values ranged from 75-89% for PBTU and between 64-74% for MBTU. Thus, the cadmium ion concentration in the aqueous layer was significantly reduced. The loading capacity indicates the ability of a certain weight (concentration) of the material used in the removal to load the largest amount of metal ion, the larger this number the small weight of the removed material (metal ion), the material is good for the removal process. We notice from [Table 1](#) that the loading capacity, Z, decreases as the concentration of MBTU or PBTU increases, the loading capacity ranges between 0.73 to 0.139 for MBTU and between 0.56 to 0.167 for PBTU.

[Table 1](#), noted that all values of the distribution coefficient, K_D , were greater than one, and this indicates the preference of the cadmium ion for the organic layer over the aqueous layer. The results showed that the efficiency of cadmium removal decreases with increasing time and that the quantitative transfer of cadmium occurs after 60 minutes where the maximum amount of metal ion was 92% and 98% when using MBTU and PBTU, respectively ([Figure 3C](#)). The removal efficiency generally decreases with

increasing temperature. At 25 °C, the efficiency reaches (92% and 98.21%) for MBTU and PBTU, respectively, which is the highest value and this indicates that benzoyl thiourea compounds have better efficiency at room temperature. It was also observed that the loading capacity decreases with the increasing temperature reaching (0.14 and 0.136) for MBTU and PBTU, respectively.

Table 1: liquid-liquid extraction of cadmium ion by MBTU and PBTU

BTU	T (°C)	t (min)	BUT (mM)	(Cd ⁺²) _{initial} (ppm)	(Cd ⁺²) _{aq} (ppm)	(Cd ⁺²) _{org} (ppm)	K _D	Z	E%
MBTU	40	60	0.01	2	0.7145	1.9355	2.709	0.73	64.27
	40	60	0.02	2	0.5455	1.4545	2.666	0.274	72.725
	40	60	0.03	2	0.5327	1.467	2.755	0.1834	73.265
	40	60	0.04	2	0.5233	1.477	2.82	0.139	73.835
	40	60	0.03	10	4.1672	5.8328	1.3997	0.7291	58.833
	40	60	0.03	8	2.986	5.014	1.679	0.627	62.68
	40	60	0.03	4	1.282	2.718	1	0.34	67.95
	40	60	0.03	2	0.5327	1.467	2.755	0.1834	73.265
	40	60	0.03	1	0.2359	0.7641	3.239	0.0955	76.41
	25	60	0.03	2	0.1428	1.857	13.006	0.232	92.86
	25	120	0.03	2	0.2421	1.7579	7.26	0.2197	87.895
	25	240	0.03	2	0.3171	1.6829	5.307	0.2104	81.415
	25	60	0.03	2	0.1428	1.8572	13.006	0.232	92.86
	40	60	0.03	2	0.5327	1.467	2.755	0.1834	73.265
	50	60	0.03	2	0.9137	1.0863	1.189	0.136	54.3
PBTU	40	60	0.01	2	0.51	1.49	2.92	0.56	74.5
	40	60	0.02	2	0.4156	1.5844	3.81	0.299	79.22
	40	60	0.03	2	0.365	1.635	4.479	0.204	82.2
	40	60	0.04	2	0.2291	1.7709	7.7298	0.167	88.55
	40	60	0.03	10	3.3774	6.6226	1.961	0.828	66.226
	40	60	0.03	8	2.04568	5.954	2.91	0.744	69.29
	40	60	0.03	4	0.858	3.142	3.662	0.39	78.55
	40	60	0.03	2	0.365	1.635	4.479	0.204	81.75
	40	60	0.03	1	0.1239	0.876	7.071	0.876	87.61
	25	60	0.03	2	0.0358	1.964	54.866	0.2455	98.21
	25	120	0.03	2	0.1552	1.8448	11.887	0.2306	92.24
	25	240	0.03	2	0.1981	1.8019	9.096	0.2252	90.095
	25	60	0.03	2	0.0358	1.964	54.866	0.2455	98.21
	40	60	0.03	2	0.365	1.635	4.479	0.204	81.75
	50	60	0.03	2	0.8488	1.1512	1.356	0.1439	57.56

4.2 Computational Study

Density function theory (DFT) was used as a basis for theoretical calculations to determine the donor atoms on benzoyl thiourea, the result clearly showed that the donor atoms are the oxygen atoms in the carbonyl group (C=O) and the sulfur atom in the thiol group (C=S). The energy gap ΔE (HOMO-LUMO) between the

HOMO and LUMO is an indicator of the reactivity of the benzoyl thiourea molecules. Based on the results recorded in Table 2, it can be said that the PBTU molecule is more effective than the MBTU molecule and this agrees with the results obtained, where the PBTU molecule showed relatively higher efficiency in removing Cadmium from MBTU, as shown in Figure (4).

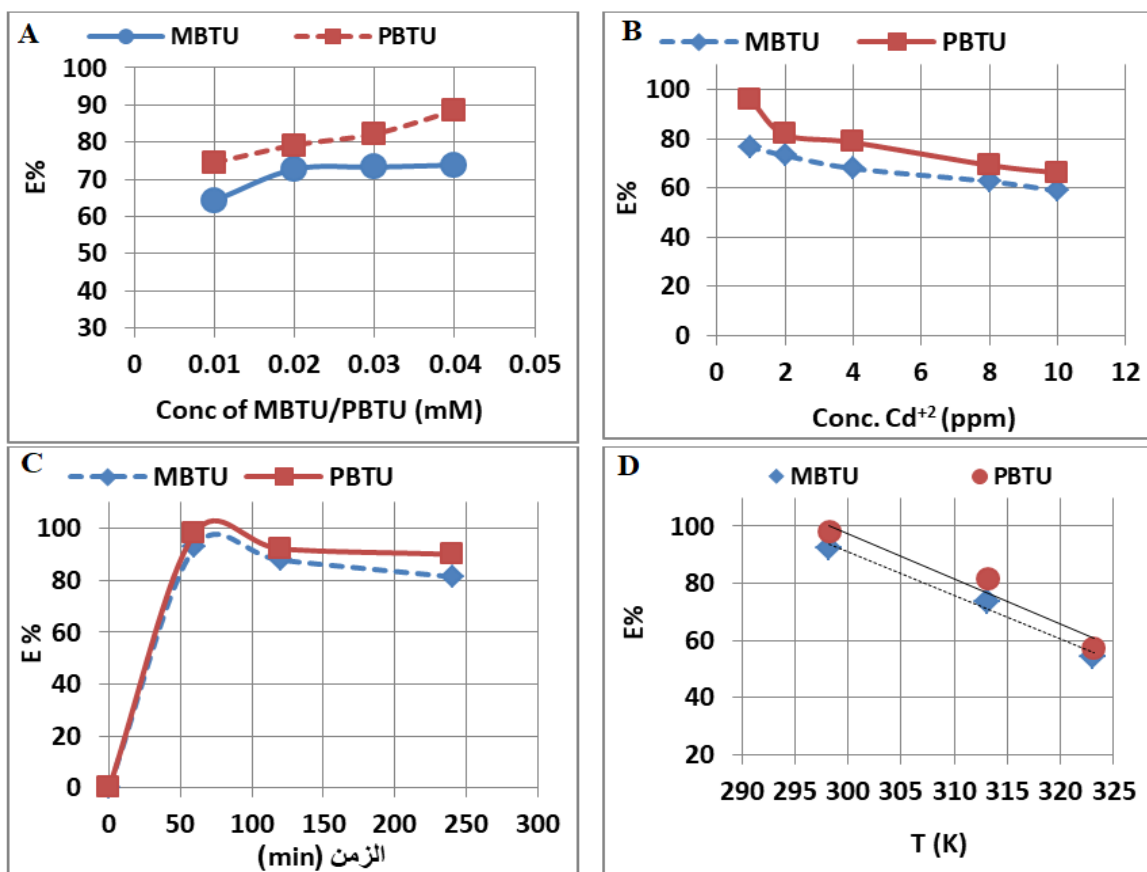


Figure 3: Cadmium removal under the effect of A) benzoyl thiourea concentration; B) cadmium ion initial concentration; C) time; D) temperature

Table 2: Energy values of the calculated orbitals of the benzoyl thiourea compounds and their complexes with cadmium(II)

Compound	HOMO (eV)	LUMO (eV)	$\Delta E_{LUMO-HOMO}$ (eV)	Binding Energy (kcal/mol)
MBTU	-5.070	-2.406	2.664	-3779.069
PBTU	-4.836	-2.740	2.096	-4646.004
[Cd(MBTU) ₂]	-4.736	-2.334	2.402	-7481.764
[Cd(PBTU) ₂]	-4.894	-2.574	2.32	-9196.268

The Binding Energy of cadmium complexes of benzoyl thiourea is an indicator of the stability of the complex. Based on the results recorded in Table (2), it can be said that the cadmium complexes are stable and are more stable than benzoyl thiourea before the reaction.

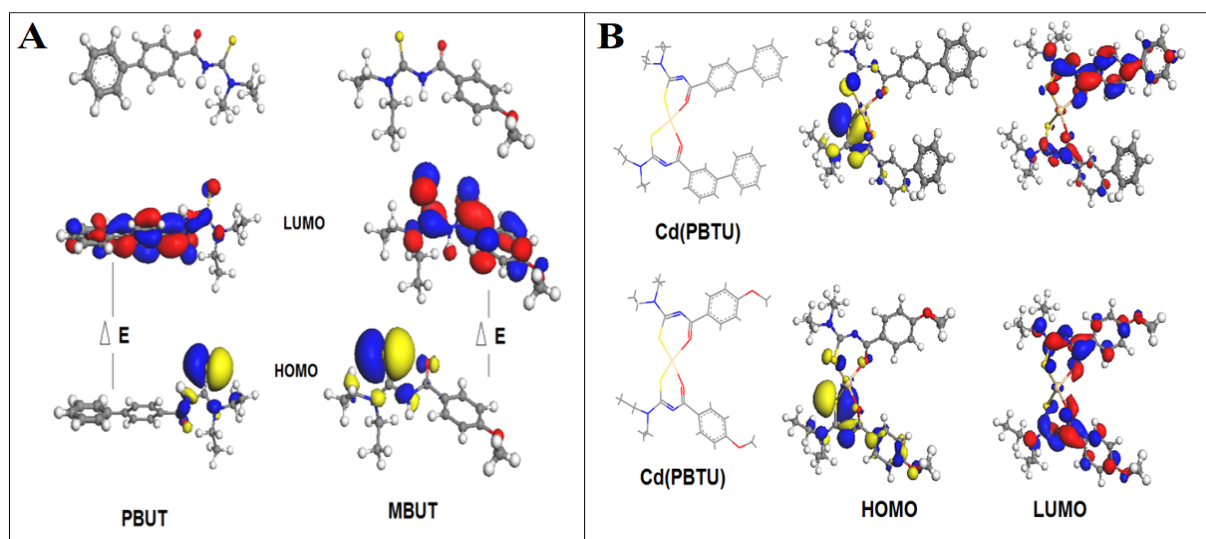


Figure 4: Geometries, HOMO and LUMO orbitals of A) MBTU & PBTU B) Cadmium-benzoyl thiourea complexes

Conclusion

In this research, the cadmium ion was successfully removed from its aqueous solution by liquid-liquid extraction using benzoyl thiourea (PBTU and MBTU) dissolved in toluene. The values of the distribution coefficients were also determined, and these values were greater than 1, which indicates that the cadmium ion distribution in the organic layer is higher than in the aqueous layer. The values of the distribution coefficient and removal efficiency increase with the increase in the concentration of each of the benzoyl thiourea compounds (MBTU and PBTU) and the cadmium ion concentration. It was also observed that the efficiency of PBTU material is better than that of MBTU material, due to the presence of the vinyl adsorbent group. The increase in contact time leads to a decrease in the removal efficiency, load capacity, and distribution coefficient. It was also observed that with increasing temperature the values of distribution coefficient and removal efficiency decreased, and the best conditions for removal are at 25°C. Computational studies have shown that the donor atoms of the bond (benzoyl thiourea) are both oxygen atoms in the carbonyl group (C=O) and a sulfur atom in the thiol group (C=S). The high value of the energy gap $\Delta E_{(HOMO-LUMO)}$ between the HOMO and LUMO energy levels of cadmium complexes with benzoyl thiourea bonds is an indication of the stability of these complexes.

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Conflict of Interest : The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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