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B. Houari, S. Louhibi, K. Tizaoui, L. Boukli-Hacene, B. Benguella, et al.. New synthetic material removing heavy metals from aqueous solutions and wastewater. *Arabian Journal of Chemistry*, 2019, 12 (8), pp.5040-5048. 10.1016/j.arabjc.2016.11.010 . hal-02443571

**HAL Id: hal-02443571**

**<https://hal.science/hal-02443571>**

Submitted on 9 Jul 2020

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## ORIGINAL ARTICLE

# New synthetic material removing heavy metals from aqueous solutions and wastewater



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Received 17 September 2016; accepted 18 November 2016

Available online 28 November 2016

## KEYWORDS

Synthesis ligand;  
Crystal structure;  
Adsorption;  
Wastewater;  
Metal

**Abstract** (E)-2-[(1H-Imidazol-4-yl)methylidene]-Hydrazinecarbothioamide ligand (EIMH) was investigated to remove heavy metal ions from wastewater. Thus, the present study leads to the adsorption/complexation of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  in aqueous solution on EIMH under various conditions such as contact time, temperature, and pH. The EIMH ligand was characterized using FTIR and X-ray diffraction. The metal ion concentration in the aqueous samples was analyzed by atomic absorption spectrophotometer. The uptake is rapid with maximum adsorption being observed within 10 min for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$ . Results obtained revealed that 99.80% of lead, 99.25% of copper and 98.68% of cadmium were removed at pH 2–8. The calculated thermodynamic parameters indicate that the adsorption of heavy metals onto EIMH is physical in nature. Finally, EIMH is able to remove the three heavy metals to a concentration less than 0.5 ppm from wastewater and with an efficiency of 96.81% for lead, 99.44% for copper and 97.76% for cadmium. © 2016 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Water is so easily polluted, for it fosters many chemical reactions. Water carries heavy metals, and inserts them into the food chain (algae, fish, etc.). Although heavy metals are usually present in trace, they are nevertheless very dangerous, since their toxicity grows and their nature is non-degradable (Jiang et al., 2010). The industry has

often favored sites near streams to facilitate the transportation of raw materials, thereby favoring the discharge of industrial effluents accidental or not. Many methods have been developed and extensively studied to remove these toxic metals and wastewater (Benguella, 2011), using physical treatment such as ion exchange, solvent extraction, reverse osmosis and adsorption (Babel and Kurniawan, 2003; Puanngam and Unob, 2008) and chemical processing such as adsorption and complexation (Cervera et al., 2003; Lorens et al., 2004).

Chemical precipitation however is not very suitable when the pollutants are present in trace amounts as amount of sludge is produced. Solvent extraction or electrolytic processes are also available but they are considered to be effective only for more concentrated solutions (Wan Ngah and Hanafiah, 2008). To improve the possibilities of recovery and removal of pollutants, few studies have focused on the use of synthetic ligands as de-polluting heavy metals. Some synthetic macroligands are able to be complex with heavy metal ions (Cervera et al.,

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2003; Lorens et al., 2004). Another group of synthetic macroligands are carboxyl methyl cellulose (Petrov and Nenov, 2004), diethylamino ethyl cellulose (Trivunac and Stevanovic, 2006), polyvinyl ethylene imine (Canizares et al., 2002), polyvinyl alcohol (Vieira et al., 2001), polyacrylic acid and polyethylene glycol (Zhang and Xu, 2003; Borbely and Nagy, 2009).

While all the above synthetic decontaminants were polymers, no monomer was used as adsorbent with a high efficiency for water decontamination of heavy metals.

The aim of our work was to test the water decontamination by complexation and/or adsorption of heavy metals using a synthetic organic ligand of pharmacological interest. Its active sites are identified by X-ray diffraction as a derivative of thiosemicarbazone.

Thiosemicarbazones represent an important class of pharmaceutical compounds with antimicrobial (Rodriguez-Argüelles et al., 2010), anti-inflammatory (Chih-Hua et al., 2009), anti-tuberculosis (Farrel, 2002) and antihypertensive (Navarrete-Vazquez et al., 2010) activities. The ability of thiosemicarbazone molecules to chelate with traces of metals in the biological system is believed to be a reason for their activity. By coordination, the lipophilicity, which controls the rate of entry into the cell, is modified, and some side effect may be decreased (Beraldo and Gambino, 2004).

The present work mainly focuses on the separation of tree heavy metal ions,  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$ , using (E)-2-[(1H-Imidazol-4-yl)methylidene]-Hydrazinecarbothioamide ligand (EIMH) as complexing and/or adsorbent agent depending on the pH.

## 2. Materials and methods

The ligand used in our work (EIMH) **1**, was synthesized from the thiosemicarbazide. It was characterized by IR and X-ray diffraction methods. The ligand regenerated **2** and the copper complex obtained by removing from wastewater **3**, were characterized by X-ray diffraction.

IR spectra were measured in the 400–4000  $cm^{-1}$  range on a 9800 FTIR spectrometer (Perkin–Elmer). The X-ray data for compounds **1**, **2** and **3** were collected on a Bruker APEX2 diffractometer using Mo  $K\alpha$  radiation (0.71073 Å). Cadmium, copper and lead ion sorption capacities were measured using a Perkin-Elmer Model 2280 atomic absorption spectrophotometer.  $Cu(NO_3)_2 \cdot H_2O$ ;  $Cd(NO_3)_2 \cdot 4H_2O$ ;  $Pb(NO_3)_2$  (Aldrich) were used as purchased. High-grade solvents (ethanol, sulfuric acid) were used for the synthesis of the EIMH ligand without further purification.

### 2.1. Synthesis of (E)-2-[(1H-Imidazol-4-yl)methylidene]-Hydrazinecarbothioamide: EIMH **1**

An equimolar amount of thiosemicarbazide 10 mmol (0.91 g) and imidazolecarboxaldehyde 10 mmol (0.96 g) was dissolved in a mixture of ethanol and water (30 ml, 50%) and refluxed for 5 h in the presence of a catalytic amount of sulfuric acid. Yellow crystals suitable for X-ray analysis were obtained after slow evaporation of the solution.

### 2.2. Metal removal kinetics

The initial metal solution concentration was 100 mg/L for all experiments. For metal-removal kinetics studies, 91 mg of EIMH was introduced in a 27 mL of metal solutions in a beaker agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature of 25 °C. In all cases, the

pH of the solution is monitored continuously using a pH meter. At appropriate time intervals, stirring was briefly interrupted while 1 mL samples of supernatant solution after decantation were pipetted from the reactor and were analyzed to determine the residual metal concentration in the aqueous solution. The metal uptake  $qt$  (mg ion metal/g EIMH) was determined as follows:

$$q_t = \frac{(C_o - C_t) \times V}{m}$$

where  $C_o$  and  $C_t$  are the initial and final metal ion concentrations (mg/L), respectively,  $V$  is the volume of solution (mL), and  $m$  is the ligand weight (g) used.

The adsorption rate constant is derived from the model established by Lagergren (1898) and developed by Ho and Kay (2000). In general, adsorption is accompanied by a thermal process that can be either exothermic  $\Delta H < 0$  or endothermic  $\Delta H > 0$ . The measurement of the heat of  $\Delta H$  is the main criterion that differentiates chemisorption from physisorption. The heat of adsorption is given by the Gibbs–Helmholtz relationship (Ramesh et al., 2005).

$$\Delta G = -RT \ln K_C; \quad \Delta G = \Delta H - T\Delta S;$$

$$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{and} \quad K_C = \frac{C_e}{C_o - C_e}$$

where  $K_C$  is the equilibrium constant,  $\Delta G$  the Gibbs free energy (joule/mol),  $\Delta H$  the enthalpy (joule/mol),  $\Delta S$  the entropy (joule/mol/K),  $T$  the absolute temperature (K),  $C_o$  and  $C_e$  the initial and equilibrium concentration of adsorbate and  $R$  the gas constant (8314 J/mol K).

### 2.3. X-ray crystallography

The structure was solved by direct method and refined in anisotropic approximation for nonhydrogen atoms with crystallographic package programs: Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SIR97 (Altomare et al., 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1999). H atoms bonded to C atoms were placed in calculated positions with C–H = 0.95 Å and refined in a riding-model approximation with  $U_{iso}(H) = 1.2U_{eq}(C)$ .

## 3. Results and discussion

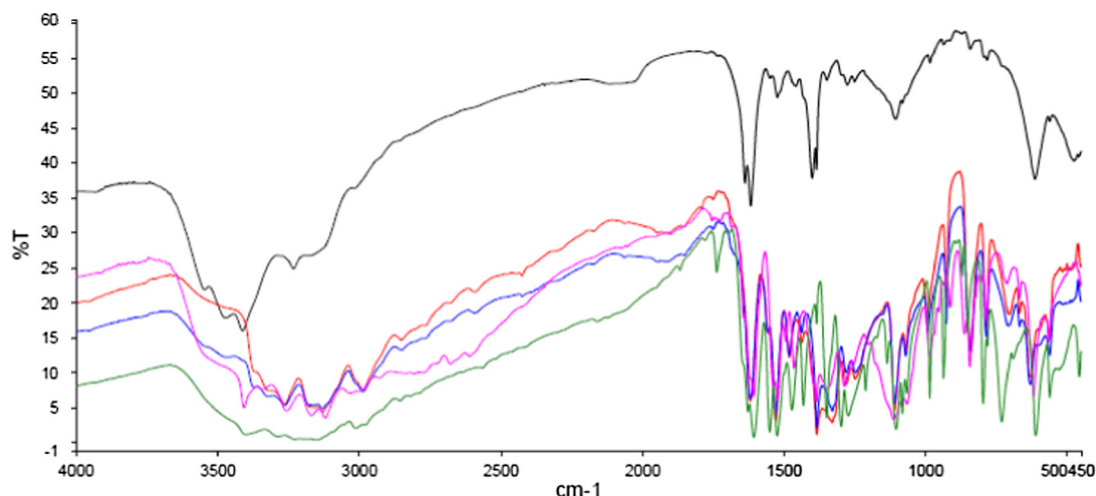
### 3.1. EIMH characterization

#### 3.1.1. FTIR analysis of EIMH ligand

The assignments of IR spectral bands most useful in establishing the structural identity of the ligand **1**, are listed in Table 1. The bands observed in the range 1115  $cm^{-1}$  and those in the range 783  $cm^{-1}$  are assigned to  $\delta(C=S)$  (Pal et al., 2002). The  $\nu(N-H)$  band is present at 3177  $cm^{-1}$ , indicating that the ligand remains in the thione form in the solid state (Bell et al., 1986). The bands corresponding to symmetric and asymmetric  $\nu(NH_2)$  appear at 3367 and 3219  $cm^{-1}$  respectively [Akinchan et al., 1996]. The azomethine and imidazolic bands  $\nu(C=N)$  appear at 1616  $cm^{-1}$ , in agreement with the literature (Bell et al., 1986).

**Table 1** FTIR characteristic peaks of EIMH before and after  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ( $\text{cm}^{-1}$ ) adsorption/complexation.

Assignment	$\sqrt{(\text{NH}_2)}$	$\sqrt{(\text{NH})}$	$\sqrt{/\delta} (\text{C}=\text{S})$	$\sqrt{(\text{C}=\text{N})}$	$\sqrt{(\text{N}-\text{N})}$	$\sqrt{(\text{C}=\text{N})}_{\text{imidazole}}$	$\sqrt{(\text{S}=\text{O})}$	$\sqrt{(\text{M}-\text{N})}$
Before	3367a/3219s	3177	1115/783	1511	972	1615	1110	
After/pH = 2	3368a/3266s	3178	1104/782	1511	972	1615,95	1384	
After/pH = 3	3342a/3264s	3130	1108/783	1529	990	1620	1384	
After/pH = 5	3344a/3264s	3133	1110/784	1529	992	1620	1384	
After/pH = 8	3474a/3414s	3133	1105/781	1523	983	1617	1385	474

**Fig. 1** FTIR spectra of EIMH: (green) before metal removal, (pink) after metal removal pH = 2; (blue) pH = 3; (orange) pH = 5; (black) pH = 8.

Moreover, the band appearing around  $1115\text{ cm}^{-1}$  in the spectrum of the ligand is assigned to  $\nu(\text{S}=\text{O})$  vibrations, for the crystallization solvent (Bell et al., 1986). This is supported by the crystal structure of EIMH (Fig. 1). The characteristic hydrated sulfate band appears on the spectrum of the ligand at  $1100\text{ cm}^{-1}$ , masked by the thione. After evaporation of solvent, this band moves to  $1380\text{ cm}^{-1}$  (Lynch, 2001).

In order to determine the functional groups involved in cadmium, copper and lead sorption onto EIMH, superposed FTIR spectra were compared (Fig. 1). The FTIR data for the used EIMH show that some peaks such as azomethine and thione groups are either weakened or shifted after removal of metals (Table 1). In the range pH 2–7, Fig. 2 shows a slight displacement of these absorption bands indicating metals adsorption. However at pH = 8, the symmetrical and asymmetrical stretching modes  $\nu(\text{NH}_2)$  as well as the azomethine and thione bands, undergo appreciable change in these spectra (Table 1). This indicates the coordination of these functions to the central metal atoms. This coordination is confirmed by the presence of a new band at  $473\text{ cm}^{-1}$ , which is assigned to  $\nu(\text{M}-\text{N})$  in complexes (Ackerman et al., 1999; Jouad et al., 2001).

### 3.1.2. X-rays analysis of EIMH ligand before (1) and after use (2)

Crystal data, data collection and structure refinement details for EIMH before and after use and EIMH Cu complex, are

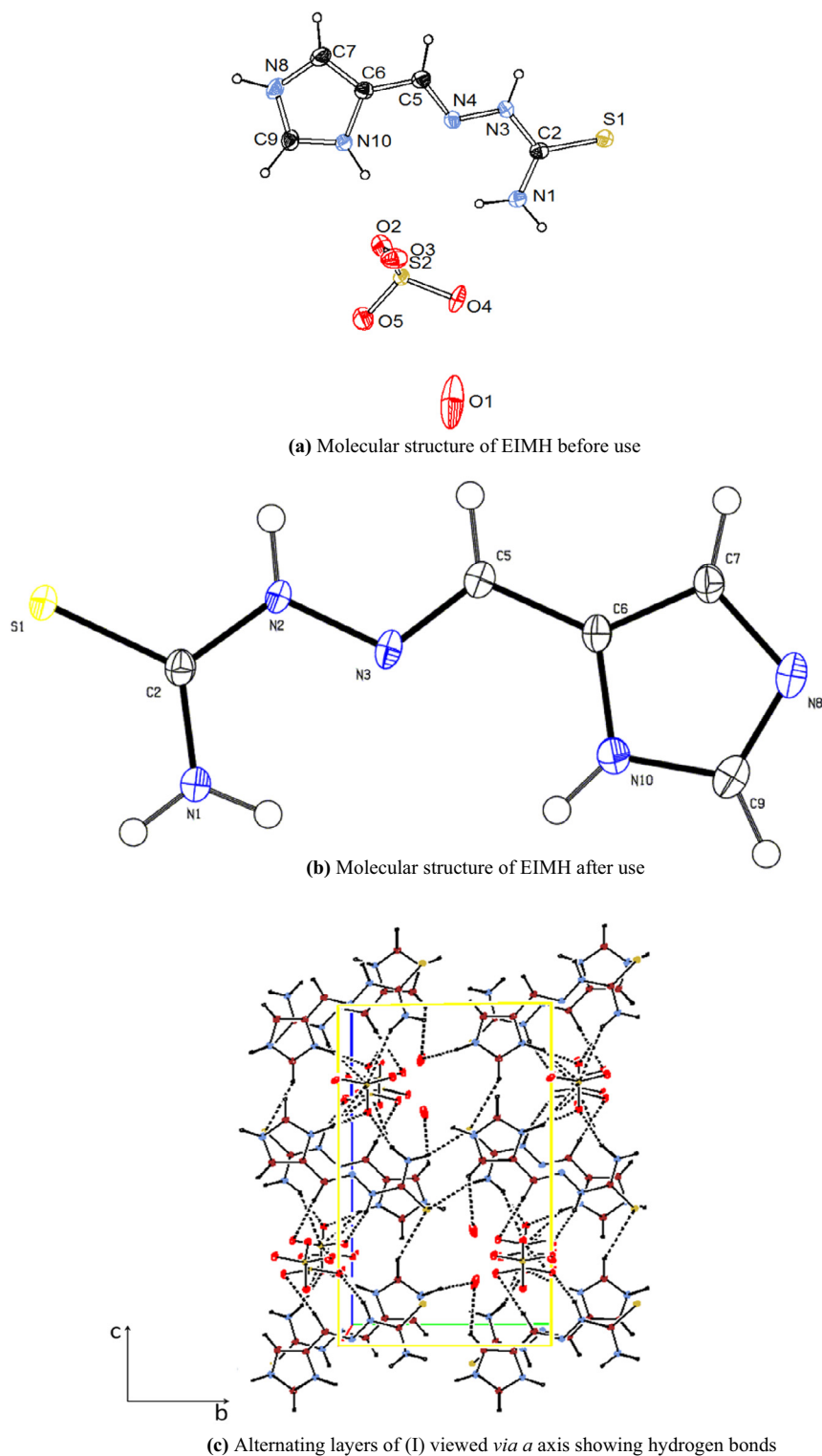
summarized in Table 2. Selected bond distances, bond angles, and torsion angles are given in Table 2.

As part of our study of thiosemicarbazone derivatives, we report herein the crystal structure of EIMH. The molecular structure of EIMH before and after use is shown in Fig. 2(a and b) respectively. The molecule 1 or 2, is approximately planar and the maximum deviation from the least squares plane through the 11 non-hydrogen atoms is  $0.0343(29)\text{ \AA}$  for the carbon C5 atom. The bond angles suggest  $\text{sp}^2$  hybridization for the C and N atoms which contributes to the planarity of the molecule. Most of nitrogen atoms are involved in hydrogen bonds as donors ( $\text{N}-\text{H}\cdots\text{S}$  for 1, 2 and  $\text{N}-\text{H}\cdots\text{O}$  for 1) forming a three dimensional network (Fig. 2c).

In contrast to our previous article (Houari et al., 2013), the entity thiosemicarbazone was protonated (imidazole N10 nitrogen) in the presence of sulfuric acid. The cationic entity (2a) crystallized with a water molecule and a disordered solvent molecule. After removal of metals, EIMH crystallizes without solvent (Fig. 2-b).

### 3.1.3. X-ray analysis of aqua copper complex

After wastewater treatment by the ligand EIMH, the Hexa-aquacopper (II) complex (3) crystallizes in ionic form. This molecule has an octahedral geometry formed by the copper (II) ion and six  $\text{H}_2\text{O}$  ligands in a square-bipyramidal configuration. The overall charge of the complex is neutralized by the presence of perchlorate ions (Fig. 3).



**Fig. 2** Molecular structure of EIMH (a) before use, (b) after use, (c) alternating layers viewed via *a* axis showing hydrogen bonds.

### 3.2. Kinetics of heavy metals removal on EIMH

Kinetic experiments were carried out to evaluate the potential of the EIMH for heavy metal removal. Different parameters related to the adsorbent, the metal and the medium can influence the kinetics of cadmium, copper and lead removal by EIMH (Benguella, 2011). In this context, the influence of var-

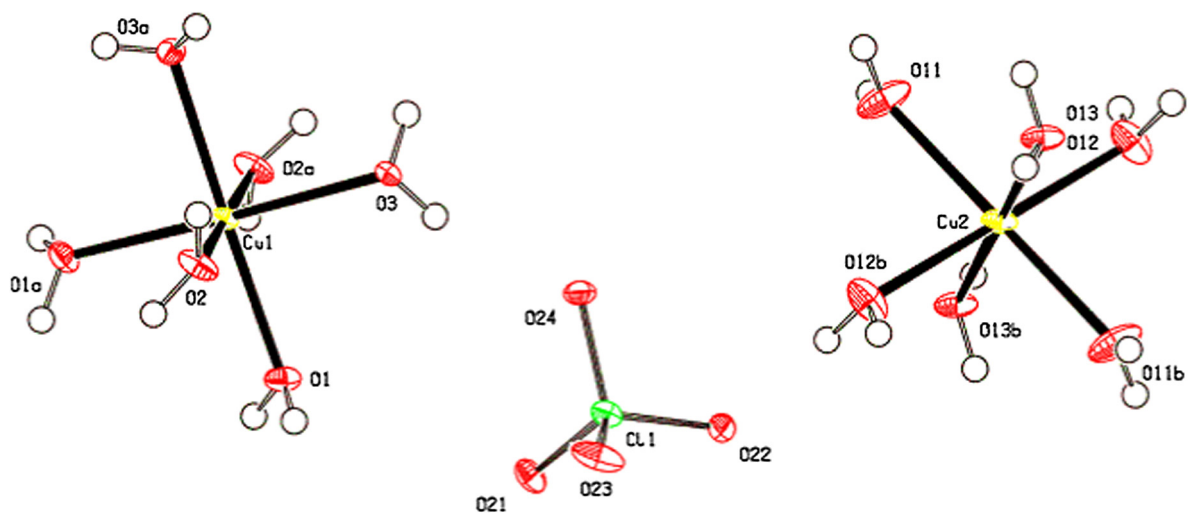
ious experimental parameters such as contact time (ligand – metal), temperature and pH of the test medium, on the kinetics of cadmium, copper and lead removal has been studied.

#### 3.2.1. Effect of contact time (ligand - metal) in aqueous solution

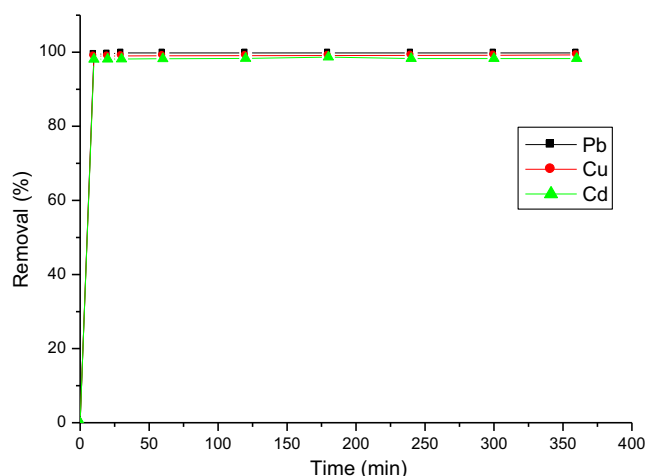
According to Fig. 4, the kinetics of cadmium, copper and lead removal by EIMH presents a shape characterized by a strong

**Table 2** Crystallographic parameters.

Compound	1	2	3		
<i>Crystallographic parameters</i>					
Formule	C <sub>5</sub> H <sub>8</sub> N <sub>5</sub> S, SO <sub>4</sub> , H <sub>2</sub> O	C <sub>5</sub> H <sub>7</sub> N <sub>5</sub> S	Cu H12 O6, Cl O4		
<i>M</i>		169.22	271.09		
System	Monoclinic	Triclinic	Monoclinic		
<i>a</i> (Å)	6.813 (5)	7.2245 (4)	9.9336 (4)		
<i>b</i> (Å)	9.258 (5)	8.1396 (4)	7.2677 (4)		
<i>c</i> (Å)	16.663 (5)	8.1350 (5)	24.1084 (12)		
$\alpha$ (°)	90.000 (5)	71.085 (2)	90		
$\beta$ (°)	98.714 (5)	70.434 (2)	98.760 (2)		
$\gamma$ (°)	90.000 (5)	86.527 (2)	90		
<i>Z</i>	4	2	8		
<i>h</i> <sub>min, max</sub>	−8, 7	−8, 9	−12, 8		
<i>k</i> <sub>min, max</sub>	−12, 11	−8, 10	−9, 9		
Space group	<i>P</i> 2/ <i>n</i>	<i>P</i> −1	<i>C</i> 2/ <i>c</i>		
<i>T</i> (K)	293 K	150 (2)	150 (2)		
<i>V</i> (Å <sup>3</sup> )	1038.9 (10)	425.79 (4)	1720.19 (15)		
<i>R</i> [ <i>I</i> > 2σ( <i>I</i> )]	1830	1736	1790		
<i>R</i> <sub>int</sub>	0.051	0.0431	0.0346		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )]	0.058	0.0475	0.0313		
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.144	0.1302	0.0844		
Selected bonds		Selected angles			
Bonds	1	2	Angles	1	2
S1—C2	1.687 (3)	1.7025 (19)	N1—C2—N3	116.8 (3)	118.3 (17)
N8—C9	1.329 (4)	1.323 (3)	N1—C2—S1	124.3 (2)	122.92 (15)
N8—C7	1.366 (4)	1.380 (3)	C5—N4—N3	117.3 (3)	117.15 (17)
C6—C7	1.360 (4)	1.374 (3)	N3—C2—S1	118.8 (2)	118.75 (16)
S1—C2	1.687 (3)	1.7025 (19)	C2—N3—N4	118.2 (2)	118.66 (16)
N8—C9	1.329 (4)	1.323 (3)	C9—N8—C7	109.2 (3)	107.28 (17)
N1—C2	1.326 (4)	1.319 (3)	C9—N10—C6	108.6 (2)	107.88 (17)
N10—C9	1.328 (4)	1.339 (3)	C7—C6—C5	131.4 (3)	131.56 (18)
N10—C6	1.388 (4)	1.339 (3)	N10—C6—C5	122.2 (3)	122.23 (17)
C6—C5	1.445 (4)	1.446 (3)	C6—C7—N8	107.2 (3)	108.09 (17)
N1—C2	1.326 (4)	1.319 (3)	N4—C5—C6	117.3 (3)	118.05 (17)
N10—C9	1.328 (4)	1.339 (3)	N10—C9—N8	108.5 (3)	110.56 (18)

**Fig. 3** Molecular structure of Cu-EIMH complex.





**Fig. 4** Efficiency of adsorption versus contact time for analyzed metal ions using model solutions with concentration 100 mg/L (adsorption time 20 min, accuracy  $\pm 0.5\%$ ).

increase in the capacity of lead, copper and cadmium removal by EIMH during the first minutes of contact between the solution and EIMH, followed by an equilibrium state. The necessary time to reach this equilibrium is about 20 min and an increase in removal time to 24 h did not show notable effects (Swaminathan et al., 2013).

Metal sorption studied by EIMH occurs with following affinity order: lead (II) (99.80%) > copper (II) (99.25) > cadmium (II) (98.72) with a slight difference in  $\Delta q$  value (Table 3). These results are significantly higher than those of the literature for natural adsorbents (Jiang et al., 2010; Yao-Jen et al., 2012).

To explain this order of affinity, we tried to summarize some specific parameters for metals involved in their ability to adsorb on EIMH (Table 3).

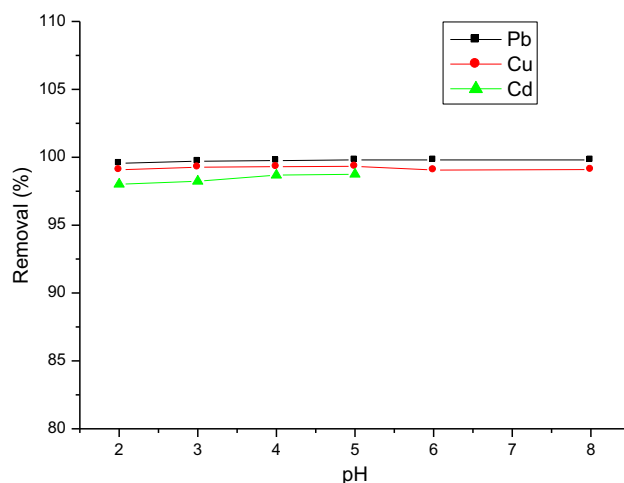
The electronegativity is an important parameter to compare the opportunities that metal ions have to set on supports. Indeed, it characterizes its ability to attract electrons when forming a chemical bond with another element. Therefore, the most readily adsorbed metal is one that has the largest electronegativity value. For this reason, the lead ions are better adsorbed than copper and cadmium.

During metal removal by EIMH, we noticed a small evolution in the value of the initial pH of the solution: from 3.73 to 3.74 for lead; from 3.42 to 3.44 for copper and from 3.43 to 3.48 for cadmium at the equilibrium. This explains that the metal removal was carried out mainly with the EIMH ligand, unlike the literature where  $H_3O^+$  ions are involved in competition for binding sites (Benguella et Benaissa, 2002).

### 3.2.2. Effect of pH

To prevent precipitation of metal hydroxides, we chose the following pH values:  $pH \leq 8$  for lead and cadmium and  $pH \leq 5$  for copper.

The effect of solution pH on the adsorption of lead (II), copper (II) and cadmium (II) using the EIMH was investigated and the results are presented in Fig. 5. It was noticed that the amount of metal removed is very high (98–99%) whatever the pH used and above that of the literature (Jiang et al., 2010; Yao-Jen et al., 2012). This is probably due to the flatness of the molecule as well as the large number of active sites in the ligand such as nitrogen, oxygen and sulfur atoms (Fig. 2), which allows an easy and fast adsorption of metals. Unlike the literature, acidic pH does not greatly affect the amount of metal removed by EIMH. For example 99.56–99.84% for Pb (II); 99.08–99.33% for Cu (II) and 98.01–98.91% for Cd (II) in the field pH (2–8) can be removed. This can be explained by the presence of two mesomeric forms of the ligand involved the conjugation of the bonds in the molecule Scheme 1a and b. Indeed, the protonation of the sulfur and/or nitrogen atom is compensated by electronic gain that discriminates the competition  $H_3O^+$ . As pH increases, the weak  $H_3O^+$  ions competing disappear as these surface active sites become more negatively charged, which enables adsorption of the metal ions through electrostatic force of attraction (Jiang et al., 2010). At pH 8, the maximum of metal is removed by complexation which is confirmed by infrared spectroscopy (Fig. 1).

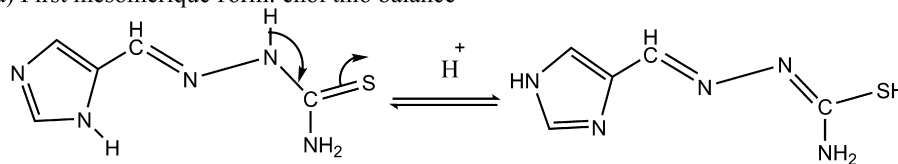


**Fig. 5** Efficiency of adsorption versus pH for analyzed metal ions using model solutions with concentrations 100 mg/L (adsorption time 20 min, accuracy  $\pm 0.5\%$ ).

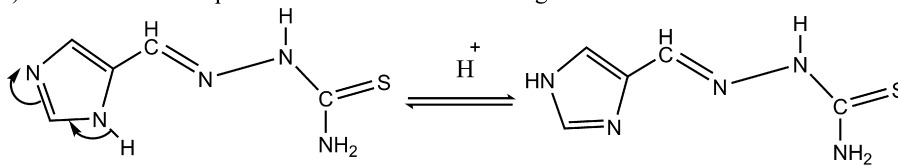
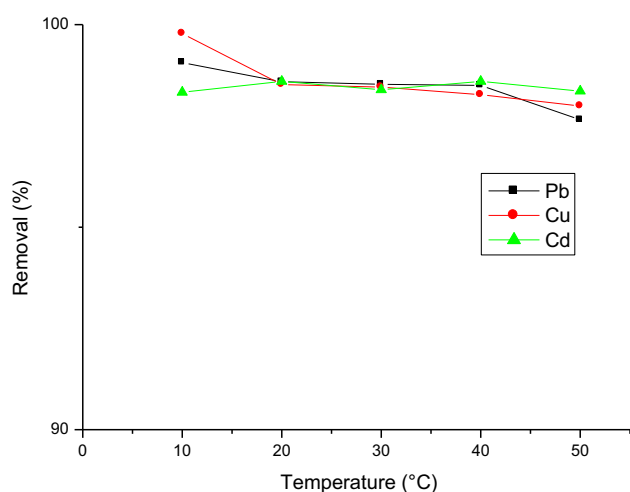
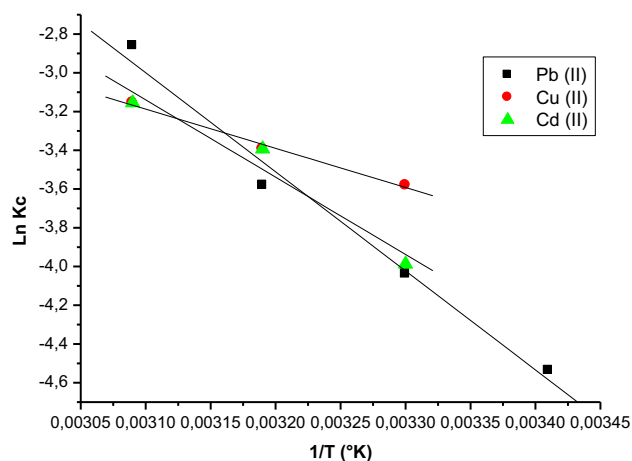
**Table 3** Relationship (amount metal removal - physical properties).

Metal	Amount of metal fixed at equilibrium (mg/g)	$M^{2+}$ removal/(%)	Load	Electronegativity
$Pb^{2+}$	29.57	99.80	2	2.33
$Cu^{2+}$	29.35	99.25	2	1.9
$Cd^{2+}$	29.25	98.72	2	1.69

(a) First mésomérique form: enol thio balance



(b) Second mésomérique form: balance imidazole ring

**Scheme 1** Mesomeric forms of EIMH ligand.**Fig. 6** Efficiency of adsorption versus temperature for analyzed metal ions using model solutions with concentration 100 mg/L (adsorption time 20 min, accuracy  $\pm 0.5\%$ ).**Fig. 7** Determination of thermodynamic parameters.

### 3.2.3. Effect of temperature on the removal of heavy metals by EIMH

To study the effect of this parameter on the kinetics of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  adsorption by EIMH, we selected the following temperatures: 10, 20, 30, 40 and 50 °C. The results obtained and presented in Fig. 6 indicate that an increase in the temperature in the interval 10–50 °C for the  $\text{Cu}^{2+}$  solution and 20–50 °C for the  $\text{Pb}^{2+}$  solution results into a decrease in these metals adsorption capacity which explains an exothermic process, whereas the cadmium removal is independent of temperature. We also note that for the three metals, the temperature did not influence the equilibrium time. Thus, environmental temperature is an important parameter that can influence the effectiveness of the adsorbent. In general, increasing the temperature weakens the physical or chemical attractive forces and reduces the sorbent ability (Benguella, 2011). For this study, the temperature increase implies a slight decrease in metal removal rate, which proves the efficiency of the ligand EIMH.

### 3.2.4. Determination of the nature of the interaction metal/ligand

In order to explain the nature of the interaction between the ligand and metal ions, it was necessary to determine the thermodynamic parameters of the contact. The thermodynamic parameters:  $\Delta H$  and  $\Delta S$  of heavy metal adsorption on EIMH are determined graphically from the plot of  $\log K$  versus  $1/T$  ( $T$  in Kelvin degrees). Fig. 7 (van't Hoff plots),  $\Delta S_0$  was determined from intercept ( $\Delta S = \text{intercept} \times 2.303R$ ) and  $\Delta H^0$  was determined from slope ( $\Delta H = -\text{slope} \times 2.303R$ ) of the curve. The values of thermodynamic properties are reported in Table 4. The negative values  $\Delta H$  for the three metals, confirm that the adsorption of heavy metals by EIMH is an exothermic process. Low values of this heat ( $< 40 \text{ K J/mol}$ ), show that this is a physical adsorption between  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions and EIMH ligand. Such interaction is due to the pH of the mixture. Indeed, in strongly acidic medium, the competition between metals and  $\text{H}_3\text{O}^+$  ions promotes adsorption, thereby preventing the metal complexation. Free energy change is negative for all temperatures (Table 4) indicating spontaneity of the process (Beraldo and Gambino, 2004).

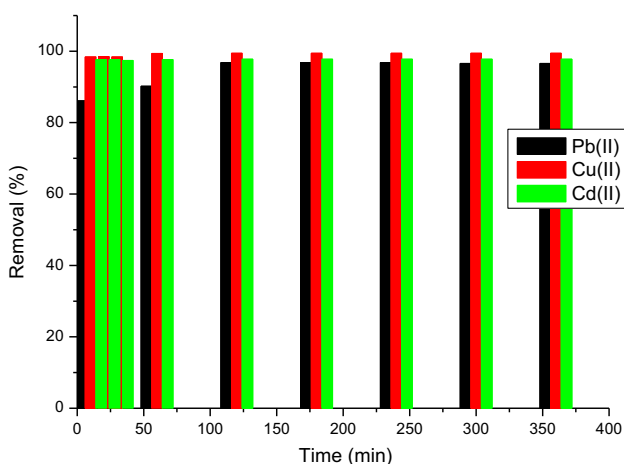


**Table 4** Thermodynamic parameters for adsorption of heavy metals by EIMH at 25 °C, 40 °C and 50 °C.

Metal	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol/K)	$R^2$	$\Delta G$ (K J/mole)		
				25 °C	40 °C	50 °C
Pb <sup>2+</sup>	-0.106	42.52	0.99	-12.77	-13.41	-13.83
Cu <sup>2+</sup>	-0.025	16.81	0.89	-5.034	-5.28	-5.45
Cd <sup>2+</sup>	-0.076	33.17	0.97	-10.13	-10.45	-10.78

**Table 5** Removal of metal ions from plating wastewater by EIMH ligand and aqueous solution.

Metal	pH	C mg/l		M <sup>2+</sup> removal/(%)	
		Before treatment	After treatment	Wastewater	Aqueous solution
Pb <sup>2+</sup>	2.93	0.44	0.063	96.81	99.80
Cu <sup>2+</sup>	2.93	371.01	2.06	99.44	99.25
Cd <sup>2+</sup>	2.93	423.17	9.45	97.76	98.68

**Fig. 8** Efficiency of adsorption versus contact time for analyzed metal ions using wastewater with concentrations 0.44 mg/L (Pb), 371 mg/L (Cu) and 423.17 mg/L (Cd),  $T = 25$  °C.

### 3.2.5. Regeneration of the ligand

20 mL of 0.01 M NaNO<sub>3</sub> was added to the EIMH sample solutions fully loaded with initially 100 mg/L of Pb(II), Cd(II) and Cu(II) and followed by stirring for 30 min. After partial evaporation of the solution, the ligand **2**, crystallized (Fig. 2-b).

### 3.2.6. Removing the metal ions from wastewater

The EIMH ligand **1** was tested using a real wastewater from a zinc electrolysis unit (ALZINC Ghazaouat). This test was carried out in order to check the possibility/capability of EIMH to remove heavy metal ions. Under the same operating conditions described earlier, 20 mL of wastewater was added to 67 and 62 mg of EIMH in 50 mL polyethylene bottles. The data are listed in Table 5. The experimental data collected (Fig. 8) clearly confirm that the Pb (II), Cu (II) and Cd (II) ions are absorbed with an efficiency of 97–99.5%. We can also observe that the amount of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> adsorbed from the wastewater, is comparable to that measured in the aqueous

solutions. This may be due to the same pH range (pH < 4) for both waters studied. Consequently, all the metal ions are removed by the electrostatic attraction force. The results show that the concentrations of lead (II), copper (II) and cadmium (II) were reduced from 0.44 to 0.014 mg/L, 371.01–2.06 mg/L and 423.17–9.45 mg/L respectively when EIMH ligand was added to the wastewater. In this case, EIMH showed a good adsorption capability at high and low concentration of metal ions. It also showed that metal ions were removed even at acidic pH as in basic medium, in the case of Pb (II) ions. This indicates clearly that EIMH ligand has a high selective adsorption toward Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup>.

Comparing lead ions and copper percentages, we note the existence of weak competition between EIMH adsorption and complexation by H<sub>2</sub>O molecules for these metals removals, which is confirmed for copper (II) by **3** crystal structures, determined by X-ray diffraction (Fig. 3). In the case of cadmium, the explanation is due to its low electronegativity value compared to those of lead and copper.

## 4. Conclusions

This work was mainly devoted to the study of removal capacity of lead, copper and cadmium water with an organic ligand. The results show that EIMH can be used to remove these metal ions with the same capacity from aqueous solution and wastewater. The kinetics of heavy metals on EIMH are characterized by a high metal adsorption (98–99%) on the ligand in the first minutes of contact solution-EIMH. Affinity adsorption of heavy metals on EIMH decreases slightly as follows: Pb<sup>2+</sup> > Cu<sup>2+</sup> > Cd<sup>2+</sup>. The metals removal performances are strongly affected by parameters such as pH and temperature.  $\Delta H$  values indicate that the interactions were primarily physical in nature like Van der Waals at acid pH while the IR spectra show chemical interactions type metal complexation in a basic medium. These interactions are carried out by the Interim cites active ligand which were characterized by single crystal X-ray diffraction. The amount of lead and copper removed by EIMH slightly decreases with temperature rise, and that of cadmium is independent of temperature.

The EIMH ligand, proved to be effective for the removal of lead, copper and cadmium in acid as in basic conditions. It also demonstrated that it can be used to a concentration less than 0.5 ppm from wastewater.

## Acknowledgment

Authors acknowledge the Algerian Ministry for Education and Research.

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