

Efficient removal of Hg^{2+} , Cd^{2+} and Pb^{2+} from aqueous solution and mixed industrial wastewater using a designed chelating ligand, 2-pyridyl-N-(2'-methylthiophenyl) methyleneimine (PMTPM)

Krishnendu Kumar Pobi, Biplab Mondal, Sumanta Nayek, Apurba K. Patra and Rajnarayan Saha

ABSTRACT

The present study is focused on the removal of Hg^{2+} , Cd^{2+} and Pb^{2+} ions from aqueous solution using a tridentate chelating agent, 2-pyridyl-N-(2'-methylthiophenyl) methyleneimine (PMTPM); and applicability of such removal from industrial wastewater using PMTPM is also investigated.

The results showed that the metal ions removal efficiency using PMTPM was in the order of Hg^{2+} (99.46%) > Cd^{2+} (95.42%) > Pb^{2+} (94.54%) under optimum reaction conditions (L:M²⁺ = 3:1, pH = 9, time = 24 h, temp. = 30 °C). Formed chelated complexes such as $[\text{Hg}(\text{PMTPM})\text{Cl}_2]$ (**1**), $[\text{Cd}(\text{PMTPM})\text{Cl}_2]$ (**2**) and $[\text{Pb}(\text{PMTPM})\text{Cl}_2]$ (**3**) were characterized by numerous spectroscopic tools and X-ray structure determination of a representative complex of Hg^{2+} . In the X-ray structure of $[\text{Hg}(\text{PMTPM})\text{Cl}_2]$, **1**, the Hg^{2+} adopted a distorted tetrahedral coordination geometry surrounding two N donors of PMTPM and two chloride ions. A similar coordination geometry surrounding the respective metal centres in **2** and **3** was established. The thermogravimetric analysis (TGA) revealed a stability order of $[\text{Cd}(\text{PMTPM})\text{Cl}_2]$ > $[\text{Hg}(\text{PMTPM})\text{Cl}_2]$ > $[\text{Pb}(\text{PMTPM})\text{Cl}_2]$. Further the comparative metal leaching behaviour of these chelate complexes exhibited higher stability in alkaline solution than in acidic. Moreover, PMTPM was applied in real mixed industrial wastewater with alkaline pH, and adequate removals of toxic metals were achieved.

Key words | chelating agent, industrial wastewater, PMTPM, removal efficiency, toxic metal

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INTRODUCTION

Toxic metals contamination in aquatic ecosystems has been a major concern to researchers and environmentalists for the last few decades. Contamination of surface waters due to industrial wastewater discharges was found by several earlier studies (Gupta *et al.* 2010; Yolcubal *et al.* 2016). Industrial wastewaters often contain detectable amounts of metals and metalloids, and their constant release into surface waters may pose severe ecological threats. Even if these are present in diluted quantities, their concentration may be magnified through natural processes such as precipitation, recalcitrance, and bio-absorption to such an extent that they become toxic for the aquatic ecosystem and existing biota (Atkinson *et al.* 1998). These toxic metals are very common in industrial effluents and wastes from chlor-alkali, pharmaceutical, metal

plating, mining activities, smelting, pesticides, coal-based thermal power plants, sponge iron, steel and alloy industries, etc. (Shah *et al.* 2013). Therefore, the release of toxic metals into the aquatic ecosystem is triggered by both natural and anthropogenic processes (Zhang *et al.* 2009), and their removal from water/wastewater has become a critical need from the local to the global point of view.

The United States Environmental Protection Agency (USEPA) has classified some toxic metals such as mercury, cadmium and lead as priority pollutants because of their toxicity (Keith & Telliard 1979). Mercury is known to have neurotoxic effects on the central nervous system, and causes malfunction of the kidneys and pulmonary disorder (Kim *et al.* 2016). Similarly, excessively high concentrations

of cadmium pose serious health risks such as renal dysfunction, liver damage, bone degeneration, lung insufficiency, and hypertension in humans, and high levels of exposure will result in death (Satarug *et al.* 2010). Chronic exposure of lead can damage the central nervous system and genital system, along with impairment of cellular and brain functions (Fu & Wang 2011). Therefore, top priority is given to the removal of such toxic metals from wastewater to avoid environmental and public health hazards.

Various techniques are being used to remove toxic metals from wastewater, including chemical treatment (Blue *et al.* 2010), phytoremediation (Rai 2009), ion exchange (Colantonio & Kim 2016), membrane technologies (Tan *et al.* 2015) and adsorption (Ge *et al.* 2016). Among them, phytoremediation and bio-adsorption are very much cost-effective techniques used to remove toxic metals in a particular study area, but they have some limitations. Chemical precipitation using a chelating agent has proved to be an excellent method to eliminate toxic metals from industrial wastewater, with significant advantages such as high metal selectivity, relatively low cost, easy operation, the ability to treat large volumes of wastewater and potential removal efficiency. In the last few decades, several research works were performed to find suitable chelating agents that can effectively remove such toxic metals from wastewater at various pH conditions. Generally, sulphur and nitrogen containing chelating agents are able to form stable metal complexes with divalent toxic metals as their precipitates and can be mechanically removed (Matlock *et al.* 2003). There are some well-known ligands such as sodium *N,N*-dimethyl dithiocarbamate (DMDTC) (Tassel *et al.* 1997), sodium trithiocarbonate (STC) (Matlock *et al.* 2002a), and sodium 1,3,5-triazine-2,4,6-trithiolate (TMT) (Henke *et al.* 2000), which have been used to remove mercury from an aqueous medium. However, their metal-ligand precipitates are quite unstable in the long term and on decomposition produce toxic substances (Hutchison *et al.* 2008). Atwood and co-workers have developed some promising chelating agents that can remove mercury, cadmium, lead, and other toxic metals from aqueous solution as their precipitates (Matlock *et al.* 2002b; Matlock *et al.* 2003; Blue *et al.* 2008). Wang *et al.* (2012) developed another promising chelating agent, namely TMBTCA (N^1, N^2, N^4, N^5 -tetrakis (2-mercaptoethyl)benzene-1,2,4,5-tetracarboxamide) which can efficiently remove toxic metals from printed circuit board (PCB) industrial wastewater. The majority of the studies have been conducted on removing the toxic metals by using chelating agents from acidic wastewater. However, limited reports are available on removal of toxic metals

using a chelating agent from wastewater in an alkaline condition (Blue *et al.* 2008, 2010; Wang *et al.* 2012; Chaudhuri *et al.* 2015). In this study, a reported (Lindoy & Livingstone 1968) chelating ligand, namely 2-pyridyl-*N*-(2'-methylthiophenyl) methyleneimine (PMTPM), is used to remove selected toxic metals; that is, Hg^{2+} , Cd^{2+} and Pb^{2+} from aqueous solution, and discovered its applicability for real alkaline mixed industrial wastewater. The investigation also explored the effects of various reaction conditions such as molar ratio of PMTPM: M^{2+} , pH, and reaction time for the removal of the aforementioned metals. The thermal stability of metal-ligand precipitates and their leaching behaviours are also investigated.

MATERIALS AND METHODS

Materials and physical measurements

All experiments were carried out using standard apparatus. All the chemicals used for the experiment and analytical purposes were of AR grade from Merck India; and pyridine-2-carboxaldehyde, 2-(methylthio)aniline obtained from Sigma-Aldrich. The chemicals were used without further purification. Solvents were distilled from an appropriate drying agent before use. Deionized water (resistivity = $18.2 \text{ M}\Omega\text{cm}^{-1}$, Sartorius Stedim Biotech, arium[®]61316) was used throughout the experiments for the preparation of solutions. The pH of the solutions was measured by using an Orion star pH meter A214, Thermo Scientific.

Synthesis of PMTPM

The Schiff base ligand (PMTPM) was synthesized by the condensation of pyridine-2-carboxaldehyde (1.076 g, 10 mmol) with 2-(methylthio)aniline (1.392 g, 10 mmol) in CH_3OH yielded (85%) yellowish crystal of PMTPM following a modified reported procedure (Roy *et al.* 2011).

Toxic metal removal study

The study was conducted to evaluate the performance of the chelating ligand (PMTPM) for the removal of toxic metals (Hg^{2+} , Cd^{2+} and Pb^{2+}) from aqueous solution, which might depend on some influencing factors, such as the molar ratio of PMTPM versus metal ions, reaction time and pH of the solution. The batch procedure was employed for the removal of toxic metals. For this purpose, an aqueous stock solution (30 ppm) of Hg^{2+} , Cd^{2+} and Pb^{2+} were

prepared separately by dissolving their chloride salts in the deionized water. Then an ethanol solution of the ligand was added dropwise to the metal solutions with continuous stirring (200 rpm) at 30 °C to ensure proper distribution of PMTPM in the solution. The solution pH was adjusted by 0.1 M HCl and NaOH. The percentage of removed toxic metals was determined under various experimental conditions using the formula as follows:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_f}{C_0} \times 100$$

where, C_0 and C_f are the initial and final concentrations of metals (mg/L) in the aliquot. The concentration of lead (Pb) and cadmium (Cd) was measured using an atomic absorption spectrophotometer (AAS) (Model: GBC, Avanta), whereas mercury (Hg) concentration was estimated by cold vapour atomic absorption. Each analysis was repeated three times, and the arithmetic mean was calculated to confirm the result for toxic metal precipitation.

Synthesis and characterization of metal complexes

The precipitation of toxic metals was performed on a larger scale to obtain sufficient precipitate for their characterization. The probable reaction pathway and structures of metal-ligand complexes are presented in Figure 1. Elemental analyses of metal precipitates were performed using a Perkin – Elmer 2400 (series-II) CHNS analyzer. The Fourier-transform infrared (FT-IR) spectra were collected from KBr pellets in the scanning range from 4,000 to 400 cm^{-1} by using a Thermo Nicolet iS10 FTIR spectrometer. ^1H NMR spectra were obtained on a JNM ECX-500, Jeol India. Mass spectra were recorded on an Impact HD, M/S Bruker Daltonik GmbH. Thermal behaviours were examined with an Okay 1200 TGA–DSC, equipped with Libratherm controller TGA-8001 at the heating rate of 10 °C/min in an N_2 atmosphere.

Synthesis of $[\text{Hg}(\text{PMTPM})\text{Cl}_2]$, (1)

Solid mercuric chloride, HgCl_2 (0.11 g, 0.409 mmol) was dissolved in 10 ml of deionized water and to this solution was added dropwise an ethanol solution (5 ml) of the ligand, PMTPM (0.10 g, 0.409 mmol). During addition of the ligand solution, a yellow precipitate was formed. The reaction mixture was further stirred for 6 h. The bright yellow solid thus obtained was filtered and washed successively with water, ether, and then dried. Crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_3CN solution of 1.

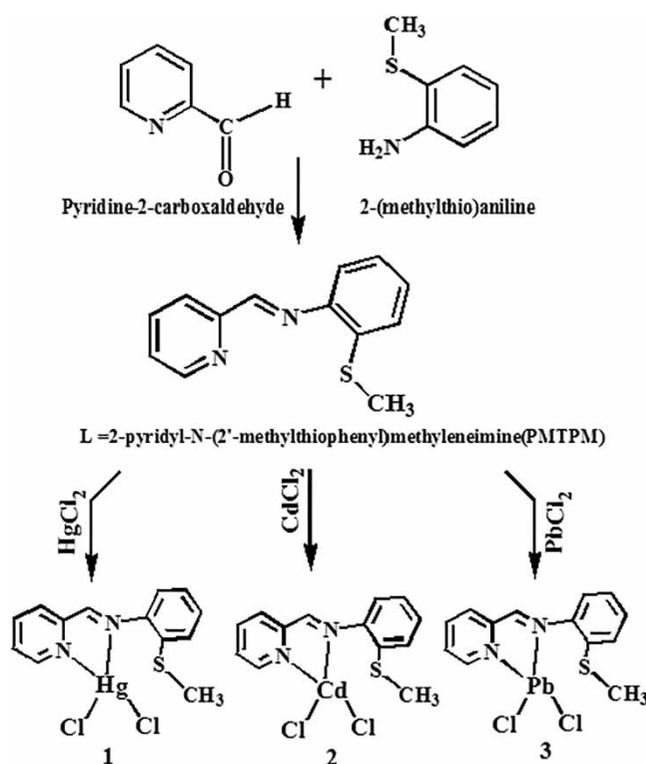


Figure 1 | Reaction scheme of metal-PMTPM complex formation (where 1, 2 and 3 represent $[\text{Hg}(\text{PMTM})\text{Cl}_2]$, $[\text{Cd}(\text{PMTM})\text{Cl}_2]$ and $[\text{Pb}(\text{PMTM})\text{Cl}_2]$ respectively).

Elemental analysis calculated for $\text{C}_{13}\text{H}_{12}\text{HgCl}_2\text{N}_2\text{S}$ (1): C 29.22, H 2.85, N 4.75; found: C 29.13, H 2.77, N 4.82. IR (KBr disk, cm^{-1} , selected peaks): 1,598 vs (C=N), 695 m (C-S); ^1H NMR (CDCl_3 , 500 MHz): δ 8.92–8.91 (2H, m, Pyridine ring proton next to N, HC=N), 8.1–8.06 (1H, m, Pyridine ring proton), 7.83 (1H, d, Pyridine ring proton), 7.74–7.71 (1H, d, Pyridine ring proton), 7.64 (1H, d, Phenyl ring proton), 7.48–7.39 (3H, m, Phenyl ring proton), 2.69 (3H, s, -SMe) where there is imine-proton resonance here (Figure S1, supplementary information, available with the online version of this paper). ESI-MS: $[\text{C}_{13}\text{H}_{12}\text{N}_2\text{S}\text{ClHg}]^+$, m/z, 465.0075, $[\text{C}_{13}\text{H}_{12}\text{N}_2\text{SNa}]^+$, m/z, 251.0595.

Synthesis of $[\text{Cd}(\text{PMTM})\text{Cl}_2]$, (2)

Solid cadmium chloride, CdCl_2 (0.15 g, 0.745 mmol) was dissolved in 10 ml of hot deionized water and to this solution was added dropwise an ethanol solution (5 ml) of the ligand, PMTPM (0.17 g, 0.745 mmol). During addition of the ligand solution, a bright yellow precipitate was formed. The reaction mixture was further stirred for 6 h. The bright yellow solid thus obtained was filtered and washed successively with hot water, ether and then dried. The yellow solid thus obtained was re-dissolved in

dimethylformamide (DMF), and diethylether diffusion to this solution afforded yellow microcrystals of **2**. Elemental analysis calculated for $C_{13}H_{12}CdCl_2N_2S$ (**2**): C 37.93, H 2.94, N 6.81; found: C 37.87, H 2.87, N 6.73. IR (KBr disk, cm^{-1} , selected peaks): 1,604 vs (C=N), 694 m (C-S); 1H NMR ($CDCl_3$, 500 MHz): δ 9.1–9.07 (1H, d, Pyridine ring proton next to N), 8.94 (1H, s, HC=N), 8.15 (1H, t, Pyridine ring proton), 7.87 (1H, d, Pyridine ring proton), 7.82–7.78 (1H, m, Pyridine ring proton), 7.75 (1H, d, Phenyl ring proton), 7.65–7.47 (3H, m, Phenyl ring proton), 2.79 (3H, s, -SMe) where there is imine-proton resonance here (Figure S2, supplementary information, available online). ESI-MS: $[M+H]^+$, m/z , 412.9675, $[L+H]^+$, 229.0716; where M = molecular weight of complex and L = molecular weight of ligand].

Synthesis of $[Pb(PMTPM)Cl_2]$, (**3**)

Solid lead chloride, $PbCl_2$ (0.10 g, 0.359 mmol) was dissolved in 10 ml of hot deionized water and to this solution was added dropwise an ethanol solution (5 ml) of the ligand, PMTPM (0.082 g, 0.359 mmol). During addition of the ligand solution, a bright yellow precipitate was formed. The reaction mixture was further stirred for 6 h. The yellow solid thus obtained was filtered and washed successively with hot water, ether, and then dried. The yellow solid thus obtained was re-dissolved in DMF and diethylether diffusion to this solution afforded yellow microcrystals of **3**. Elemental analysis calculated for $C_{13}H_{12}PbCl_2N_2S$ (**3**): C 30.83, H 2.39, N 5.53; Found: C 30.60, H 2.28, N 5.45. IR (KBr disk, cm^{-1} , selected peaks): 1,593 vs (C=N), 695 m (C-S); 1H NMR ($CDCl_3$, 500 MHz): δ 8.71 (1H, d, Pyridine ring proton next to N), 8.57 (1H, s, HC=N), 8.34 (1H, d, Pyridine ring proton), 7.83 (1H, t, Pyridine ring proton), 7.39–7.37 (1H, m, Pyridine ring proton), 7.3–7.26 (1H, m, (1H, d, Phenyl ring proton merged with $CHCl_3$ peak), 7.24–7.21 (1H, m, Phenyl ring proton), 7.2–7.16 (1H, m, Phenyl ring proton), 7.08 (1H, d, Phenyl ring proton), 2.79 (3H, s, -SMe) where there is imine-proton resonance here (Figure S3, supplementary information, available online). ESI-MS: $[M+H]^+$, m/z , 507.2686, $[L+Na]^+$, 251.0592; where M = molecular weight of complex and L = molecular weight of ligand.

The study of X-ray crystal structure of complex **1**

Single crystal X-ray data of **1** were collected at 150.00(10) K by using Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) on a four-circle diffractometer equipped with a CCD plate detector. Data collection, reduction and cell refinements were carried out

using the CrysAlisPro package (Agilent Technologies 2014). The structure was solved by direct methods of SHELXS-97 and refined by full-matrix least squares refinement methods based on F^2 with the SHELXL-97 programme (Sheldrick 2008). Crystal data, data collection and structure refinement details are summarized in Table 1(a), and the selected bond lengths and bond angles are shown in Table 1(b).

Leaching study

Leaching studies were performed to ascertain the metals' leachability and long-term stability of $[Hg(PMTPM)Cl_2]$, $[Cd(PMTPM)Cl_2]$ and $[Pb(PMTPM)Cl_2]$ precipitates. The batch leaching experiments were performed followed by the

Table 1 | (a) Details of refinement data and (b) selected bond length (\AA) and bond angles ($^\circ$) for complex **1**

(a)			
Empirical formula	$C_{13}H_{12}Cl_2HgN_2S$		
Formula weight	499.80		
Crystal system	Monoclinic		
Space group	P 1 21/n 1		
a (\AA)	7.6681(4)		
b (\AA)	9.0769(5)		
c (\AA)	21.4050(15)		
β ($^\circ$)	95.532(5)		
Volume (\AA^3)	1,482.89(15)		
Radiation type	Mo $K\alpha$		
Radiation wave length (\AA)	0.71073		
Measurement temperature	150 K		
Z	4		
ρ_{calc} (g/cm^3)	2.239		
F(000)	936		
θ range(deg)	1.91–28.27		
Goodness-of-fit	1.079		
Data/restraints/parameters	3252/0/173		
Final R1, wR2 [$I > 2\sigma(I)$]	0.0269, 0.0651		
R indices (all data)	0.0321, 0.0684		
(b)			
Bond length (\AA)			
Hg – Cl(1)	2.4161(12)	Hg – Cl(2)	2.3706(13)
Hg – N(1)	2.498(4)	Hg – N(2)	2.371(4)
Bond angles ($^\circ$)			
Cl1 Hg1 N1	117.38(9)	Cl2 Hg1 Cl1	134.32(4)
Cl2 Hg1 N1	100.19(9)	Cl2 Hg1 N2	124.95(10)
N2 Hg1 Cl1	93.94(10)	N2 Hg1 N1	68.61(13)

Hutchison leaching method (Hutchison *et al.* 2008). As mercury, cadmium and lead are common in various acidic, alkaline, or even neutral wastewaters, therefore stability of metal chelate precipitates in certain environments may ensure their stability by their leaching tests. For this purpose, buffer solutions (pH- 4.0 ± 0.05 , pH- 7.0 ± 0.05 and pH- 9.2 ± 0.05) were prepared using Merck Buffer pHDrion capsules with 100 ml deionized water. Each precipitate, 0.249 ± 0.02 g of $[\text{Hg}(\text{PMTPM})\text{Cl}_2]$, 0.366 ± 0.02 g of $[\text{Cd}(\text{PMTPM})\text{Cl}_2]$ and 0.244 ± 0.02 g of $[\text{Pb}(\text{PMTPM})\text{Cl}_2]$ was taken in above three types of 100 ml buffer solutions separately, and stirred vigorously for 15 min. Then the solutions were covered with parafilm and kept under a fume hood for a month. Aliquots of 10 ml each, filtered using $0.2 \mu\text{m}$ syringe filters, were taken after 7, 15 and 30 days and metal concentrations analyzed in AAS.

Collection and analysis of mixed industrial wastewater

The metal removal efficiency of PMTPM was also investigated for real mixed industrial wastewater samples. For this purpose, wastewater samples were collected from a common wastewater channel in the Durgapur industrial zone, carrying effluents and discharges from various industries such as iron-steel, thermal power plant, chlor-alkali, and ferro-alloy industries (Kisku *et al.* 2000; Gupta *et al.* 2013). This channel is also used to drain the municipal wastewater originating from the residential areas. The wastewater samples were collected in wide mouth pre acid washed polythene bottles and rinsed with sample wastewater before filling up to the capacity (1 L) from three sampling stations along the contaminated wastewater channel and were immediately brought to the laboratory and stored at 4°C until further use. The pH and electrical conductivity (EC) of wastewater samples were measured on site using a portable hand analyzer (Multi-Parameter PCSTestrTM 35, Oakton). For toxic metal analysis, wastewater samples were digested with a mixture of concentrated HNO_3 and HClO_4 (3:1, v/v) at 80°C (APHA 1998) and the metal concentration quantified using AAS.

RESULTS AND DISCUSSION

Toxic metal removal study

Effect of variation of ligand concentration

The chelation efficiency of PMTPM with Hg^{2+} , Cd^{2+} and Pb^{2+} ions was gradually increased as the molar ratio (PMTPM: M^{2+}) increased from 1:1 to 3:1, then remain unchanged up to 3.5:1

(Figure 2(a)). In alkaline condition (pH = 9), the highest removal of Hg^{2+} , Cd^{2+} and Pb^{2+} ions from their aqueous solutions was observed as 99.5%, 95.54% and 94.62% respectively at 3.5:1 molar ratio after 24 h. Whereas the optimum removal efficiency was observed as 99.46%, 95.42% and 94.54% for Hg^{2+} , Cd^{2+} and Pb^{2+} respectively at PMTPM: M^{2+} = 3:1 (Figure 2(a)). The above results revealed that the higher concentration of ligand leads to better metal precipitation, which is consistent with the earlier researchers (Blue *et al.* 2008; Hutchison *et al.* 2008). The competitive precipitation of metal ions from aqueous medium was found to be $\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ for PMTPM and the results suggest that a higher PMTPM: M^{2+} leads to more effective chelation of toxic metals, whereas the selective removal efficiency of PMTPM towards Hg^{2+} is the best among the others under certain experimental conditions. Additionally, the comparative analysis of the toxic metals removal efficiency of PMTPM with a traditional inorganic agent (such as Na_2S); and some well-known ligands (such as DMDTC, STC and TMT) has been summarized in Table S1 (supplementary information, available with the online version of this paper), which indicated PMTPM has comparable or even higher metal removal capability than the others and may be considered as a promising chelating agent for toxic metal remediation from water/wastewater.

Effect of reaction time

The effect of contact time for the degree of completion of PMTPM with Hg^{2+} , Cd^{2+} and Pb^{2+} ions in aqueous solution was also investigated. For this purpose, 10 ml of samples were periodically collected after 1, 6, 12 and 24 h intervals from the reaction mixture and filtered using $0.2 \mu\text{m}$ syringe filters, and the analyzed metal concentrations are represented in Figure 2(b). The results (Figure 2(b)) clearly show an increase in removal efficiency of metal ions by PMTPM with the reaction time. A sharp increase in removal efficiency was noted during the initial stage (1–12 h), and then it slowed down (12–24 h) until an equilibrium state was reached, which was common for all three examined metal ions. The removal percentages of Hg^{2+} , Cd^{2+} and Pb^{2+} after 1 h were 90.50%, 86.25% and 85.42%, respectively, whereas the optimum removal efficiencies were achieved after 24 h following the order of Hg^{2+} (99.46%) > Cd^{2+} (95.42%) > Pb^{2+} (94.54%).

Effect of pH

The pH of the solution is the most significant factor governing the chemical precipitation of toxic metals by the ligand

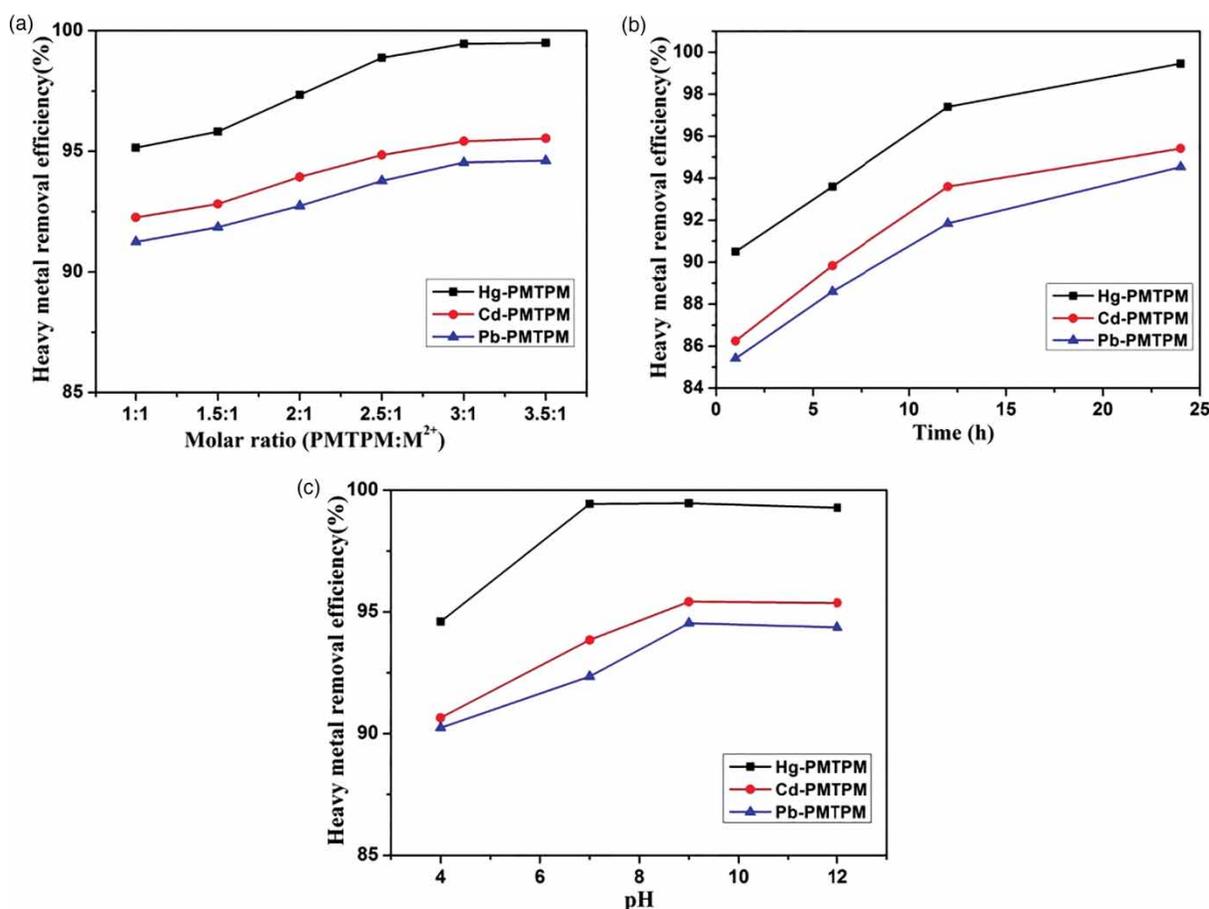


Figure 2 | (a) Toxic metal removal efficiency at different molar ratios of PMTTPM:M²⁺ (C₀ = 30 ppm, pH = 9, time = 24 h, and temp. = 30 °C); (b) the effect of reaction time for toxic metal removal from aqueous solution by PMTTPM (C₀ = 30 ppm, molar ratio, PMTTPM:M²⁺ = 3:1, pH = 9, and temp. = 30 °C); (c) toxic metal removal efficiency study with variation of pH (C₀ = 30 ppm, molar ratio, PMTTPM:M²⁺ = 3:1, time = 24 h, and temp. = 30 °C).

(Hutchison *et al.* 2008). The investigation of chemical precipitation of Hg²⁺, Cd²⁺ and Pb²⁺ ions using PMTTPM at different pH (over a range of 4–12) was conducted and is represented in Figure 2(c). In this study, the sharp increase in removal efficiency of metal ions from aqueous solution was noted up to pH = 9, after which no significant changes in removal efficiencies of the examined metals were observed. The removal efficiency of PMTTPM for Hg²⁺, Cd²⁺ and Pb²⁺ at pH = 4 were 94.6%, 90.65% and 90.24% respectively, while under identical reaction conditions the optimum removal efficiency was achieved as 99.46%, 95.42% and 94.54% for Hg²⁺, Cd²⁺ and Pb²⁺ respectively at pH = 9. However, at higher pH range when hydroxide of metals dominated, the metal ions were still present in soluble form without precipitation and there was no significant change in metal concentrations in the absence of ligand when initial metal concentrations were not so high (Chaudhuri *et al.* 2015). The metal removal efficiency of PMTTPM was comparatively higher in an alkaline medium (pH = 9)

than the others (such as Na₂S, DMDTC, STC and TMT) (Table S1, supplementary information) and suggested the use of PMTTPM for toxic metal remediation from alkaline water/wastewater.

Synthesis and characterization of metal complexes

The chloride salt of Hg²⁺, Cd²⁺ and Pb²⁺ reacted with PMTTPM ligand to form their corresponding mononuclear complexes in a mixed ethanol-water medium at ambient temperature. The yields for the metal complexes were obtained as 0.18 g (87%) for [Hg(PMTTPM)Cl₂], 0.24 g (75%) for [Cd(PMTTPM)Cl₂] and 0.13 g (71%) for [Pb(PMTTPM)Cl₂]. The newly formed complexes were stable under ambient conditions and partially soluble in acetonitrile, DMF and DMSO etc. These complexes were further characterized by physicochemical and spectroscopic tools. The FT-IR study of free PMTTPM ligand displayed strong stretches at 1,622 and 693 cm⁻¹ (Figure S4,

supplementary information, available online) which corresponds to $\nu_{\text{C=N}}$ (of imine) (Nakamoto 1970) and $\nu_{\text{C-S}}$ (of thioether) respectively (Roy *et al.* 2011). The $\nu_{\text{C=N}}$ of PMTPM for complex **1** ($1,598\text{ cm}^{-1}$), **2** ($1,604\text{ cm}^{-1}$) and **3** ($1,593\text{ cm}^{-1}$) are red shifted than the $\nu_{\text{C=N}}$ of the free ligand ($1,622\text{ cm}^{-1}$), indicating imine N coordination to metal ions (Figure 3). The high similarity of the FT-IR spectrum of complex **1**, **2** and **3** (Figure 3) suggested the chemical compositions and the structures remain the same.

Description of crystal structure of complex **1**

Crystal structure of **1**: The ORTEP view of **1** is shown in Figure 4, and the selected bond lengths and angles are listed in Table 1(a) and 1(b). A distorted tetrahedral

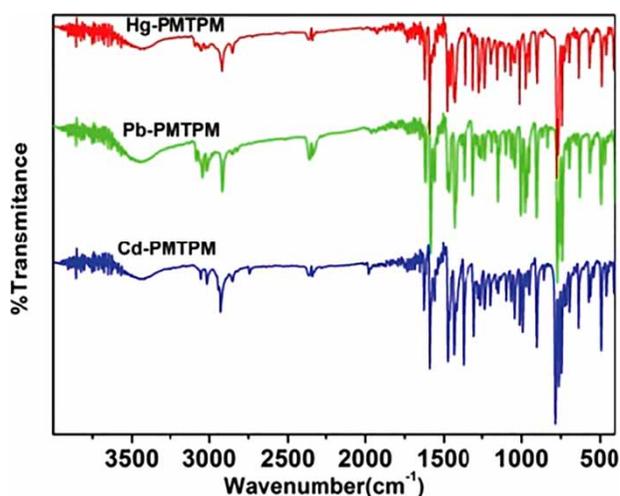


Figure 3 | FT-IR spectrum of the complexes of $[\text{M}(\text{PMTPM})\text{Cl}_2]$, ($\text{M} = \text{Hg}^{2+}$, Cd^{2+} and Pb^{2+}).

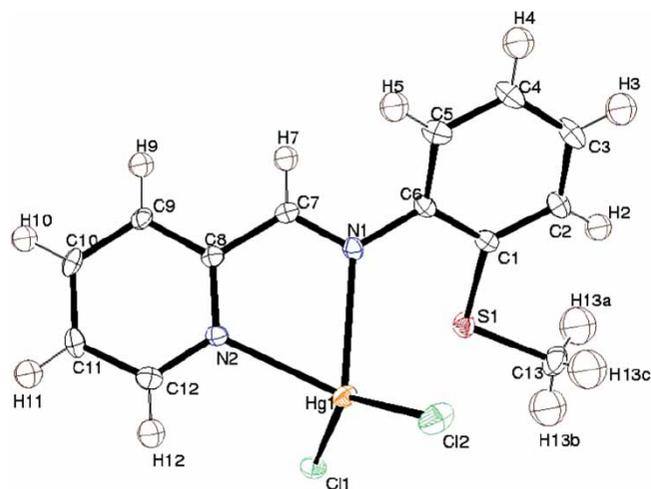


Figure 4 | Crystal structure of $[\text{Hg}(\text{PMTPM})\text{Cl}_2]$ complex.

coordination geometry around Hg is observed with two chlorine and the two N atom of PMTPM situated at the vertices of the tetrahedron. The complex is monomeric, no secondary interaction with adjacent monomeric units is structurally evident. The Hg–Cl distances of $2.4161(12)$ and $2.3706(13)\text{ \AA}$ were observed and are comparable to the previously reported X-ray structure (Hernández *et al.* 2015). Although PMTPM is a tridentate ligand that contains a soft thioether-S donor, the structure shows no coordination to Hg. Two N atoms of PMTPM are ligated to Hg adopting a five-membered chelate ring. The Hg–N distances of $2.498(4)\text{ \AA}$ and $2.2371(4)\text{ \AA}$ are observed and are comparable to the Hg–N distances of other reported complexes (Hernández *et al.* 2015). The smallest and the largest bond angles around the central Hg atom observed are $\text{N}(1)\text{--Hg}(1)\text{--N}(2)$ $68.61(13)^\circ$ and $\text{Cl}(2)\text{--Hg}(1)\text{--Cl}(1)$ $134.32(4)^\circ$.

Thermal analysis of complexes

Thermal stabilities of the compounds were examined by thermogravimetric analysis (TGA) applying a temperature range of $30\text{--}800\text{ }^\circ\text{C}$ in a static atmosphere of nitrogen. The TGA graphs of examined complexes are represented in Figure 5(a)–5(c), and data showed that the metal complexes resulted in two stages of decomposition. In the first stage, water and volatile organic components in the complexes were evaporated and complex **1**, **2** and **3** were stable up to $206\text{ }^\circ\text{C}$, $245\text{ }^\circ\text{C}$ and $196\text{ }^\circ\text{C}$, respectively. While in the second stage, further decomposition of metal complexes resulted in a sharp weight loss, as shown in the respective figures. After complete decomposition, metal oxides (probably HgO, CdO and PbO) were obtained as final residue (Roy *et al.* 2014).

Leaching study

For better understanding of the leachability of metal ions, and the stability characteristics of metal-ligand precipitates, a leaching study was performed. Earlier investigations showed appreciable metal ion removal efficiency by using various commercial chelating agents, but the produced precipitates were quite unstable in various pH media (Henke *et al.* 2000; Liao *et al.* 2008). The comparative leaching behaviour of metal ions from their respective metal-ligand complexes in various pH at different time intervals (7, 15 and 30 days) are shown in Table 2. The analytical results of leaching characteristics of metal complexes revealed that in all cases, the leachate metal concentration was increased over time and also suggested

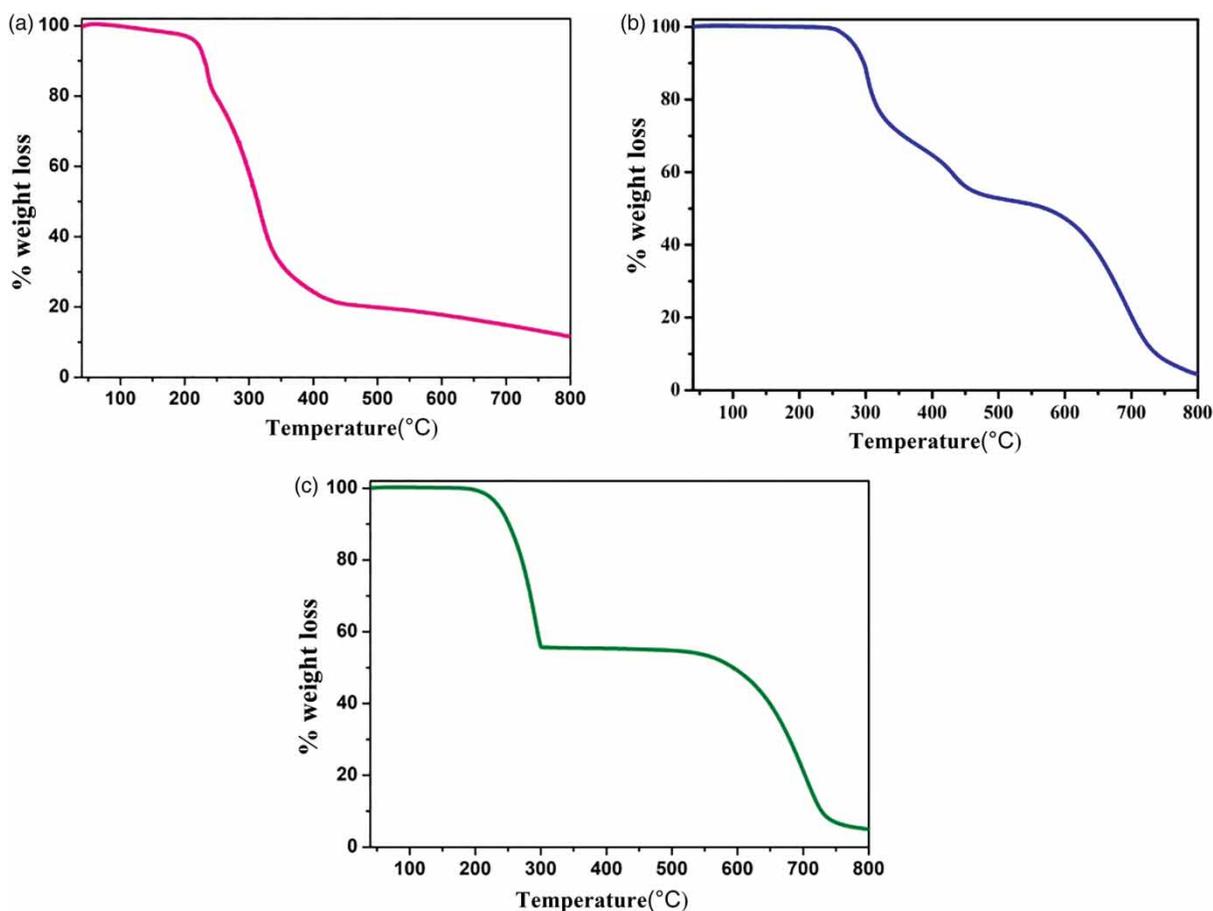


Figure 5 | TGA curve of (a) [Hg(PMTPM)Cl₂] complex, (b) [Cd(PMTPM)Cl₂] complex and (c) [Pb(PMTPM)Cl₂] complex.

Table 2 | Results of leachability and stability characteristics of [Hg(PMTPM)Cl₂], [Cd(PMTPM)Cl₂] and [Pb(PMTPM)Cl₂]

Metal	pH	Leachate metal concentration after 7 days(ppm)	Leachate metal concentration after 15 days(ppm)	Leachate metal concentration after 30 days(ppm)
Hg	4.0	0.014	0.018	0.023
	7.0	0.006	0.009	0.011
	9.2	0.007	0.009	0.010
Cd	4.0	0.026	0.034	0.065
	7.0	0.012	0.014	0.022
	9.2	0.008	0.012	0.016
Pb	4.0	0.032	0.046	0.074
	7.0	0.022	0.028	0.044
	9.2	0.021	0.024	0.032

the time for sludge removal. After 30 days' observation, the concentrations of Hg²⁺, Cd²⁺ and Pb²⁺ ions were observed as 0.023, 0.065 and 0.074 ppm, respectively, at pH = 4, whereas the concentrations of Hg²⁺, Cd²⁺ and Pb²⁺ ions were 0.01, 0.016 and 0.032 ppm respectively

at pH = 9.2. Thus the stability characteristics of metal complexes were in the order of [Hg(PMTPM)Cl₂] > [Cd(PMTPM)Cl₂] > [Pb(PMTPM)Cl₂] and showed a noticeable higher stability in alkaline condition than in acidic. The leaching phenomenon of metal precipitates was due to the variation of the stability constant of metal-ligand precipitates (Wu *et al.* 2015), and the rate of protonation and hydrolysis of imine N of metal precipitates (Wang *et al.* 2009).

Application of PMTPM in mixed industrial wastewater

Application of chemical precipitation using a chelating agent proved to be an excellent method for extracting toxic metals from industrial wastewater (Halawa & Zabin 2017). PMTPM was further applied to eliminate selected toxic metals (i.e. Hg, Cd, and Pb) from the mixed industrial wastewater sample. The pH and EC values of real industrial water samples were found as 8.77 ± 0.15 and 2.42 ± 0.35 mS.cm⁻¹ respectively. The initial concentrations of

Hg, Cd and Pb were 1.14 ± 0.12 mg/L, 0.38 ± 0.01 mg/L and 3.35 ± 0.51 mg/L, respectively. In order to find the efficiency of PMTPM in removing the metal ions from 100 ml of wastewaters, at 3:1 PMTPM:M²⁺ stoichiometry dose with stirring at 200 rpm at 30 °C was performed. After 24 h, the formation of precipitate PMTPM-M²⁺ could almost remove Hg, Cd and Pb from mixed wastewater and the removal efficiencies were found to be 99.31%, 95.26% and 94.15%, respectively. The results clearly showed that PMTPM has a higher affinity towards Hg than Cd and Pb in mixed industrial wastewater. The slight variations in metal ion removal efficiency using PMTPM may be attributed to the complex formation with other coexisting metal ions present in the mixed industrial wastewater (Blue et al. 2010). Final concentrations of metal ions (viz., Hg, 0.008 mg/L; Cd, 0.018 mg/L; Pb, 0.196 mg/L) in mixed wastewater were well under the permissible limits (i.e. 0.01 mg/L for Hg, 2.0 mg/L for Cd and 0.1 mg/L for Pb) as per BIS standards (IS 2490 Part I: 1981) and suggested PMTPM can be chosen as a suitable chemical precipitating agent for the elimination of toxic metals from real industrial wastewater.

CONCLUSIONS

In this study, a chelating agent, namely 2-pyridyl-N-(2'-methylthiophenyl) methyleneimine (PMTPM), containing pyridine and imine nitrogen and thioether-S moiety was used. This ligand, using its N-donors, could effectively remove the selected toxic metals (such as Hg²⁺, Cd²⁺ and Pb²⁺) through chemical precipitation from aqueous solution. The formed metal precipitates were characterized by FT-IR, ESI-MS, ¹H-NMR and single crystal XRD ([Hg(PMTPM)Cl₂] complex) analysis, which exhibited a distorted tetrahedral coordination geometry to the corresponding metal ions. The efficacy of metal ion removal from aqueous solution employing different experimental conditions, such as pH, contact time and metal ligand molar ratio (L:M²⁺) was investigated. The experimental results revealed that PMTPM has good binding potentiality and removal efficiency for all three metal ions at slightly higher pH values. The metal ion selectivity of PMTPM in aqueous solution followed the order of Hg²⁺ > Cd²⁺ > Pb²⁺ under optimum experimental conditions. The results also demonstrated that PMTPM could efficiently extract Hg, Cd and Pb from the real alkaline mixed industrial wastewater and reduce the metal concentrations to below their discharge limits as per BIS standards. The leaching tests

revealed higher stability of metal precipitates in alkaline condition than in acidic. TGA study showed that the thermal stability of [Hg(PMTPM)Cl₂], [Cd(PMTPM)Cl₂] and [Pb(PMTPM)Cl₂] was up to 206 °C, 245 °C and 196 °C respectively. The observation based on experimental results infers that PMTPM can effectively remove selected toxic metal ions from aqueous solution and mixed industrial wastewater and therefore can be considered as a convenient method for industrial wastewater treatment.

ACKNOWLEDGEMENTS

Authors gratefully acknowledge DST-FIST (SR/FST/CSI-267/2015 (C)) and National Institute of Technology (NIT), Durgapur, for creating and providing infrastructural facility throughout the research work.

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First received 16 September 2018; accepted in revised form 12 March 2019. Available online 22 March 2019