Abstract—The environmental pollution by heavy metals became more problematic nowadays. To solve the problem of Cadmium accumulation in human organs which lead to dangerous effects on human health, and to determine its concentration, the organic legand 1-phenyl-3-benzoyl-2-thiourea was used to extract the cadmium ions from its solution. This legand as one of thiourea derivatives was successfully synthesized. The legand was characterized by NMR and CHN elemental analysis, and used to extract the cadmium from its solutions by formation of a stable complex at neutral pH. The complex was characterized by elemental analysis and melting point. The concentrations of cadmium ions before and after the extraction were determined by Atomic Absorption Spectrophotometer (AAS). The data show the percentage of the extract was more than 98.7% of the concentration of cadmium used in the study.

Keywords — Thiourea derivatives, cadmium extraction.

I. INTRODUCTION

UREA is the first organic compound that was synthesized in lab in 1928, which became the important synthesis step in the history of synthetically organic chemistry and played important physiological and biological roles in animal kingdom [1]-[3].

Thiourea is the analogue compound to urea with Replacement of oxygen atom in urea by sulphur atom, also thiourea have a considerably wide range of applications. The properties of urea and thiourea differ significantly because of the difference in electronegativity between sulfur and oxygen [4].

Thiourea compounds works as building blocks in the synthesis of heterocyclic compounds [5]. Substituted thioureas have recently gained much interest in the preparation of wide variety of biologically active compounds [6], [7].

Thioureas are important organic compounds: possess high biological activity, act as corrosion inhibitors and antioxidant, and are polymer component [8]. Thiourea and urea derivatives show a broad spectrum of biological activities as anti-HIV, antiviral, HDL-elevating, antibacterial and analgesic properties [9]-[12]. Acyl thiourea derivatives are well known for wide range of biological activities like bactericidal, fungicidal, herbicidal, insecticidal action and regulating activity for plant growth [13], [14].

The synthesis of the thiourea derivatives can be easily done with good yield [15]. Thiourea and its derivatives represent well-known important group of organic compounds due to the diverse application in fields such as medicine, agriculture, coordination, and analytical chemistry [16]. On the other hand, some thiourea derivatives have been used in commercial fungicides [17]. They are also can be used as selective analytical reagents, especially for the determination of metals in complex interfering materials [18]-[20].

As one of important thiourea derivatives is benzoyl thiourea compounds which have a wide range of biological activities including antiviral [21], antibacterial [22], [23], antifungal [24], antitubercular [25], [26], herbicidal [27], insecticidal [28], and pharmacological properties [29] and acting as chelating agents [30], [31].

In addition, benzoyl thiourea derivatives were often used in analytical and biological applications [32]. The compounds of N-benzoyl-N'-alkylthiourea and N-benzoyl-N,N'-dialkylthiourea have recently attracted interest in view of the potential use of these compounds as highly selective reagents for the concentration and separation of metal cations [33]. One specific use for these substances is the coordination of harmful compounds, which can be achieved in the organism by one or several ligands of adequate structure. The metal complexes of thiourea are neutral and their colors vary with the nature of the metal ions. These chelating agents have been remarkable ones for analytical chemistry [34].

Thiourea derivatives and their transition metal complexes have been known since the beginning of the 20th century [32]. Also these complexes display a wide range of biological activity including antibacterial, antifungal properties [35], [36]. Metal complexes of ligands containing sulfur as donor atoms are known to possess antifungal and antibacterial activities [20]. Thiourea and its derivatives coordinate to several transition metal ions to form stable complexes. Thiourea is versatile ligands, able to coordinate to metal centres either as neutral ligands, monoanions, or dianions [37], [38].

The complex with thiourea derivatives which has biological activity has been successfully screened for various biological actions: antidepressant, anticonvulsant, anthelmintic, antihistaminic, anesthetic, antitussive, analgesic etc. [39].

II. RESULTS AND DISCUSSION

Benzoyl isothiocyanate was produced by the reaction of benzoyl chloride with an equal molar amount of potassium thiocyanate in dry benzene. 1-phenyl -3-benzoyl-2- thiourea (PhBTU) was synthesized from benzoyl isothiocyanate and aniline in dry benzene. Fig. 2 outlines the synthesis of thiourea derivatives. The ligand (PhBTU) were purified by

Abdulfattah M. Alkherraz and Zaineb I. Lusta are with the Misurata University, Faculty of Education, Department of Chemistry, Misurata, Libya (e-mail: abdo_7979355176@yahoo.co.uk).

Ahmed E. Zubi is with the Misurata University, Faculty of Science, Department of Chemistry, Misurata, Libya.
recrystallization from ethanol and obtained in 75% yield. The synthesized compound structure was confirmed by Melting point, H-NMR spectra, FT-IR spectra, and elemental analysis data.

The presence of a benzoyl group in this thiourea derivative permits the coordination of cadmium ions to form stable neutral complex.

The extraction of cadmium ions from its solution was done using 1-phenyl -3-benzoyl-2- thiourea (PhBTU). During the extraction at neutral pH, the ligand (PhBTU) will react with cadmium ions in ratio of 1:2 to form a yellow complex. Complex structure was shown in Fig. 1 [40], and the data of the extraction process were shows in Table I below.

![Fig. 1 Cadmium Complex Structure](image)

From the table, it can be seen that the concentration of cadmium ions after extraction were less than instrument sensitivity for all concentration except that with very high concentration (55.828 ppm) which has extraction percentage about 98.7%. The results show high with confidence the ability of present ligand to be used to extract cadmium from its solution.

Table I shows the mean of cadmium concentration before and after extraction and the standard deviations (the value were obtained from three experiments).

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Cd(^{2+}) before extraction (ppm)</th>
<th>Cd(^{2+}) after extraction (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55.00±:0.193</td>
<td>0.72±:0.711</td>
</tr>
<tr>
<td>2</td>
<td>5.60±:0.026</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>3</td>
<td>3.35±:5.7 x10(^{-4})</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>4</td>
<td>2.80±:5.7 x10(^{-3})</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>5</td>
<td>1.67±:0.029</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>6</td>
<td>1.10±:7.0 x10(^{-3})</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>7</td>
<td>0.55±:9.5 x10(^{-4})</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

The instrument sensitivity limit is 0.01

### III. EXPERIMENTAL

#### A. Chemicals and Standard Solutions

All the chemicals and solvents used for the synthesis of these compounds were purchased from Aldrich and Merck and used without further purification. Double-distilled deionized water was used throughout the experiments.

The following compounds were synthesized according to Fig. 2 given below the benzoyl thiourea derivative was prepared by a similar procedure that was reported in the literature [32]. The benzoyl thiourea derives were purified by recrystallization from ethanol. The synthesized compounds were characterized by elemental analysis which was done by using carbon and nitrogen analyzers, Melting points were determined in Gallenkamp Hot stage. The IR spectral study of the synthesized compounds was done by using infra-red spectrophotometer (Bruker, ISS 25), KBr disc method was used. The NMR spectral study was performed on NMR spectrometer 300 MHz. The cadmium concentrations before and after extraction were determined by atomic absorption spectrometer 300 MHz. The cadmium concentrations before and after extraction were determined by atomic absorption spectrometer 300 MHz.

#### B. Preparation of Benzoyl Isothiocyanate

A solution of benzoyl chloride (0.5mol, 69.25g) in dry benzene (30ml) was added drop wise to a solution of potassium thiocyanate (0.5mol, 48.5g) in dry benzene (30ml). The reaction mixture was heated (120°C) under reflux for 12h and then cooled to room temperature. The resulting solid was filtered; the solvent was evaporated under high pressure to obtain benzoyl isothiocyanate as heavy oil (130g, 80% yield).

#### C. Preparation of 1-Phenyl-3-Benzoyl-2-Thiourea (PhBTU)

Aniline (0.1mol, 9.3g) was added dropwise with stirring to the solution of benzoyl isothiocyanate (0.1mol, 16.3g) in dry benzene (30ml). The reaction mixture was heated under reflux for 1h and then cooled in ice bath. A solid compound precipitated which filtered, washed with cold benzene. The resulting white solid product 1-phenyl -3-benzoyl-2- thiourea was recrystallized from ethanol and dried in vacuo (75% yield), (dried sample): m.p.143-144°C, Anal. Calcd. For C14H12N2OS (%): C, 65.61; H, 4.72; N, 9.68. 1H NMR: (300 MHz, DMSO): 4.0 ν(C=O), 1628-1501 ν(C=S), 800-770 ν(C=S).
D. Preparation of Standard Solution of Cadmium  
To prepare a stock solution of cadmium ions (55.82 ppm), 55.00g of cadmium chlorided (CdCl₂.H₂O) was transferred to 1L volumetric flask and dissolved in deionized water. A series of different concentrations of cadmium ion (0.55, 1.10, 1.67, 2.80, 3.35, 5.60 ppm) were prepared by dilution of the solution with deionized water.

E. Extraction of Cadmium by 1-Phenyl-3-Benzoyl-2-Thiourea (PhBTU)  
In ratio of 2:1 a solution of 1-phenyl -3-benzoyl-2-thiourea in hot ethanol was added to 25ml standard solution of cadmium ions (Cd²⁺). The mixture was heated at 100°C under reflux for 1h and then cooled to room temperature. The resulting yellow solid product (cadmium complex) was filtered. The filterer solution was used to determine cadmium concentration by using atomic absorption spectrophotometer model Hitachi 30 – 180.

IV. CONCLUSIONS  
Biological importance of thiourea is well known as mentioned earlier under the review of literature. This prompted us to synthesize thiourea derivatives. The synthesis of the proposed thiourea was successfully done.

From the extraction data it can be conclude that, the ligand 1-phenyl -3-benzoyl-2-thiourea has high ability to bond and extract cadmium ions from its solution, that mean it can be used in precipitate, determine, separate and extract the cadmium ions from low concentration solutions, and can be used for concentrated cadmium solutions by repeating the extraction process.

ACKNOWLEDGMENTS  
We would like to thank all the stuff of faculty of Education Misurata University especially for Dr Almahdi Amer for kindly support, also thanks goes to advanced chemicals analysis laboratory in Tripoli and we would like to thank Mr. Mohamed Albaour from the chemical laboratory in Libyan iron and steel company.

REFERENCES  

World Academy of Science, Engineering and Technology  
International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering Vol:8, No:2, 2014