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# Molecular design of a novel ligand for Menshutkin complexation of Bi(III) from aqueous acidic copper sulfate electrolyte solutions and experimental investigations<sup>†</sup>

Jyotsna S. Arora and Vilas G. Gaikar\*

5-Amino-2,9-diphenoxy-1,10-phenanthroline functionalized silica is designed to reversibly adsorb bismuth impurities from strongly acidic aqueous copper sulfate solutions. The ligand interacts with Bi(III) ions through weak non-covalent interactions due to the presence of the arene- $\pi$  electron cloud of the phenyl moiety. The stronger complexation of Bi(III) as compared to Sb(III), As(III) and Cu(II) ions with the ligand was explored using Density Functional Theory (DFT) under solvated conditions. The theoretical predictions were validated by experimental studies with Bi(III)/Cu(III) mixtures in aqueous acidic solutions. The ligand shows very high selectivity ( $\alpha = 978$ ) towards Bi(IIII) in the presence of a high concentration of Cu(III) in the acidic solutions.

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# 1 Introduction

Copper is one of the most important strategic metals manufactured by electrolytic refining of blister copper anodes. The electrorefining process consists of electrochemically dissolving copper from impure anodes in aqueous sulfuric acid solutions and selectively plating the dissolved copper in a pure form onto copper cathodes. The principal interfering impurities in copper anodes are As, Bi, Fe, Ni, Pb, Sb, Se and Te.1,2 Of these impurities, most parts of Sb, As and Bi are electrochemically dissolved into the acidic solutions. Hence, the concentrations of these impurities in the electrolyte solutions increase in the course of the continuous electro-refining process.<sup>1</sup> In addition, the electrode potential of Bi(III) is very close to that of Cu(II) making it probable to plate on the Cu cathode, thus affecting the quality of copper.3 Hence, to accomplish the ASTM standards of Cu electrode, the contamination by Bi(III) ion needs to be controlled.<sup>2</sup>

Various authors have proposed the use of organophosphorus,<sup>1,4</sup> organothiophosphorus<sup>1,5</sup> compounds and hydroxamic acids<sup>1,4</sup> as ligands for removal of Bi(m) by liquid–liquid extraction. Even the use supported liquid membranes (SLM) for recovery of bismuth from aqueous solutions has been reported.<sup>2,6</sup> Co-precipitation of bismuth by addition of Ba-, Sr-/Pbcarbonates to the electrolytic solutions is also suggested by Hyvarinen *et al.*,<sup>7</sup> because of poor solubility characteristics of sulfates. However, precipitation is not advisable taking into consideration the environmental concerns associated with these heavy metal sludge generated in the process.<sup>3</sup>

Several studies have demonstrated the separation of heavy metals by adsorption.8 Wang et al.9 reported the selective adsorption of Bi(III) (98%) from copper electrolyte solutions at pH 2 (percentage adsorption (% R) of Cu(II) = 0.02) using bayberry tannin (ortho-phenolic hydroxyl groups)10 loaded collagen fiber. Though the collagen fiber is selective, it will not be able to withstand the highly acidic conditions of a typical copper electrolyte solution; viz. >18% H<sub>2</sub>SO<sub>4</sub>. The other reported adsorbents for the removal of contaminants from acidic copper solutions are chelating resins and activated carbons.8 Nagai et al.<sup>11</sup> reported the chelation of Bi(III) and Sb(III) by imino-bismethylene phosphonic acid groups bound to a phenolic matrix. However, this chelating resin suffered from the strong co-extraction of Fe(III) ion as well as its subsequent slow elution with 6 M HCl resulted in a poor quality cathode copper and loss of precious metal. Ogata et al.12 disclosed the use of a phosphomethylamine chelating resin for the selective removal of bismuth and/or antimony from the sulfuric acid solutions. However, batch adsorption experiments exhibited only ~49% and  $\sim$ 77% adsorption of bismuth and antimony, respectively, with significant copper uptake (~7%). Sasaki et al.13 used Eporous MX-2 ion exchange resin and Dreisinger et al.14 reported the use of DUOLITE C-467 and UR-3300 resins, all functionalized with aminomethylene phosphonic acid groups on a polystyrene-divinylbenzene matrix for separation of Bi(III).

For eluting and recovering Bi, most of these resins require a large excess of a strongly acidic stripping solution, typically 4–

Department of Chemical Engineering, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai-19, India. E-mail: vg.gaikar@ictmumbai.edu.in; Fax: +91-22-33612020; Tel: +91-22-33612013

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6 M concentration.<sup>14</sup> Further, for the regeneration of the stripped resin, a large volume of base would be required to treat the residual acid, making the entire process laborious, expensive as well as it generates a large amount of salt solution that must be disposed off.<sup>15,16</sup>

To overcome these problems, specific ligands need to be designed for highly selective separation of Bi(III) ions. Recent reports have explained the non-covalent interactions of arenes with heavier group 15 elements (pnictogens). These pnictogens-arene interactions play an important role in various chemical and biological processes including molecular recognition, crystal engineering, enzymatic mechanisms and supramolecular assembly design.<sup>17-21</sup> Watt et al.<sup>22</sup> described bismuth ion (Lewis acid) and aromatic ring ( $\pi$ -base) complex as "Menshutkin complexes", where donor orbitals on the arene interact with the acceptor orbitals on the metal center. Further, 1,10phenanthroline and its derivatives exhibit interesting metal complexation properties because they possess two nitrogen donor atoms situated in the same plane.<sup>23</sup> The phenanthroline moiety is locked by integrated benzo rings, which benefits thermodynamic stabilization by avoiding σ-bond rotation in their bipyridine analogues.<sup>24</sup> 1,10-Phenanthroline, therefore, often acts as a chelating ligand exhibiting high affinity towards metal ions.<sup>23,24</sup> Bi(III) ion forms a stable 5-membered chelate complex with 1,10-phenanthroline-2,9-dicarboxylic acid as Bi(III) ion possesses the right size to fit in the cleft of the diacid.<sup>25</sup>

The present study involves density functional theory (DFT) assisted design of a ligand which is highly selective towards bismuth even in the presence of large concentration of Cu(II) in aqueous H<sub>2</sub>SO<sub>4</sub> solutions. These theoretical studies were also performed with Sb(III) and As(III) ions<sup>26</sup> in order to explore the competitive complexation behaviour of Bi(III) in presence of other pnictogens and  $Cu(\pi)$  ions with the ligand. These studies provide a deeper insight of metal-ligand interaction and thus assist in the design of highly Bi-specific ligands. The complete synthesis of the ligand is described along with its covalent attachment to the silica backbone that exhibits low interaction/ binding of the target analytes<sup>27,28</sup> as well as provides chemical, mechanical and operational stability. The adsorption-desorption characteristics of the functionalised adsorbent for Bi(m) uptake in the presence of large concentration of copper ions are explored by batch adsorption experiments to support the theoretical predictions.

### 2 Computational methodology

All DFT calculations were conducted using Gaussian 09 program.<sup>29</sup> For investigating the structural and electronic properties of the designed ligand and its complexes, the dispersion corrected DFT-D3 *viz.* BP86-D3 level of theory was chosen as dispersion is important to explain the pnictogen– $\pi$  complexes.<sup>19</sup> The copper( $\pi$ ) (possessing one unpaired electron) has doublet multiplicity, while in pnictogen( $\pi$ ) ions there are no unpaired electrons. Hence, for the simulation studies of Cu( $\pi$ )–phen–arene complex surrounded by anions (HSO<sub>4</sub><sup>-</sup>), unrestricted formalism (*viz.* UBP86-D3) was considered.<sup>30</sup> The basis sets used for H, C, O, N, S was 6-31+G(d)<sup>31</sup> considering the

computational feasibility of the calculations with significant accuracy while LANL2DZ was employed for the metal ions<sup>32-34</sup> as the computed geometries of metal complexes show good agreement with the experimental data. In order to account for relativistic effects, the inner electrons were substituted by an effective-core potential (ECP).35 Natural Bond Order (NBO) charge analysis was performed using the NBO package as implemented in Gaussian 09 in order to compute the quantum chemical properties. The geometry optimization of the free ligand as well as that of the complexes was performed under solvated conditions using the Integral Equation Formalism Polarized Continuum Model (IEFPCM), which includes implicit long-range hydration, without imposing any initial symmetry restriction.<sup>36</sup> The solvent dielectric constant ( $\varepsilon$ ) was taken as 78.4, viz. the same as bulk water. The absence of imaginary frequencies during the Hessian calculations characterized the optimised structures as stationary points.

# 3 Materials and methods

### 3.1 Materials

Special chemicals, such as 1,10-phenanthroline monohydrate, 1,3-dibromopropane, potassium t-butoxide, phosphorus oxychloride, phosphorus pentachloride, hydrazine hydrate (99%), 10% Pd/C, sodium hydride, phenol (all AR grade), solvents and bulk chemicals like 98% H<sub>2</sub>SO<sub>4</sub> and 68% HNO<sub>3</sub> solutions, were used as received from s.d. Fine Chemicals, Mumbai. (1-Chloropropyl)triethoxysilane (CPTES) (>99%) and silica having pore volume of 0.8 cm<sup>3</sup> g<sup>-1</sup>, specific surface area of 550 m<sup>2</sup> g<sup>-1</sup>, and an average pore diameter of 60 Å, were obtained from Alfa-Aesar, Mumbai. Bi(III) and Cu(II) stock solutions were prepared using bismuth sulfate (Thomas Baker, >99%) and copper sulfate (s. d. Fine Chemicals, >99%), respectively, by dissolving in aqueous H<sub>2</sub>SO<sub>4</sub> solutions of appropriate strength. Standard solutions of bismuth(III) and copper(II) (ICP grade, 1000 mg  $dm^{-3}$ ) were obtained from Sigma-Aldrich, Mumbai. Deionized (DI) water obtained from Millipore, was used for all experiments.

#### 3.2 Experimental methodology

**3.2.1** Synthesis of the designed ligand. The synthesis of silica based functionalized adsorbent was investigated by the *"Retrosynthetic approach"* as described in Scheme 1, while the synthetic method for the phen-arene functionalized adsorbent is described in Scheme 2.

The first 3 intermediates, starting from 1,10-phenanthroline to 2,9-dichloro-1,10-phenanthroline (**III**), were synthesized according to the procedure reported by Guo and co-workers.<sup>37</sup> 1,10-Phenanthroline was initially protected by reacting with excess (1 : 5 molar ratio) of 1,3-dibromopropane in toluene resulting in the formation of (**I**) (97% yield). The oxidation of (**I**) was achieved with air in the presence of excess *t*-BuOK in *t*-BuOH producing the brown solid (**II**), which was used directly for the next step without any purification while the filtrate was evaporated to dryness and the solid residue obtained was purified using silica column. The total yield of (**II**) was 73%



Scheme 1 Retrosynthetic approach for phen-arene synthesis.



Synthesis of 5-nitro-2,9-dichloro-1,10-phenanthroline (IV). Sulfuric acid (20 cm<sup>3</sup>; 98%) was added over 5 min to (III) (3.3 g, 13.3 mmol) at 0-5 °C and stirred for 30 min at the same

temperature. To the resulting dark-brown solution, the nitrating mixture (HNO<sub>3</sub> :  $H_2SO_4 = 1 : 1$ ) (3.5 cm<sup>3</sup>) was added over a period of 10 min with vigorous stirring. The reaction mass was then stirred for another 45 min at the same temperature, and then the temperature of the reaction mass was raised to 60 °C



Scheme 2 Synthetic route of phen-arene formation and its covalent functionalisation on silica.

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with continuous stirring for 8 h. The reaction mass was cooled to room temperature and then carefully poured over crushed ice to afford a bright yellow solid. The solid was filtered off, washed with cold water and recrystallized from hot aqueous THF (THF : water = 4 : 0.25,  $60 \,^{\circ}$ C) to give (**IV**) as a golden yellow solid. The crystallized solid was dried at 80  $^{\circ}$ C for 8 h (2.53 g, yield 65%).

Synthesis of 5-amino-2,9-dichloro-1,10-phenanthroline (V). The nitro compound (IV) (2.5 g, 8.5 mmol) was dissolved in methanol (60 cm<sup>3</sup>) under refluxing for 30 min. The solution was then cooled and purged with N<sub>2</sub> for 30 min to remove oxygen, as its presence may result in the deactivation of the catalyst. Hydrazine hydrate (4 cm<sup>3</sup>, 8.8 mmol) and 10% Pd/C (0.5 g) were added to this solution. The reaction mixture was then refluxed for 5 h under N<sub>2</sub> atmosphere after which it was filtered under hot conditions (50 °C). The filter cake was washed well with hot methanol (45 °C). The combined filtrates were then concentrated under reduced pressure to afford the golden brown amine (V). The obtained solid is vacuum dried at 80 °C for 5 h (1.84 g, 82%).

Synthesis of 5-amino-2,9-diphenoxy-1,10-phenanthroline (VI). Alcoholic sodium hydroxide (0.64 g, 16 mmol) solution (5 cm<sup>3</sup>) was added to the mixture of phenol (1.5 g, 16 mmol) and methanol (10 cm<sup>3</sup>). To this mixture, the amino compound (V) (2.0 g, 7.6 mmol), dissolved in methanol (10 cm<sup>3</sup>), was added over a period of 15 min. The reaction mixture was refluxed for 4 h. After this, the reaction mass was cooled and poured into ice cold water and stirred. The solid was filtered, then washed with water (20 cm<sup>3</sup> × 2) and recrystallized using chloroform. The crystallized solid was vacuum dried at 80 °C for 8 h (2.18 g, 76%).

Synthesis of  $(\gamma$ -chloropropyl)triethoxysilane (CPTES)functionalized silica (silica-Cl) (**VII**). Silica-Cl (**VII**) synthesis was performed according to the procedure reported by Wang *et al.*<sup>38</sup> A total of 4 g of silica was suspended in 100 cm<sup>3</sup> of dry toluene containing 4 g of ( $\gamma$ -chloropropyl)triethoxysilane (CPTES) as silylation reagent. The reaction mixture was stirred for 24 h at 90 °C under N<sub>2</sub> atmosphere. The resulting powder, denoted as silica-Cl (**VII**), was filtered and washed with toluene (30 cm<sup>3</sup> × 2), ethanol (30 cm<sup>3</sup> × 2), and diethyl ether (30 cm<sup>3</sup> × 2), respectively. The solid was dried in vacuum at 80 °C for 12 h.

Synthesis of silica bound phen-arene ligand (VIII). Hybrid mesoporous material (silica-phen-arene) was synthesized by an elimination reaction of silica-Cl (VII) with phen-arene ligand (VI). 2.0 g of silica-Cl was dispersed in 70 cm<sup>3</sup> toluene under N<sub>2</sub> atmosphere. To this mixture, a solution of (VI) (1.52 g, 8 mmol) in toluene was added over 10 min. The reaction mass was refluxed for 24 h in N<sub>2</sub> atmosphere. The resulting product was filtered and washed with toluene ( $30 \times 2 \text{ cm}^3$ ), methanol (20 cm<sup>3</sup>), and diethyl ether ( $20 \text{ cm}^3$ ), in sequence, to obtain (VIII) as yellowish solid. The solid was dried in vacuum at 80 °C for 10 h (yield = 2.86 g).

**3.2.2 Batch adsorption studies.** The first set of adsorption experiment was conducted with aqueous acidic Bi(m) solutions without Cu(n). Batch sorption studies were conducted by suspending varying amounts (0.1–0.5 g) of the silica–phene–arene in stoppered conical flasks, each containing initially 20 cm<sup>3</sup> of

aqueous acidic bismuth solution (free  $H_2SO_4$  concentration = 180 g L<sup>-1</sup>; [Bi] = 96.9 ppm). The flasks were kept on an orbital shaker with an agitation rate of 100 strokes per min at an ambient temperature of  $60 \pm 2$  °C (ref. 6 and 8) for 24 h. The residual metal-ion concentration was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) as described later in this report.

The kinetics of Bi(m) uptake was studied separately at  $60 \pm 2$  °C using 100 cm<sup>3</sup> ( $V_0$ ) of aqueous acidic Bi(m) solution in 2 M H<sub>2</sub>SO<sub>4</sub> and 1.5 g of silica–phen–arene. The samples ( $V_t = 1$  cm<sup>3</sup>) were withdrawn at regular intervals from the solution and to maintain the volume of the solution constant during the experiment, an equal amount of 2 M aqueous H<sub>2</sub>SO<sub>4</sub> solution was added to the solution.

For competitive batch sorption of Bi(m) in the presence of Cu(n), the adsorbent was equilibrated with 20 cm<sup>3</sup> of copper electrolyte solution ( $[H_2SO_4] = 180 \text{ g L}^{-1}$ ;  $[Cu] = 36\ 000 \text{ ppm}$ , [Bi] = 96.9 ppm). The flasks were kept on an orbital shaker with an agitation rate of 100 strokes per min at an ambient temperature of  $60 \pm 2$  °C for 24 h to reach equilibrium. The residual metal-ion concentrations were measured by ICP-OES.

The elution of Bi(m) was performed by using 0.02 M aqueous EDTA solutions as an eluent.<sup>9</sup> The Bi(m) loaded phen–arene functionalized silica was equilibrated with the eluent for 3 h at 30 °C. The mixture was then filtered and the resulting solution was analysed for Bi(m) and Cu(n) concentration on ICP-OES. The adsorbent was washed thoroughly with DI water, dried at 80 °C and was recycled in the subsequent four-cycles of adsorption–desorption experiments.

#### 3.3 Characterization methods

The infrared spectra of the intermediates, the ligand and the ligand functionalised silica were recorded using Bruker-VERTEX 80V vacuum FTIR spectrophotometer aligned with Ultra-Scan interferometer in KBr pellets. The Thermo-Finnigan Mass Spectrometer was used to perform mass spectrometry electrospray ionization (MS/EI) of the organic compounds by dissolving the samples in methanol. D<sub>2</sub>O and CDCl<sub>3</sub> were used as solvents to record the <sup>1</sup>H NMR spectra using a Bruker DPX-300 (300 MHz) spectrometer at 25 °C. All of the chemical shifts were reported in the standard  $\delta$  notation of parts per million. The solvent proton signals are observed at: D<sub>2</sub>O 4.66 ppm and CDCl<sub>3</sub> 7.27 ppm. The CHN(O) contents in the grafted adsorbent were determined on the Perkin-Elmer 240B Elemental Analyser. The surface area of the grafted adsorbent was obtained from nitrogen adsorption-desorption isotherms using the Micrometrics ASAP2020 instrument. Prior to the testing, the samples were degassed at 100 °C overnight in the degassing port of the adsorption analyzer. The Barrett-Joyner-Halenda (BJH) algorithm on the adsorption branch was used to calculate the pore size distribution while the pore volume was investigated at the  $P/P_0$  0.973 single point.

The metal ion concentrations during the adsorption studies were determined using ICP-OES (Thermo Fisher Scientific, iCAP, 6000). The charge-coupled device (CCD) was used along with a radiofrequency (RF) generator exhibiting power and frequency of 1400 W and 27.12 MHz, respectively. Argon with flow rates of 0.8, 1 and 12  $dm^3 min^{-1}$ , respectively, was used as the nebulizer gas, auxiliary gas, and also for the generation of plasma. The pump speed was maintained at 50 rpm for injecting the samples into the plasma.

# 4 Results and discussion

### 4.1 Ligand design

The structure of the ligand to coordinate with a particular metal is determined by four factors: (1) *chemical hardness and softness of the metal ion*; (2) *types of donor atoms* (3) *ligand pre-organization* and (4) *coordination geometry*.<sup>39,40</sup> According to Pearson's hard and soft acid–base principle, Bi(III) and Cu(II) are both borderline metal cations.<sup>41</sup> Hence, donors like sp<sup>2</sup> hybridized aromatic nitrogen would be the best choice in highly acidic solutions.<sup>42</sup> 1,10-Phenanthroline and its derivatives have shown interesting properties because they have two nitrogen donor atoms situated in the same plane and often act as a chelating ligand due to their high affinity to metal ions.<sup>18,19,42</sup> Further, Cu(II) belongs to the 1<sup>st</sup> transition series while Bi(III) ion is a group 15 element, which are also known as pnictogens. Several authors have reported pnictogen– $\pi$  interaction which has wide applications in supramolecular assembly design.<sup>17–21</sup> On the other hand; these metal– $\pi$  interactions are not very regular for copper ions. Hence, to ensure selective uptake of only Bi(III) ions, a ligand comprising of both: sp<sup>2</sup> hybridized aromatic nitrogen from 1,10-phenanthroline and an arene moiety capable of donating its  $\pi$  electrons was designed.

### 4.2 Optimized structure of the ligand

The optimized structure of the ligand under solvated conditions shows the phenanthroline ring to be planar while phenolate moieties at 2 and 9 positions of 1,10-phenanthroline ring are perpendicular to ring (Fig. 1(A)). This results in formation of an open cavity which is rich in electrons, contributed by the 'N' atoms of phenanthroline and the  $\pi$  electron cloud of two parallel phenyl rings. Hence, the mapped electrostatic potential energy (MESP) surface as shown in Fig. 1(B) exhibits significant negative charge within the open cavity which should be capable



Fig. 1 (A) Optimized structure, (B) MESP surface (C) HOMO and (D) HOMO-1 of phen-arene ligand.

Table 1 Geometrical parameters of optimized phen-arene ligand

Paper

Bonds	Bond distances (Å)	Bonds	Bond distances (Å)	Bond angle	Degree
C15=C16	1.445	C5=C6	1.399	C19-O29-C5	122.2
C15=N23	$1.374(1.352)^{a}$	C5-C4	1.397	O29-C5-C6	122.4
N23=C19	$1.317(1.322)^a$	C6-C1	1.401	C19-N23-C15	118.8
C19-O29	1.401	C4-C3	1.403	C16-N24-C20	$119.3 (119.1)^{a}$
O29-C5	1.418				

<sup>*a*</sup> The experimental XRD values for similar system are given in parenthesis (Warad *et al.*<sup>43</sup>).

of attracting the metal ions. The optimized parameters of the ligand (VI), before the metal complexation, are given in Table 1. The bond distances and bond angles of the ligand (VI) are compared with the XRD values of a similar compound *viz.* 2,9-dimethyl-4,7-diphenyl[1,10]phenanthrolinedium crystals: the  $C_1$ =N ('C' of central benzyl ring of phenanthroline) = 1.352 Å, N=C\_2 ('C' of the pyridinyl ring) bond distance = 1.322 Å and  $C_1$ -N- $C_2$  bond angle is 119.1°.<sup>43</sup> These experimental values are in close agreement with the computed values of the ligand.

The orbital analysis of the ligand shows that the highest occupied molecular orbital (HOMO) has major contributions from the 'C' (C22, C11, C16 = 10% each while C15 = 11%; C12 and C13 = 22% each) and 'N' (N24 = 10%) atoms of phenanthroline. For the next occupied molecular orbital (HOMO-1), the orbital density is mainly due to the contributions of C11 (14%), C18 (12%) as well as the phenolate moiety (O28 = 12%, C4 = 10%, C31 = 10%). Hence, both HOMO and HOMO-1 would be involved in the metal complexation (Fig. 1(C) and (D)).

#### 4.3 Optimized structures of the complexes

The interaction between phen–arene ligand and the metals (Bi( $\pi$ ), Sb( $\pi$ ), As( $\pi$ ) and Cu( $\pi$ )) along with its counterions can be discussed in terms of the quantum chemical properties. The parameters, electronegativity ( $\chi$ ), hardness ( $\eta$ ) and the electrophilicity index ( $\omega$ ) were calculated using eqn (1)–(3), respectively (Table 2).

$$\chi = \left(\frac{-(E_{\rm LUMO} + E_{\rm HOMO})}{2}\right) \tag{1}$$

$$\eta = E_{\rm LUMO} - E_{\rm HOMO} \tag{2}$$

$$\omega = \chi^2 / 2\eta \tag{3}$$

Pearson<sup>44</sup> affirmed that electronic flow will occur from the molecule with the lesser electronegativity ( $\chi$ ) (the organic

 
 Table 2
 Electronegativity and electrophilicity index values for metalanion complex and the ligand

χ	η	ω
0 1383	0 1382	0.0720
0.2563	0.3104	0.1058
0.2175	0.2546	0.0929
0.2016	0.2291	0.0887
0.1987	0.2287	0.0863
	χ 0.1383 0.2563 0.2175 0.2016 0.1987	χ         η           0.1383         0.1382           0.2563         0.3104           0.2175         0.2546           0.2016         0.2291           0.1987         0.2287

molecule) towards that of higher value (metal ion) when considering an interacting system of two species differing in the electronegativities. Moreover, the more reactive nucleophile is supposed to have a lower value of  $\omega$  while the opposite is affirmed for an electrophile.<sup>45</sup> In the present study, the ligand exhibits lower  $\chi$  and  $\omega$  values as compared to the metal-anion species (Table 2). These values signify that the phen-arene ligand is nucleophilic and thus interacts well with the metal ions forming complexes.

The optimized geometries of the individual complexes of bismuth, antimony, arsenic and copper ions, surrounded with counterions  $(\text{HSO}_4^{-}/\text{SO}_4^{2-}/\text{OH} \text{ ions})$ , are shown in Fig. 2. The  $[\text{HSO}_4^{-}]/[\text{SO}_4^{2-}]$  ratio of 1.4–1.7 was reported by Margarella *et al.*<sup>46</sup> at 2.0 M H<sub>2</sub>SO<sub>4</sub>. Hence, to maintain the electroneutrality of the complexes, the metal ions (Bi, Sb and Cu) are surrounded by appropriate number of  $\text{HSO}_4^{-}$  and  $/\text{SO}_4^{2-}$  counterions.<sup>47</sup> However, As(III) does not exhibit coordination with  $\text{HSO}_4^{-}$  and  $/\text{SO}_4^{2-}$  counterions. Casas *et al.*<sup>48</sup> discussed the aqueous speciation of arsenic in cupric sulfate–sulfuric acid solutions and predicted that at the high H<sub>2</sub>SO<sub>4</sub> concentration (pH < 2), the dominant As(III) species is neutral H<sub>3</sub>AsO<sub>3</sub>. The bond distance values as well as the interaction energy ( $\Delta E$ )<sup>45</sup> of the complexes, estimated by using (eqn (4)), are given in Table 3.

$$\Delta E = E_{\text{complex}} - (E_{\text{ligand}} + E_{\text{metal-anion species}})$$
(4)

where, *E* is the total energy of the optimized structure. The interaction energies of all the metal complexes are negative showing attractive interactions of the metal ions with the ligand. Out of the three pnictogens, Bi(m) interacts strongly with the phen–arene ligand followed by Sb(m), As(m) and least interaction is observed for Cu(n) ions. Further, the  $\Delta E$  value for Bi(m) complex is almost twice that of the Cu(n) complex.

The greater tendency for Bi(m) complexation by the ligand is due to the presence of weak non-covalent interactions between the Lewis acid pnictogen and Lewis base  $\pi$ -electrons in addition to the 'N' atoms of the phenanthroline ring. Of the four oxygen atoms in the HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions, only one of the oxygen atoms coordinates with Bi(m) ion. Similar observation was discussed by Andrews *et al.*,<sup>49</sup> where the oxygen atoms of SO<sub>4</sub><sup>2-</sup> exhibited  $\eta^1$  coordination mode with bismuth in [Bi<sub>8</sub>(O<sub>3</sub>-SMes)<sub>20</sub>(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>] complex. Further, the lowered interaction of As(m) (existing as H<sub>3</sub>AsO<sub>3</sub>) can be attributed to its lowered Lewis acidity (compared to Bi(m) and Sb(m)) and its presence within the hostile electron rich cavity of the ligand. Similar trend of pnictogen interaction with benzene was reported by



Bi(III)+phen-arene

Sb(III)+phen-arene



### As(III)+phen-arene



Cu(II)+phen-arene

Fig. 2 Optimized structures of metal-ligand complexes.

Table 5 Optimized geometrical parameters of metal-ligand complexes and its comparison with reported AND value	Table 3	Optimized geometric	cal parameters of meta	al-ligand complexes	and its comparison wit	h reported XRD values
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		M–O, Å		M-N, Å		M-pi, Å	
Complex	$\Delta E$ , kcal mol <sup>-1</sup>	Calc.	XRD	Calc.	XRD	Calc.	Lit.
Bi(m)	-498.15	$2.19 (SO_4^{2-})$	2.29*	2.31	2.53**	3.56-3.77	#3.47-3.96
Sb(III)	-405.87	2.25 (HSO <sub>4</sub> ) 2.31 (SO <sub>4</sub> <sup>2-</sup> ) 2.24 (HSO <sup>-</sup> )	<sup>1a</sup> 2.42, <sup>1b</sup> 2.25	2.33, 2.35	<sup>1c</sup> 2.24, 2.39	3.59-3.78	<sup>1d</sup> 3.20–3.61
As(m) Cu(п)	-321.62 -257.64	$\begin{array}{c} 2.34 \ (\mathrm{HSO}_4^-) \\ 1.78, \ 1.80, \ 1.84 \ (\mathrm{OH}) \\ 2.21 \ (\mathrm{HSO}_4^-) \end{array}$	<sup>1e</sup> 1.78 <sup>a</sup> 1.94–2.39	2.72 1.99	<sup>b</sup> 2.03	3.34-3.47 3.63-3.88	<sup>1d</sup> 3.20–3.45 —

<sup>*a*</sup> \*Graunar & Lazarini,<sup>50</sup> \*\*Feng *et al.*,<sup>51</sup> <sup>1a</sup>Zimmermann *et al.*,<sup>52</sup> <sup>1b</sup>Mercier *et al.*,<sup>53</sup> <sup>1c</sup>Yin and Zhai,<sup>54</sup> <sup>1d</sup>Watt *et al.*,<sup>22</sup> <sup>1e</sup>Farquhar *et al.*,<sup>55</sup> <sup>#</sup>Auer *et al.*<sup>21</sup> <sup>a</sup>Yang *et al.*,<sup>56</sup> <sup>b</sup>Yan-Ju *et al.*;<sup>57</sup> Zhang *et al.*,<sup>58</sup>

Bauzá *et al.*<sup>19</sup> The geometrical parameters for the complexes are compared with the reported XRD values of similar systems (Table 3).

Next, the effect of counterion (*viz.*  $Cl^-$  and  $SO_4^{2-}/HSO_4^-$ ) coordinating the metal was observed on Bi(m) and Cu(n) complexation with the ligand. Here too Bi(m) which is surrounded by  $Cl^-$  ions interacts more with phen-arene as compared to Cu(n) ions. The DFT optimized geometry of the complexes and their parameters are given in Fig. 3 and Table 4, respectively. These optimized parameters are compared with XRD parameters for similar systems.

As compared to the  $SO_4^{2-}/HSO_4^{-}$  anions, when Cl<sup>-</sup> counterions are surrounding the metal, slightly greater interaction between the metal and ligand is observed. According to the Hofmeister series, the  $SO_4^{2-}$  anions as classified as *kosmotropic* (*viz.* hydration shell around the anion influences its interaction with the metal) while Cl<sup>-</sup> ions are *chaotropic* (anions interact directly with the metal).<sup>63</sup> This influence of direct Cl<sup>-</sup> binding to the metal, thus significantly influences the metal–counterion–ligand complexation. This observation is similar to the results discussed by Vaid *et al.*<sup>64</sup> for Cu(II) adsorption in Cl<sup>-</sup> and  $SO_4^{2-}$  media.



Cu(II)+phen-arene

Fig. 3 Optimized structures of metal-ligand complexes surrounded by Cl<sup>-</sup> ions.

Santiago-Santiago et al.<sup>2</sup> have reported the use of HCl/H<sub>2</sub>SO<sub>4</sub> mixed media for the separation of Bi(m) and Sb(m) using Cyanex 921 on SLM. But in the present study, the focus was to selectively separate Bi(III) from the copper-sulfuric acid solution without any addition of HCl solution. Hence for experimental studies, the selectivity of Bi(m) in presence of large concentration of Cu-sulfuric acid solution was investigated.

5-Amino-2,9-diphenoxy-1,10-phenanthroline is a symmetrical molecule and hence the 2<sup>nd</sup> and the 9<sup>th</sup> positions of phenanthroline ring can be easily arylated. The details of complete characterization (FTIR, ESI-MS and <sup>1</sup>H-NMR) of the intermediates (IV and V) and the ligand (VI) are given in ESI along with their <sup>1</sup>H-NMR spectra (Fig. S1 to S3<sup>†</sup>).

The functionalization of the ligand (VI) to the silica backbone was achieved by covalent bonding of (VI) to the silica backbone via the amino group at the 5<sup>th</sup> position of 1,10-phenanthroline ring and the chloro group of  $\gamma$ -chloropropyl silica (VII). This is achieved by primarily chlorinating the silica surface. The presence of three new bands at 618 cm<sup>-1</sup> indicates C-Cl stretching while the bands at 2854 and 2959 cm<sup>-1</sup> correspond to  $v_s$  and  $v_{as}$  aliphatic C-H stretching frequencies (Fig. S4<sup>†</sup>). These frequencies are absent in the untreated silica. The specific BET surface area of silica-Cl was 436  $m^2 g^{-1}$  with an estimated pore size and pore volume of 47 Å and 0.67  $\text{cm}^3 \text{ g}^{-1}$ , respectively (Table 5).

The covalent attachment of the ligand (VI) on silica-Cl surface (VII) is characterized by the presence of new bands for C=N stretching (1640  $\text{cm}^{-1}$ ), C-O stretching (1026  $\text{cm}^{-1}$ ) and

Table 5 Textural properties of the adsorbent

Material	Specific BET surface area $(m^2 g^{-1})$	Pore size (Å)	Pore volume $(cm^3 g^{-1})$
Silica	550	60	0.8
Silica-Cl	436	47	0.67
Silica-phen-arene	321	39	0.59

aromatic C-H stretching (3065 cm<sup>-1</sup>) with the elimination of C-Cl band. In addition to this, slight shifts in the symmetric plus asymmetric bands of aliphatic C-H as well as the characteristics bands of silica explain the functionalization of ligand on the silica backbone (Fig. 4). The physicochemical properties of the functionalized adsorbent (VIII) were: specific BET surface area = 321 m<sup>2</sup> g<sup>-1</sup>, pore size = 39 Å, pore volume = 0.59 cm<sup>3</sup> g<sup>-1</sup> and amine loading = 30% (Table 5).

The presence of chemically bound ligand on silica support ensures improved operational stability and pre-organization of the ligand. This adsorbent is different from chelating resins as it does not involve ion exchange and has the following advantages: (1) enhanced metal ion uptake rates, due to higher porosity, open pore structure and non-swelling characteristics; (2) resistance to chemical oxidation; and (3) easy and selective regeneration.65 The advantage of having phenanthrolinephenolate ligand functionalized on silica backbone in the current study is the exceptional stability of silica in sulfuric acid solutions and the presence of selective non-covalent interaction of ligand with bismuth (Lewis acid) by the arene- $\pi$  electrons provided by phenolate moiety. This pnictogen-arene noncovalent interaction can thus enable higher affinity and selective interaction of bismuth (pnictogen ion) with the ligand as compared to copper (transition metal ion).

#### 4.4 Batch adsorption studies

4.4.1 Effect of the adsorbent concentration. For the efficient uptake of the metal ion from the aqueous solutions, the adsorbent concentration plays a vital role. Hence for quantitative uptake of the metal by the adsorbent, the adsorbent concentration needs to be optimized.66 Therefore, the quantitative sorption of Bi(III) from the acidic solution was studied by varying the adsorbent concentration between 0.1 and 0.5 g. The

Table 4 Optimized geometrical parameters of metal-ligand complexes surrounded by chloride ions and its comparison with reported XRD values<sup>a</sup>

	$\Delta E$ , kcal mol <sup>-1</sup>	M–Cl, Å		M-N, Å		M–pi, Å	
Complex		Calc.	XRD	Calc.	XRD	Calc.	Lit.
Bi(m)	-505.65	2.48 2.50	<sup>\$</sup> 2.44-2.51 <sup>\$</sup>	2.45	<sup>\$\$</sup> 2.48	3.34-3.49	#3.47-3.96
Cu(II)	-282.27	2.53 2.27 2.31	$^{f}2.34$	2.46 1.99	$^{*^{\$}2.53}_{f1.98}$	3.52-3.71	_

<sup>a</sup> <sup>\$</sup>Vezzosi et al.,<sup>59</sup> <sup>\$\$</sup>Imran et al.,<sup>60</sup> \*<sup>\$</sup>Feng et al.,<sup>51</sup> <sup>f</sup>Mao et al.,<sup>61</sup> <sup>g</sup>Zhang et al.,<sup>62</sup> <sup>#</sup>Auer et al.<sup>21</sup>



Fig. 4 Comparison of the FTIR spectra of silica-Cl and phen-arene functionalized silica.

metal ion uptake was estimated as (% R) (eqn (5))<sup>45</sup> and adsorption capacity per unit weight of adsorbent,  $Q_{av}$ , given by eqn (6),<sup>45</sup> respectively.

$$\% R = \frac{(C_{\rm o} - C_{\rm e})}{C_{\rm o}} \times 100$$
(5)

$$Q_{\rm av} = \frac{(C_{\rm o} - C_{\rm e}) \times V_{\rm s}}{W_{\rm s}} \tag{6}$$

where  $C_o$  and  $C_e$  are the initial and residual metal ion concentrations,  $V_s$  is the volume of the aqueous metal solution while  $W_s$  is the weight of the adsorbent. The uptake of Bi(m) increased with the increase in the amount of the suspended adsorbent from 0.1–0.3 g (Fig. 5(A)). However, on addition of 0.4 and 0.5 g of the adsorbent, % *R* remained almost constant, achieving equilibrium. Thus, 0.3 g of the adsorbent was used for competitive adsorption experiments (Fig. 5(A)).

**4.4.2** Adsorption kinetics. The metal uptake at any time  $(Q_{t,i}) \pmod{g^{-1}}$  is given by eqn (7)<sup>67</sup>

$$Q_{t,i} = \frac{(C_{\rm o} - C_{t,i}) \times V_0 - \sum_{2}^{i-1} C_{t,i-1} \times V_t}{W_{\rm s}}$$
(7)

where,  $C_{t,i}$  is the metal concentration at any time  $t_i$ . The kinetic data for Bi(m) adsorption on phen–arene functionalized silica was modeled using *pseudo* first-order kinetics as given in eqn (8).<sup>45</sup>

$$\log(Q_{\rm e} - Q_t) = \left(-\frac{k_1}{2.303}\right)t + \log Q_{\rm e}$$
 (8)

where  $Q_e$  and  $Q_t$  are the amounts of Bi(m) adsorbed onto the functionalized adsorbent at equilibrium and at time t, respectively, while  $k_1$  is the rate constant. At first, the adsorption rate increases rapidly due to the availability of fresh active sites for metal complexation and reaches 63% in about 6 h. However, with increase in time, adsorption becomes slower and reaches equilibrium (~92%) after 24 h. Hence, the acidic metal solution was equilibrated with the adsorbent for minimum of 24 h. As seen from Fig. 5(B) the experimental data exhibits a satisfactory



Fig. 5 (A) Effect of adsorbent concentration on % adsorption of Bi(III) (B) adsorption kinetic data (C) adsorption-desorption cycle.

fit with the *pseudo*-first-order kinetic model. The parameter,  $Q_{e,exp} = 4.04 \text{ mg g}^{-1}$  is in agreement with the  $Q_{e,cal} = 4.03 \text{ mg}$  $g^{-1}$  and the rate constant  $k_1$  is 0.236 g (mg h)<sup>-1</sup>.

**4.4.3 Co-adsorption studies.** To evaluate the selectivity of the ligand towards Bi(m) from copper electrolytic solutions, the competitive sorption studies were performed at 60 °C for 24 h. The distribution coefficient,  $K_d$  (dm<sup>3</sup> g<sup>-1</sup>) and selectivity ( $\alpha$ ) were calculated using eqn (9) and (10), respectively.<sup>45</sup>

$$K_{\rm d} = \frac{(C_{\rm o} - C_{\rm e}) \times V_{\rm s}}{W_{\rm s} \times C_{\rm e}}$$
(9)

$$\alpha = \frac{K_{\rm d,Bi}}{K_{\rm d,Cu}} \tag{10}$$

It was found that Cu(II) exhibited almost negligible complexation with the adsorbent while Bi(III) interacted strongly with the functionalized adsorbent. The adsorption constants  $K_d$  (eqn (9)) for the binary mixture of Bi(III) and Cu(II) are 0.548 and  $5.6 \times 10^{-4}$ 

Table 6 Competitive adsorption of Bi(III) from copper electrolytic solution at 60  $^\circ\text{C}$ 

W <sub>s</sub> , g	C <sub>o</sub> ; ppm	<i>C</i> <sub>e</sub> ; ppm	% R	$Q_{\rm av}$ ; mg g <sup>-1</sup>	$K_{\rm d};{\rm dm}^3~{\rm g}^{-1}$	α
0.3	Bi 96.9	10.5	89.2	5.76	0.548	978
	Cu 36 000	35 730	0.83	19.9	0.00056	

dm<sup>3</sup> g<sup>-1</sup>, respectively (Table 6). The selectivity factor ( $\alpha_{Bi(III)/Cu}$ ) (eqn (10)) for Bi(m) and Cu(n) mixture with 0.3 g of adsorbent is 978. These results clearly indicate stronger interaction of Bi(m) with the functionalized adsorbent as compared to Cu(n).

For the reusability of the functionalized adsorbent, the metal loaded adsorbents were equilibrated with 0.02 M EDTA. Fig. 5(C) shows the % *R* of Bi(III) on the immobilized adsorbent for four consecutive adsorption–regeneration cycles. The % *R* for Bi(III) slightly decreased from (89.2 to 86.3%) in all the four cycles. However, the % desorption is very high ~98% for Bi(III) ions. This behavior should be attributed to the intensive chelating interaction between Bi(III) with EDTA (stability constant log  $\beta$  of Bi(III)–EDTA complexes is 22.8),<sup>39</sup> hence resulting in almost complete desorption of Bi(III) from silica–phen–arene. Furthermore, % *R* of Cu(II) ions decreased from 0.57 to 0.36 in the four adsorption cycles, while the % desorption was nearly 90–93% for the four consecutive runs. The reported stability constant (log  $\beta$ ) of Cu(II)–EDTA complex is 18.8.<sup>68</sup>

The selective adsorption of Bi(m) from copper electrolytic solution by silica–phen–arene adsorbent was compared with some of the reported adsorbents. Majority of the reported adsorbents are ion-exchangers in which the phosphoaminomethyl moiety is the active functional group. *UR-3300S Resin* and *Duolite C-467 Resin* reported by Gabai *et al.*<sup>8</sup> exhibited ~95% Bi(m) uptake as compared to the existing phen–arene adsorbent which exhibits ~89% adsorption in presence of large Cu(n) ions. However, Gabai and coworkers<sup>8</sup> have not discussed the selectivity of the ion-exchangers towards Cu(n) ions. In addition, the phosphomethylamino chelate resin reported by Ogata *et al.*<sup>12</sup> exhibits ~49% Bi(III) and ~7% Cu(II) uptake. As compared to the current adsorption study, these reported metal uptake values are ~0.5 times less for Bi(III) while ~12 times higher for Cu(II) ions.

Further, the estimated product cost for silica functionalized phen-arene adsorbent was evaluated. It comprised of raw material and reagents costs along with utilities. The cost estimates for the lab-scale production of the sorbent is  $\sim$ \$19.5 per g. The recovery and reuse of solvents, catalysts, and few other reagents can further help to offset the overall production cost making this novel adsorbent affordable and feasible for industrial applications. The cost comparison of phen-arene with the available ion-exchangers is difficult to obtain due to lack to enough database providing the price of these resins.

Thus, the silica-phen-arene adsorbent is effective for Bi(m) removal from Cu(n) solution that can surmount the shortcomings of the usual ion-exchange process, demonstrating efficient separation of Bi(m) from acidic copper solutions.

### 5 Conclusions

An effective adsorbent for selective removal of Bi(m) from aqueous acidic copper solution was designed and synthesized. The ligand exhibited weak non-covalent metal– $\pi$  interactions with Bi(m) surrounded by counterions. The geometrical parameters evaluated from the DFT studies of the ligand and the metal–ligand complexes are in good agreement with the bond distance values for similar compounds. The experimental studies show high selectivity ( $\alpha = 978$ ) for Bi(m) over copper even when the latter is present large excess. The adsorbent can be repeatedly used over four adsorption–desorption cycles without a significant drop in the metal uptake values.

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