

# Effective removal of mercury ions using combination of ionic liquid and activated charcoal in industrial organic and aqueous waste

Upender S. Sisodia<sup>a</sup>Seema Khothari

Department of Chemistry, Pacific University, Udaipur, Rajasthan 313003, India

**Abstract-** A highly effective and neat reaction protocol for the removal of mercury ions from the industrial effluents and organic compounds using a selective combination of ionic liquid such as 1-butyl-3-methylimidazolium hydrogen sulfate [BMIM] [HSO<sub>4</sub>] and activated charcoal. This combination has been proved to be more successful as compared to conventional methods for the removal of such heavy metals.

**Index Terms-** Ionic liquid, 1-butyl-3-methylimidazolium hydrogen sulfate, liquid-liquid extraction, mercury, activated charcoal.

## I. INTRODUCTION

Mercury is a naturally occurring element that exists in several forms such as elemental or metallic mercury, organic and inorganic mercury compounds etc. Elemental or metallic mercury is a shiny, silver-white metal that is liquid at room temperature. Elemental mercury can evaporate to become an invisible, odorless toxic vapor. Inorganic mercury compounds take the form of mercury salts that are generally a white powder or crystalline, with a notable exception being mercuric sulfide, which is red. Organic mercury compounds, such as methyl mercury, are formed when mercury combines with carbon. Microscopic organisms convert inorganic mercury into methyl mercury, which is the most common organic mercury compound found in the environment. Mercury is bio-accumulative in nature. Mercury is one of the prevalent toxic heavy metals with significant environmental concern because of its persistent accumulation, high toxicity, wide use and large distribution [1-2]. Room temperature ionic liquids (RTILs) increases interest for their promising role as alternative media in synthesis [3-10], separation [11-13] and electrochemistry [14-15], as a result of

their unique chemical and physical properties [16-18]. RTILs can dissolve a wide spectrum of organic, organometallic, and inorganic compounds [19-20]. Also, they have no detectable vapor pressure and are relatively thermal stable. So, there is no loss of solvent through evaporation with ionic RTILs. This will avoid environmental and safety problems due to volatilization, as is the case in traditional organic solvents. Therefore, they are proposed as novel solvent systems to replace traditional solvents that are generally toxic, flammable, and volatile.

The conventional mercury treatment processes are generally non-selective and only roasting or retorting recovers pure mercury. The other methods involve an additional purification step for the complete recovery and all generate secondary waste. It is well known that separation processes based on the ion-exchange technique yield high purity compounds. However, these processes are time consuming and inherently expensive. Methods based on liquid-liquid extraction emerged as novel and unique technique for the separation of metal ions owing to its simplicity, versatility and ready adaptability to scaling up of the process.

Therefore, here we proposed a cost effective and industrial reliable process for the removal of mercury ions by using ionic liquids. Recycling of the spent solvent is yet another attractive feature of this technique. Hence, in the present work the liquid-liquid extraction technique has been developed using ionic liquids and activated charcoal doing selective separation procedures to recover mercury ion from industrial organic or aqueous waste.

The use of task specific ionic liquid (TSILs) as potential extracting agents for the removal of heavy metals such as mercury, and so on explores interesting results. The removal of these heavy metals from the industrial effluents / contaminated

water bodies using these ionic liquids has been proved to be more successful than conventional methods such as precipitation, cementation, reverse osmosis, ion exchange and adsorption [21-23]. Therefore, in this present work, we have attempted to remove heavy metals such as mercury ion from their effluents using synthesized acidic ionic liquids with the combination of activated charcoal.

## II. MATERIALS AND METHOD

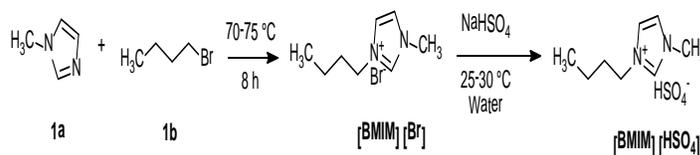
Synthesized compounds were analyzed by highly advanced spectroscopic and analytical techniques such as NMR and MASS. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were determined in CDCl<sub>3</sub> solution on ZEOL 400MHz spectrometer. Elemental analysis was carried out on Elemental Vario EL-III Carlo Erba 1108 Model.

### A. Synthesis of Ionic liquid: 3-butyl-1-methyl-1H-imidazol-3-ium bromide [BMIM] [Br]

To the stirring solution of compound 1a (50g, 0.609 mol) was added drop wise compound 1b (83.33g, 0.6699 mol). Reaction mixture was stirred at 80 °C for 12h. Completion of reaction on TLC, light yellow viscous reaction mass was obtained as desired [BMIM] [Br]. Into this reaction mixture toluene was added and stirred again for 30 minutes. Layer was separated and lower layer was distilled under high vacuum at 90-100°C. Desired product was isolated as crude. Crude was crystallized by ethyl acetate and then evaporates a white solid obtained with 92% yield.

### B. Synthesis of 3-butyl-1-methyl-1H-imidazol-3-ium hydrogensulfate [BMIM] [HSO<sub>4</sub>]

Anion-exchange- To the stirring solution of compound [BMIM] [Br] (15g, 0.059mol) add water 22gm than added lot wise Sodium bisulfate (7.56g, 0.63 mol). Reaction mixture was stirred for 12h. Reaction mass distilled out at 70-75°C under reduces pressure at 550mmHg. Add dichloromethane 20gm into the crude mass. Stir for 1hrs than filter by watmaan filter paper. Filtrated complete distilled out at 60-65°C without vacuum. Light yellow liquids obtained pH acidic. The purity of final product was characterized with <sup>1</sup>H NMR, <sup>13</sup>C NMR, (Figure 1). The yield was about 95%.



**Figure1.** Preparation of Ionic liquid [BMIM] [HSO<sub>4</sub>]

### C. Procedure for the removal of mercury (Hg) ion

#### Monophasic System

Experiments were carried out in reaction flask by adding 10% w/w ionic liquid [BMIM] [HSO<sub>4</sub>] and 1% w/w activated charcoal in organic solution containing concentration of mercury ions around 500 to 800ppm. Stir for 1hrs at 25 to 30°C followed by filtration on celite and whatman filter paper. Concentrations of mercury ions were found to be 10 to 15ppm in filtrate. The mercury concentrations were determined using inductively coupled plasma / Mass spectrometry (ICP/MS) iCAP 6000 series Thermo scientific.

#### Biphasic System

Experiments were performed by ionic liquid in dichloromethane and an aqueous solution of metal ion, stirred the above solution for 2hrs followed by layer separation. Here liquid/liquid extraction was carried out by specific volumes of ionic liquid and mercury solution with known concentration, kept under stirring at constant temperature. The mercury concentrations in the aqueous phase were determined before and after extraction, by using Inductively Coupled Plasma / Mass Spectrometry (ICP/MS) ICAP 6000 series Thermo scientific instrument.

Extraction efficiencies (E) were calculated by

$$E (\%) = \frac{(C_i)_{aq} - (C_f)_{aq}}{(C_i)_{aq}} \times 100$$

where (C<sub>i</sub>)<sub>aq</sub> and (C<sub>f</sub>)<sub>aq</sub> are the concentration of H(II) ions in aqueous phase before and after extraction.

1mg/L=1ppm

1ppm=1000ppb

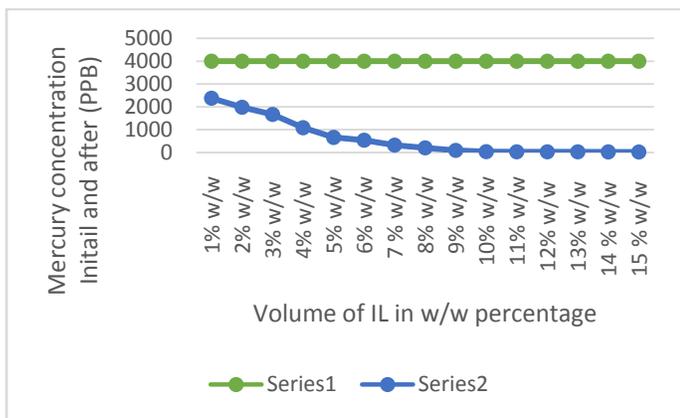
### III. RESULTS AND DISCUSION

There is different process conditions were carried out and to obtain best conditions for maximum remove mercury ions Hg (II) in monophasic and biphasic system. Experiments are conducted to find the effect of:

- Ionic liquid concentration;
- Effect of pH;
- Effect of Temperature;
- Effect of Contact Time
- Strength of IL in monophasic and biphasic system

#### IONIC LIQUID CONCENTRATION

To find out the role of the ionic liquid as a simple medium or as an active partner in a molecular interaction, a series of experiments were carried out by varying amount of the ionic liquid in w/w percentage w.r.t to reaction volume at constant mercury concentration of 4000ppb and at a temperature of 25°C or 950 rpm stirring speed for time 1hr. The results were shown in (Figure 2) which shows that the extraction strength of Hg (II) increases powerfully with increase in the concentration of ionic liquid in the range of 1 to 10 % w/w and after the max concentration 10% w/w there were no significant increase was acquired.



**Figure 2.** Effect of ionic liquid concentration at constant Hg (II) concentration of 4000ppb and Temp. 25°C, time=1hrs,950rpm starring speed.

#### EFFECT OF pH IN EXTRACTION OF MERCURY

Different experiment were carried out with different pH in range of 2 to 10 by using hydrochloric acid or sodium hydroxide solution, at constant strength of ionic liquid, Hg(II), temperature, time or 950rpm stirring speed and then it was observed that extraction of mercury increases with decrease in the acidity and was found to be maximum in the range pH 5 to 6 as shown in (Figure 3).

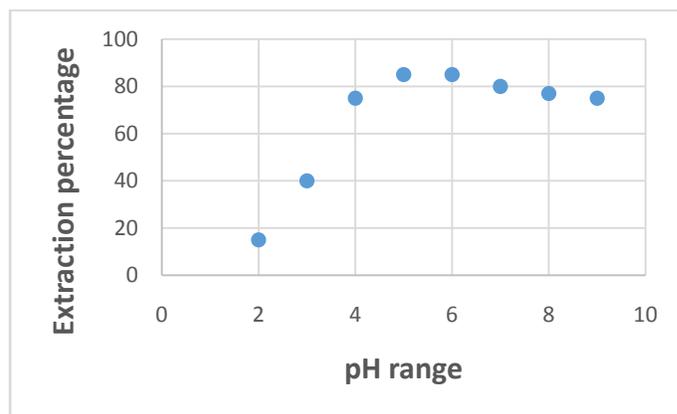


Figure 3. Effect of initial pH of aqueous solution on the extraction efficiencies of Hg(II)

#### EFFECT OF TEMPERATURE AND CONTACT TIME ON EXTRACTION

Various experiments were carried by varying temperature and contact time and it was found that a minimum of 40 to 60 min of stirring and a temperature of 25 to 30°C is needed for maximum extraction of mercury (II). The elongated stirring has no progressive effect on the extraction of Hg(II).

#### STRENGTH OF IONIC LIQUID IN MONOPHASIC AND BIPHASIC SYSTEM

To find out the efficiency of ionic liquid in monophasic and biphasic system different experiment were carried out at constant temperature 25°C and contact time 1hrs on different strength of Hg(II) ions in monophasic and biphasic system with constant volume of ionic liquid (10% w/w) and it was observed that in

monophasic system ionic liquid extracted mercury(II) more efficiently as compared to biphasic system as shown in (Table 01).

Exp. No.	Initial Hg conc. Ppb	Phase	Final Hg conc. Ppb
1	3280	monophasic	36
2	3108	monophasic	22
3	2922.51	monophasic	32
4	1572.63	monophasic	28
5	3252.9	diphasic	204
6	2922.51	diphasic	186
7	1572.63	diphasic	152
8	2252.9	diphasic	165

**Table 01:** 100g of organic or aqueous layer treated with 10% w/w ionic liquid and 1% w/w activated charcoal.

*The purity of Synthesis of ionic liquid [BMIM] [HSO<sub>4</sub>] was characterized with <sup>1</sup>H NMR, <sup>13</sup>C NMR,*

**<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; δ/ppm relative to TMS)**

0.97(3H, t, CH<sub>2</sub>CH<sub>3</sub>), 1.38-1.34 (2H, m, CH<sub>2</sub>CH<sub>3</sub>), 1.95-1.91 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>), 2.99 (3H, s, NCH<sub>3</sub>), 3.42-3.38 (2H, t, NCH<sub>2</sub>), 7.74 (1H, d, NCHCHN), 10.01 (1H, s, NCHN).

**<sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub> δ/ppm relative to TMS)**

δ 137.50 (s), 124.29 (s), 121.06 (s), 47.01 (s), 34.39 (s), 29.73 (s), 19.88 (s), 14.02 (s).

**Elemental analysis (%):Found:** C, 40.23; H, 6.34; N,11.42; S,13.86.C<sub>8</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S **calcd:** C, 40.66; H, 6.83; N, 11.86. S, 13.57.

**IV. CONCLUSION**

In conclusion, we have developed a versatile, useful and environment benign method for the removal of highly toxic mercury (II) ions by a biphasic or monophasic liquid-liquid

extraction system using a combination of ionic liquid and activated charcoal.

**ACKNOWLEDGMENT**

The authors are thankful to the Head of Department of Chemistry, Pacific University, Udaipur (Raj.), for providing laboratory facilities and the Head of Department of Pharmacy for providing spectral and analytical data.

**REFERENCES**

- [1] Rapsomanikis S, Craig P J, Anal Chim Acta, 1991, 248, 563–567.W.-K. Chen, *Linear Networks and Systems* (Book style). Belmont, CA: Wadsworth, 1993, pp. 123–135.
- [2] Collasiol A, Pozebon D, Maia S M, Anal Chim Acta, 2004, 518,157–164.
- [3] Wilkes J S, Zaworotko M J, J. Chem. Soc., Chem. Commun.,1992, 965.
- [4] Suarez P A Z, Dullius J E L, Einloft S, de Souza R F, Polyhedron., 1996, 15, 1217.
- [5] Adam C J, Earle M J, Robert G, Sneddon K R, Chem.Commun., 1998, 2097.
- [6] Dyson P J, Ellis D J, Parker D.C, Welton T, Chem.Commun., 1999, 25.
- [7] Adam C J, Earle M J, Sneddon K R, Green Chem., 2000, 2, 21.
- [8] Toma G, Gotov B, Solcaniova E, Green Chem., 2000,2, 149.
- [9] Song C E, Roh E J, Chem. Commun., 2000, 837.
- [10] Rosa J N, Afonso C A M, Santos A G, Tetrahedron., 2001, 57, 4189.
- [11] Huddleston J G, Willauer H D, Swatloski R P, Visser A N, Rogers R D, Chem. Commun., 1998, 1765.
- [12] Blanchard L A, Hancut D, Beckman E J, Brennecke J F, Nature, 1999, 399, 28.
- [13] Fadeev A G, Meagher M, Chem. Commun., 2001, 295.
- [14] Hussey C L, Mamantov G, Popov A I, VCH, New York, 1994.
- [15] Sun I W, Hussey C L, Inorg. Chem, 1989, 28, 2731.
- [16] Freemantle M, Chem. Eng. News, 2001, 79, 21.
- [17] Wasserscheid P, Keim V, Angew. Chem. Int. Ed., 2000, 39, 3772.
- [18] Welton T, Chem. Rev, 1999, 99, 2071.
- [19] Anthony J A, Maginn E J, Brennecke J F, J. Phys. Chem., 2001, 105 10942.
- [20] Huddleston J G, Visser A E, Reichert W M, Willauer H D, Broker G A, Rogers R D, Green Chem., 2001, 3, 156.
- [21] Papaicomomou N, Lee J M, Salimen J, Stosch M V and Prausnitz M J, J Chem EnggData, 2007.
- [22] Mikkola J P, Virtanen P, and Sjöholm P, Green Chem., 2006, 8, 250.
- [23] Kogelnig D, Stojanovic A, Galanski M, Groessl M, Terahedron Lett., 2008, 49, 2782-2785.

**AUTHORS**

**First Author** – Upendra Singh Sisodia, Department of Chemical Sciences, Pacific University, Udaipur, Rajasthan.Email.Id, upendra.mlsu08@gmail.com

**Second Author** – Seema Khothari, Department of Chemical Sciences, Pacific University, Udaipur, Rajasthan.Email.Id, seemavkothari@rediffmail.com

