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Azomethine-functionalized task-specific ionic liquid for diversion of toxic metal ions in the aqueous environment into pharmacological nominates

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ABSTRACT

By this work, a new azomethine-supported task-specific ionic liquid (ABIIL) was fabricated based on bis-(butylimidazolium hexafluorophosphate) salicylidene Schiff base. The successful formation of ABIIL was confirmed form its microanalytical and spectral results. The excellent aqueous-ethanolic solubility coupled with the high chelating capacity of ABIIL enabled it to act as a multifunctional scavenger for removing of Cu(II) and Fe(III) ions from aqueous environments. Not only has that, but also transformed these toxic ions into promising pharmacological candidates. ABIIL showed an excellent scavenging efficiency, as it can uptake up to 98.9% and 96.7% of Fe(III) and Cu(II) ions, respectively, from aqueous-ethanolic effluents. Besides, it could be easily regenerated and reused for six cycles without significant loss in its efficiency. The scavenging outputs (M-ABIIL) exhibited excellent and broad-spectrum antimicrobial activity, with a slight preference toward fungi than bacteria. Fe-ABIIL is the most potent antimicrobial nominate as revealed from its MIC values (μg/mL): 16.8 (*C. albicans*) < 18.9 (*S. aureus*) < 19.5 (*A. flavus*) < 23.1 (*E. coli*). Additionally, this complex is more cytotoxic (IC_{50} 3.40 ± 0.53 μg/mL) than the clinical anticancer drug (Vinblastine, VB) (IC_{50} 3.79 ± 1.01 μg/mL) toward colon cancer cells (HTC116), whereas it is less cytotoxic (IC_{50} 85.66 ± 1.44 μg/mL) than VB (IC_{50} 57.12 ± 1.95 μg/mL) to normal human cells (HeLa). Thus, ABIIL has great potential for removing toxic Cu(II) and Fe(III) ions from aqueous environments, converting them into chemotherapeutic agents.

1. Introduction

Ionic liquids (ILs) have been categorized as eco-friendly alternatives for traditional toxic organic solvents due to their amazing characteristics such as promoted mechanical and thermal stability, high solubilization power, reusability, tunable chemical/ physical properties, non-volatility, non-flammability, and intrinsic conductivity [1]. Moreover, the toxicity study revealed that most of ILs showed relatively low toxic impacts toward several biological systems [2]. These unique features of ILs make them the best choice for many researchers to design and refine their chemical structures (i.e. fine-tuning the cation and/or anion), rendering them inimitably suited for many applications [3]. These functionalized ILs often referred to as task-specific ionic liquids (TSILs) which have been designed, fabricated, and tuned by modification their chemical constituents according to the user's needs. For instance, they explored their specific efficiency in organic synthesis [4], nanomaterials fabrication [5], catalysis [6], extraction [7], electrochemistry [8], analytical chemistry [9], active pharmaceutical ingredients (API) [10] and so far [3]. Recently, utilized as scavengers for primary amines [11] and a turn-on pH nano-fluorosensor [12].

Previous studies demonstrated that the TSILs could offer promising scavengers for the removal of metal ions from aqueous effluents [13,14]. Despite there are many TAILs that have been investigated for extraction and separation of metal ions from aqueous solutions based upon physical interactions [13–15]; a few trials have been performed to endow coordinating groups to the ionic liquid, rendering them more fiercely for extraction of metal ions. These few trials involve supporting of ionic liquid with thiourea [16], macrocyclic ethers [17], 2-hydroxybenzylamine [18], ethylene glycol [19], carboxylic groups [20], and recently aminothiazolyl Schiff bases [21] or porous organic co-polymer [22]. The preference of the chelating TSILs over non-chelating ones is due to the availability of the functional group which provides

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them the advantage of the ability to chelate diverse metal ions with pH-controlled selectivity and pH-dependent stability [23].

Amongst toxic heavy metal ions (HMIs) popularly distributed in aqueous environments, cupric (Cu(II)) and ferric (Fe(III)) ions were deemed as potential toxicity sources [24,25] due to their capacity to generate free radicals and reactive oxygen species (ROS) in the live cells [24,26], inducing their programmed death. The major sources of the toxic ferric ions in aqueous environments are; steel tempering, mining, coal coking, and metallurgical industries [27].On the other hand, cupric ions have emitted in aqueous effluents as a result of many industrial processes, such as electroplating, metal finishing, etching, and plastics [28]. As the Cu(II) and Fe(III) ions are very toxic metal even at low concentrations, therefore, the cupric- and ferric-polluted wastewater should be remediated before discharging into the aquatic environment [27,28].

Few trials have been reported to remove cupric and ferric ions from aqueous solutions using TSILs. For instants, imidazolium-supported TSILs have been applied as scavengers for M(II/III) ions (M = Cu, Co, Ni, Zn, Cd, Fe) from their respective aqueous solutions; by chelating them [20,29]. In addition, ammonium-based TSILs showed moderate to good effect in removing and recovering of several metal ions (Cu (II), Pb(II), Zn(II), Cd(II), Ni(II), Co(II), and Fe(III)) from aqueous effluents [29,30]. Recently, microcapsules composed of styrene and divinylbenzene were used to encapsulate pyridinium TSILs for Zn(II) and Cu(II) recovery from aqueous media [31]. Nevertheless, these reported TSILs are limited and their routes of fabrication are sophisticated and expensive.

All these aforementioned facts prompted us to design and fabricate a new azomethine-supported bis-butylimidazolium chelating task-specific ionic liquid (**ABIIL**) which will be utilized not only for the removal of Cu(II) and Fe(III) ions from the aqueous solutions but also to convert these ions to metals-based pharmacological nominates.

2. Experimental part

2.1. Materials and instrumentation

Chemicals, solvents, and practical procedures utilized in the preparation of salicylaldehyde-supported butylimidazolium ionic liquids (SBIILs) (**2a,b**) and 1-(3-aminopropyl)-3-butyl-1H-imidazolium hexafluorophosphate (**5**) coupled with the instrumentation used for the comprehensive characterization of prepared compounds were described in the online electronic supplementary information (**ESI†**).

2.2. Synthesis of ABIIL

Into a 100 mL round-bottomed flask (RBF), a *solution of* SBIIL (**2b**) (1.62 g, 4 mmol) in ethanol (35 mL) was gradually added to an ethanolic solution (25 mL) of the aminopropyl derivative (**5**) (1.31 g, 4 mmol) containing a catalytic amount of glacial acetic acid (three drops) under stirring. Then, the reaction mixture was heated under reflux and continuous stirring for 3–5 h (TLC was used to monitor the completion of reaction). After reaction completion, the solvent was partially evaporated followed by cooling of the content of RBF to ambient temperature. The precipitated product was filtered, washed with cold ethanol and ether, (3 × 5 mL) for each, dried, and then recrystallized from aqueous ethanol to give ABIIL as yellow fine crystals. Yield (2.49 g, 89%), mp 98–99 °C. FTIR (KBr, cm^{-1}): 3336 (m, br), 3079 (m, br), 2982 (m, sh), 2959 (m, sh), 2889 (m, sh), 1631 (vs, sh), 1567, 1549, 1466 (s, sh), 1335 (m, sh), 1279 (s, sh), 1150 (s, sh), 965(m, sh), 836 (vs, sh), 735 (m, sh). ^{1}H NMR (200 MHz, DMSO-d_6) δ (ppm): 10.19 (s, 1H), 9.43 (s, 1H), 9.12 (s, 1H), 9.04 (s, 1H), 8.11–7.96 (m, 2H), 7.82–7.76 (m, 2H), 7.39 (d, 1H, J = 7.1 Hz), 7.06–7.01 (m, 2H), 5.69 (s, 2H), 5.10 (t, 2H, J = 6.9 Hz), 4.26 (t, 2H, J = 7.2 Hz), 4.11 (t, 2H, J = 6.9 Hz), 3.99 (t, 2H, J = 6.8 Hz), 2.25–2.09 (m, 6H), 1.96–1.81 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 161.33, 158.21, 137.86, 136.22, 133.14, 132.42, 125.02, 123.07, 122.70, 118.74, 117.63, 57.62, 55.91, 54.81, 51.970, 49.02, 36.13, 32.97, 31.61, 31.09, 21.34, 19.17 and 13.61. ^{31}P NMR (202 MHz, DMSO-d_6): δ −142.95 (hept, J = 711.2 Hz). ^{19}F NMR (471 MHz, DMSO-d_6) δ: −70.57 (d, J = 711.2 Hz). ESI-MS: in positive mode peaks at m/z 568.4 ($[C_{25}H_{37}F_6N_5OP]^+$, M – PF_6^-) a.m.u. and 211.6 ($[C_{25}H_{37}N_5O]^{2+}$, M – 2 PF_6^-) a.m.u. Anal. Calcd. for $C_{25}H_{37}F_{12}N_5OP_2$ (M = 713.53 g/mol): C, 42.08; H, 5.23; N, 9.82%. Found: C, 41.99; H, 5.31; N, 9.78%.

2.3. Deprotonation constant (pKa) of ABIIL

The dissociation constant (pK_a) of ABIIL was estimated at 298 K in its aqueous solution (10^{-4} M) of ionic strength of 0.04 M (KNO_3) by titration with an aqueous NaOH solution (1.6×10^{-3} M).

2.4. Scavenging of Cu(II) and Fe(III) ion by ABIIL extractant

A general protocol mimic to the common solid-phase extraction (SPE) technique [32] has been utilized for removal of heavy metal ions (HMIs) (Cu(II) and Fe(III)) from aqueous ethanolic solutions by ABIIL as an extracting agent. In brief, a solution of metal ion (0.5 mmol, 0.10 g $Cu(CH_3CO_2)_2 \cdot 2H_2O$; 0.302 g $Fe(NO_3)_3 \cdot 9H_2O$) in distilled water (5 mL) was slowly added to the pale-yellow solution of ABIIL (0.71 g, 1.0 mmol) in ethanol (30 mL) containing 100 μL of 0.1 M $NaOH_{aq}$. Then, the reaction mixture was heated under reflux with stirring for 1 h. After cooling to ambient temperature, the isolated colored solids were collected by filtration, washed with cold ethanol and diethyl ether, (2 × 3 mL) for each, and dried in a desiccator. Samples of the obtained complexes were analyzed as follow;

[Cu(ABIIL)$_2$] (Cu-ABIIL): Dark yelowish green crystals, Yield 69%. FTIR (KBr, cm^{-1}): 3125 (w, br), 1647 (m, sh), 1622 (s, sh), 1549 (s, sh), 1457 (m, sh), 1336 (m, sh), 1271 (m, sh), 1150 (m, sh), 837 (vs, sh), 643 (m, br), 525 (w, br), 478 (m, sh). ESI-MS: in positive mode peaks at m/z 1315.3 ($[C_{48}H_{68}CuF_{18}N_{10}O_2P_3]^+$, M - PF_6^-) a.m.u., 585.2 ($[C_{48}H_{68}CuF_{12}N_{10}O_2P_2]^{2+}$, M – 2 PF_6^-) a.m.u., 341.6 ($[C_{48}H_{68}CuF_6N_{10}O_2P]^{3+}$, M – 3$PF_6^-$) a.m.u., and 220.0 ($[C_{48}H_{68}CuN_{10}O_2]^{4+}$, M – 4 PF_6^-). Anal. Calcd. for $C_{48}H_{68}CuF_{24}N_{10}O_2P_4$ (M = 1460.54 g/mol): C, 39.47; H, 4.69; N, 9.59%. Found: C, 39.42; H, 4.71; N, 9.38%.

[Fe(ABIIL)$_2$(H$_2$O)(NO$_3$)] (Fe-ABIIL): Dark purple powder, Yield 65%. FTIR (KBr, cm^{-1}): 3453 (m, br), 3122 (w, br), 1620 (s, sh), 1549 (s, sh), 1458 (m, sh), 1336 (s, sh), 1272 (m, sh), 1151 (m, sh), 839 (vs, sh), 653 (m, br), 506 (w, br), 458 (w, br). ESI-MS: in positive mode peaks at m/z 1387.6 ($[C_{48}H_{70}F_{18}FeN_{11}O_6P_3]^+$, M – PF_6^-) a.m.u., 621.2 ($[C_{48}H_{70}F_{12}FeN_{11}O_6P_2]^{2+}$, M – 2 PF_6^-) a.m.u., 365.7 ($[C_{48}H_{70}F_6FeN_{11}O_6P]^{3+}$, M – 3 PF_6^-) a.m.u., and 238.1 ($[C_{48}H_{70}FeN_{11}O_6]^{4+}$, M – 4 PF_6^-). Anal. Calcd. for $C_{48}H_{70}F_{24}FeN_{11}O_6P_4$ (M = 1532.86 g/mol): C, 37.61; H, 4.60; N, 10.05%. Found: C, 37.52; H, 4.63; N, 9.98.

2.5. Regeneration of ABIIL scavenger

An aqueous solution containing a mixture of HCl (1.0 M, 3 mL) and thiourea (4% *w/v*) was added to the extracting products (M-ABIIL complexes) (100 mg). Thereafter, these mixtures have subjected to ultrasonic irradiation for 30 min. The color change of the reaction solution from colorless to yellow color was an indication of the progress of the ABIIL-recovering process. After reaction completion, the reaction mixture was neutralized with an aqueous $NaHCO_3$ solution (1.0 M) which leads to the precipitation of the parent scavenger (ABIIL). The recovered ligand (ABIIL) was collected by filtration, washed several times with Milli-Q water to remove the undesired byproducts (M-thiourea complexes). Then, this scavenger was dried under reduced pressure and can be used for a further removal process.

2.6. Pharmacological performance study

2.6.1. Antimicrobial activity

The antimicrobial performance for the scavenging products (Cu(II)-/Fe(III)-ABIIL complexes) was assessed in comparison to the native scavenger (ABIIL) and clinical drugs (antibacterial, ampicillin; antifungal, amphotericin B), against different microbial strains including *Staphylococcus aureus* (*S. aureus*, ATCC-25923) as a Gram-positive bacterium, *Escherichia coli* (*E. coli*, ATCC-25922) as a Gram-negative bacterium, and *Aspergillus flavus* (*A. flavus*) & *Candida albicans* (*C. albicans*, NCIM No. 3100) as fungal species. This study was performed according to the usual antimicrobial evaluation protocol followed in our earlier reported works [11,33]. The diameter of zone of inhibition (ZOI, mm) and minimum inhibitory concentration (MIC) were used as antimicrobial activity indices for the tested compounds.

2.6.2. Anticancerl activity

The anticancer efficacy of the scavenging products was evaluated in comparison to a clinical anticancer drug (Vinblastine, VB) against two human cell lines; colon carcinoma (HCT116) and normal cells (Hela). Again, this work was carried out using the standard MTT protocol described in our previous study [34]. The cell viability% and IC_{50} values were utilized as cytotoxicity activity markers for the examined compounds.

3. Results and discussion

3.1. Synthesis of new scavenger (ABIIL)

The synthesis of new task-specific ionic liquid (TSIL) based on salicylidene moiety and butylimidazolium ionic liquids (BIILs) terminals involves seven chemical reactions. Initially, quaternization of 1-butylimidazole with *N*-(2-bromoethyl)phthalimide (**1**) to generate 1-(2-(phthalamido)ethyl)- 3-^{n}butylimidazolium bromide (**2a**), which is readily transformed into the corresponding hexafluorophosphate salt through an anion metathesis reaction using an aqueous HPF_6. Then, the 3rd step involves a dephthaloylation of compound **2b** by the traditional hydrazinolysis reaction using hydrazine monohydrate in an ethanolic medium followed by simple extraction with dichloromethane (DCM), filtration, and evaporation of solvent to separate a pure 1-(2-aminoethyl)-3-butyl-imidazolium hexafluorophosphate (AEBI, **3**). Other sets of reactions were dedicated for the preparation of salicylaldehyde-supported butylimidazolium ionic liquids (SBIILs); in the fourth reaction, a bromomethylation process was performed on salicylaldehyde to obtain 5-(bromomethyl) salicylaldehyde (**4**) which is utilized as an alkylating agent for the quaternization of 1-buty limidazole to produce salicylaldehyde-based butylimidazolium bromide (**5a**). Thereafter, a bromide exchange in compound 6a with hexafluorophosphate anion was performed to prepare compound **5b**. Eventually, a classical Schiff base condensation was carried out between the amino component (**3**) and SBIIL (**5b**) in ethanolic solution to fabricate the desired scavenger, 1-butyl-3-(3-(((2-(1-butyl-midazolium-3-yl)ethyl)imino)methyl)-4-hydroxybenzyl)-imidazolium hexafluorophosphate (ABIIL). It was obtained in an excellent yield with high purity and structurally characterized based on the elemental analysis and spectroscopic methods (FTIR, UV–Vis, NMR (^{1}H, ^{13}C, ^{19}F, ^{31}P) and ESI-MS).

3.2. Structural characterizations of new scavenger (ABIIL)

Regarding solubility, ABIIL is insoluble in water (Solubility in water = 9.7 g/L) and methanol but soluble in ethanol and has aqueous stability in basic and neutral solutions (pH = 10–5); while it is readily decomposed, by dissociation of azomethine bond, at low pH values (pH < 4) like the behavior of most Schiff bases [35]. The elemental analysis of new scavenger (ABIIL) gave satisfactory results which in good consistent with the suggested molecular formula of it (see experimental part).

The positive mode electrospray ionization mass spectra (ESI-MS) of ABIIL displayed four distinctive peaks at *m/z* 568.4 and 211.6 corresponding to the successive departure of hexafluorophosphate counter anions to generate a single-charged $[M - PF_6^-]^+$ and double-charged $[M - 2\ PF_6^-]^{2+}$ cations. Also, these data agree with the molecular formula proposed by the elemental analyses.

The appearance of two sets of absorption bands (characteristic for AEBI and SBIIL) and vanishment of others along with the emergence of new ones in the spectrum of the new scavenger (ABIIL) (see Fig. S1, ESI) confirms its successful fabrication. Just to name few, the two main peaks centered at 3336 and 1279 cm^{-1} are assigned to the vibration of hydroxyl and aryl-O fragments of the phenolic group in the SBIIL segment. However, absorption bands noticed at 1466, 965, and 836 cm^{-1} are ascribed to the vibration of imidazolium and PF_6^- fragments of ionic liquids terminals in the AEBI and SBIIL segments. On the other hand, vanishment of the stretches of the NH_2 group (at 3501 and 3398 cm^{-1} in AEBI spectrum) and aldehyde moiety (at 2820 and 1658 cm^{-1} in SBIIL spectrum), coupled with the growth of new stretch at 1631 cm^{-1} (assignable for the vibration of azomethine group) in the spectrum of ABIIL; proves the successful formation of the new scavenger (ABIIL) by Schiff base condensation of the amino group of AEBI with an aldehyde moiety of SBIIL.

The coexistence of two groups of NMR signals in the ^{1}H NMR spectrum of ABIIL (Fig. 1) confirms the successful condensation of AEBI with SBIIL to form ABIIL. (See Scheme 1.)

As shown in Fig. 1, the first set of ^{1}H NMR peaks are centered at chemical shift values of 10.19, 9.04, 8.11–7.96, 5.10, 4.26, and 3.99 ppm (distinctive for the aminoethyl butyl imidazolium (AEBI) part); while the other group which is positioned at 9.12, 7.82–7.01, 5.69, and 4.11 ppm are characteristic for SBIIL segment. Interestingly, the emergence of a new singlet at δ 9.43 ppm corresponding to the resonance of azomethinic proton, coupled with the downfield shift of the phenolic (–OH) proton to δ 10.19 ppm are ascribed to the intramolecular H-bonding (O-H•••N) between the azomethine (-CH=N-) and ortho-hydroxyl groups in ABIIL.

Additionally, the ^{13}C NMR technique provides informative structural insight concerning the carbon-atoms distribution map in the skeleton of ABIIL scavenger. The ^{13}C NMR spectrum of ABIIL revealed the presence of C-atoms distinctive for both AEBI and SBIIL segments (see Fig. 2A). Noteworthy, this spectrum exhibited two characteristic peaks at δ 161.33 and 158.21 ppm due to the nuclear resonances of phenolic (C—O) and azomethinic (-CH=N) carbon atoms, respectively. Powerful evidence for anchoring of ionic liquids on the terminals of ABIIL is the appearance of a septet signal (centered at δ −142.95 ppm, J = 711.2 Hz) and a doublet peak (centered at δ −70.57 ppm, J = 711.2 Hz) in the ^{31}P (Fig. 2B) and ^{19}F NMR (Fig. 2C) spectra of ABIIL, respectively.

3.3. pH-potentiometry

As the chelating capacity of any protic ligand is strongly correlated to the extent of its ionization and the stability of its ionizable form at different pH values, so, it is of importance to examine the deprotonation process and dissociation constant of ABIIL. In this context, the dissociation performance of ABIIL was examined by a pH-potentiometric method in an aqueous ethanolic solution at ambient temperature. Moreover, the stability of ABIIL in aqueous media was inspected by a pH-potentiometric titration of its solution (10^{-4} M) against NaOH (10^{-3} M) (Fig. S2, ESI†). This titration curve showed a single abrupt change corresponding to the departure of one proton form ABIIL without losing its identity at a wide pH-range (4.8–10.5). The average number of acidic protons in ABIIL (n̄A) was calculated at serial pH values according to Irving–Rossotti equation (Eq. (1)) [36]:

$$n_A^- = Y - \frac{V_1 N^\circ}{(V_1 + V^\circ)\,T_l} \quad (1)$$

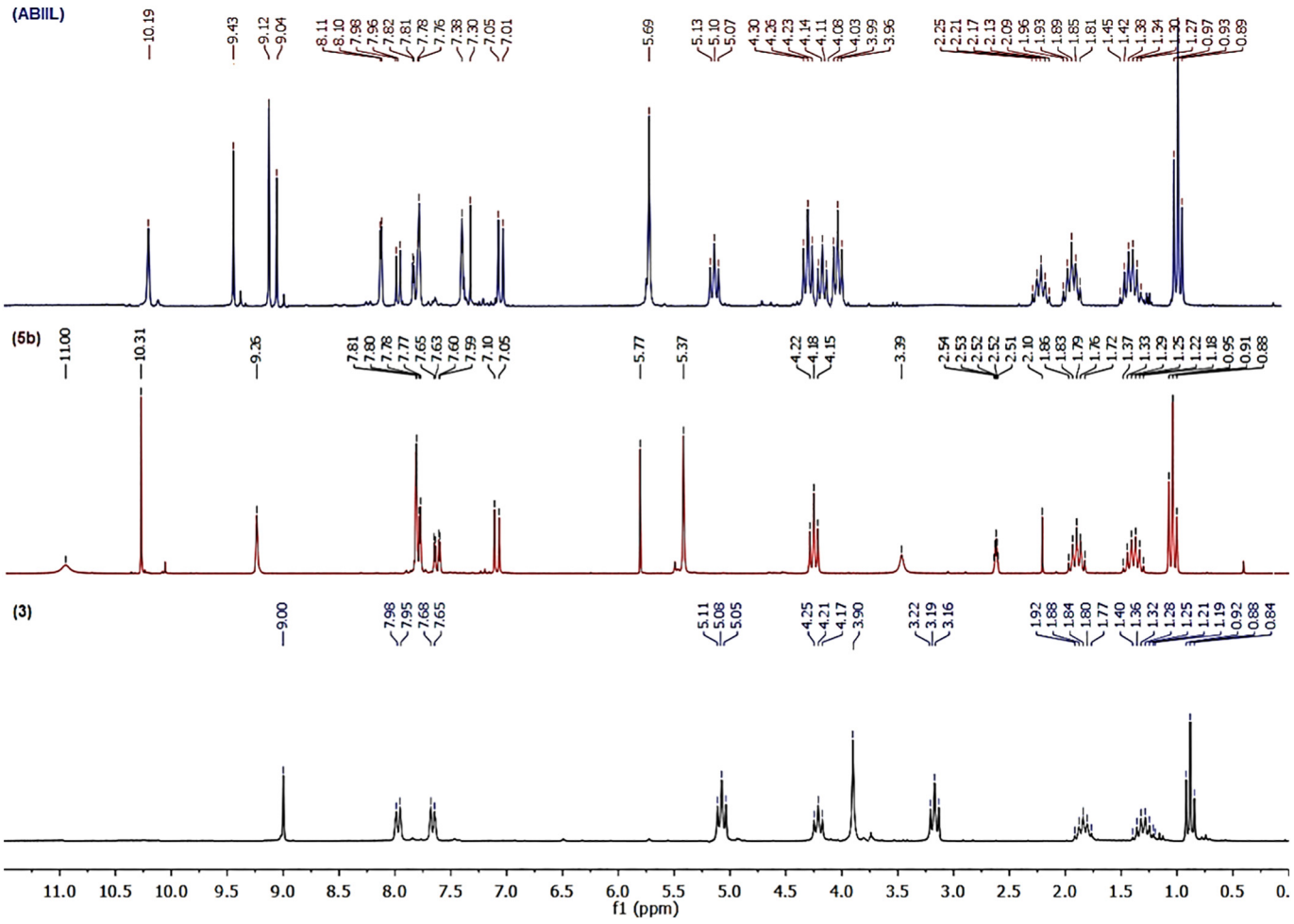


Fig. 1. ^{1}H NMR spectra of AEBI (**3**), salicylaldehyde-supported butylimidazolium hexafluorophosphate (**5b**), and ABIIL scavenger in d_6-DMSO at 300 MHz.

Y = number of dissociable protons; $\mathbf{V_1}$ = volume of NaOH added; $\mathbf{V_o}$ = initial volume (25 mL); ***N°*** = concentration of NaOH (1.6×10^{-3} M).

Plots of the nA vers pH values (Fig. S3, ESI†) show a maximum at ñA = ~1, proving that the ABIIL contains one ionizable acidic proton. The acid dissociation constant (pKa) of ABIIL was estimated within the studied pH-range using half method (HM) (pKa = 7.35) and further verified by the least square method (LSM) (pKa = 7.34). In summary, ABIIL behaves as a monoprotic ligand [37].

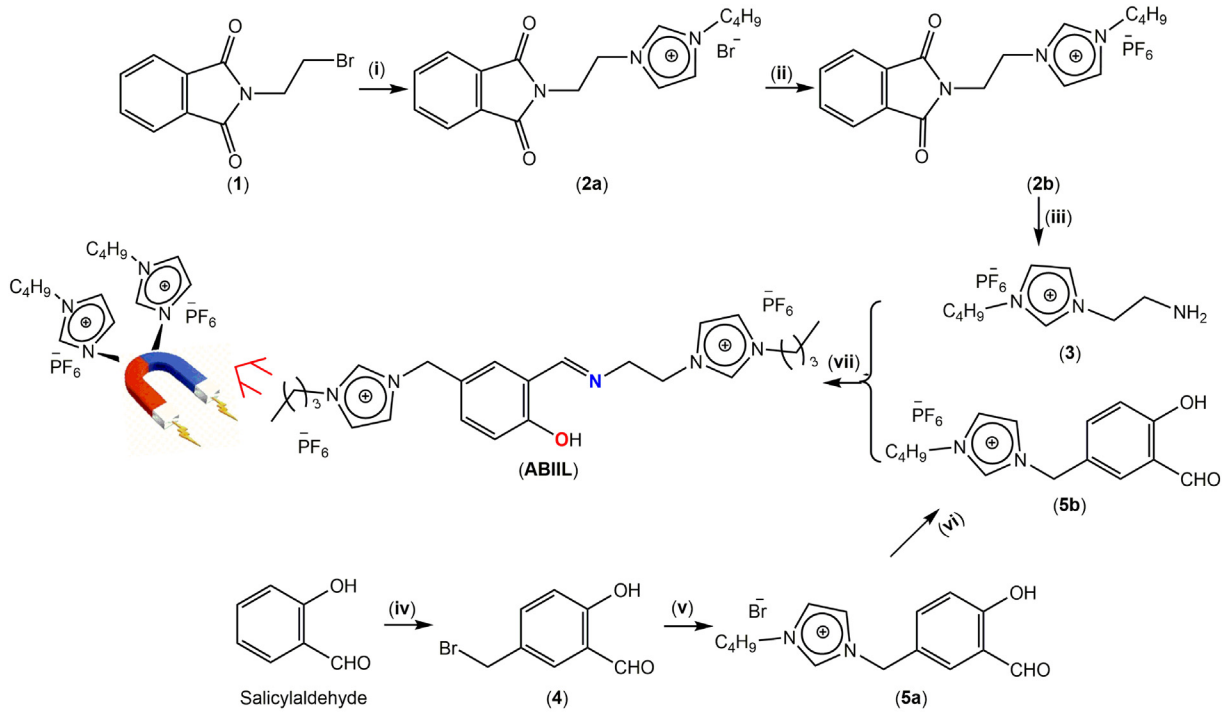
3.4. Conversion of toxic metal ions into pharmacological nominates

The ability of bis-(butylimidazolium) salicylidene (ABIIL) to scavenge the toxic metal ions (Cu(II) and Fe(III)) from their respective aqueous ethanolic solutions, coupled with their conversion into pharmacological nominates, was investigated using our previous protocol. Initially, the optimum conditions for this remediation process were determined by studying the scavenging of Cu(II) ions by ABIIL from cupric acetate solution under different experimental conditions. Only 67.3% of Cu(II) ions have been removed by ABIIL and converted into the corresponding complex (Cu(*II*)ABIIL) by heating under reflux for 5 h. On the other hand, the addition of NaOH to the remediation media has significantly improved the Cu(II) uptake to 96.7% during only 1 h at ambient temperature. The scavenging outputs for the toxic metal ions (Cu(II) and Fe(III)) using ABIIL are the corresponding complexes, $[M(ABIIL)_2(NO_3)_x(H_2O)y]$ (M = Cu(II), x = y = 0; M = Fe(III), x = y = 1) (see Scheme 2).

Alteration of the physicochemical properties of the scavenging products (M(II/III) ABIIL complexes) in comparison to the reaction inputs, (Cu(II)/ Fe(III) ions and ABIIL), along with the structural characterization of these outputs based upon their elemental and spectral analysis confirms the success of our scavenging protocol. Interestingly, the uptake of metal ions by the ABIIL molecule can reach up to 98.9% (see Table 1).

3.5. Optimization of ABIIL recovering conditions

The regeneration of the scavenger is an important and crucial issue to minimize operating costs and increase the feasibility of this process investment. In this context, recovering of ABIIL from its scavenging products was carried out under different conditions using various metal-desorbing agents (HCl–thiourea, HNO_3–thiourea, HCl–thiosulfate, HNO_3–thiosulfate), according to our earlier work [21], to determine the best conditions or regeneration of ABIIL scavenger. Again and in the consistent with our previous study, HCl-thiourea mixture (1 M HCl containing 4% (*w*/*v*) thiourea) was proven to be the ideal metal-desorbing agent for the regeneration of native scavenger (ABIIL). The total recovery ratio of ABIIL from scavenging products (Cu(II)-/Fe(III)-ABIIL) and its further reuse without significant loss in its efficacy is remarkably high as revealed from Fig. 3. After six cycles, the ABIIL still sustained 94% and 92% of its initial scavenging ability for Cu(II) and Fe(III) ions, respectively.



(**i**) 1-^{n}butylimidazole, toluene, stir, 80 °C, N_2, 48 h; (**ii**) 60% HPF_6, Milli-Q H_2O, rt, 1 h; (**iii**) $N_2H_4.H_2O$, EtOH, 75 °C, 4 h; (**iv**) CH_2O, H_2SO_4, HBr_{aq}, HBr_g, 70 °C, 20 h; (**v**) 1-^{n}butylimidazole, toluene, stir, 80 °C, N_2, 24 h; (**vi**) 60% HPF_6, Milli-Q H_2O, rt, 1 h; (**vii**) EtOH, AcOH, reflux, stir, N_2, 6 h.

Scheme 1. The stepwise schematic protocol for the preparation of 1-(2-aminoethyl)-3-butyl-imidazolium hexafluorophosphate (AEBI, 3), salicylaldehyde-supported butylimidazolium ionic liquids (SBIILs), and ABIIL scavenger.

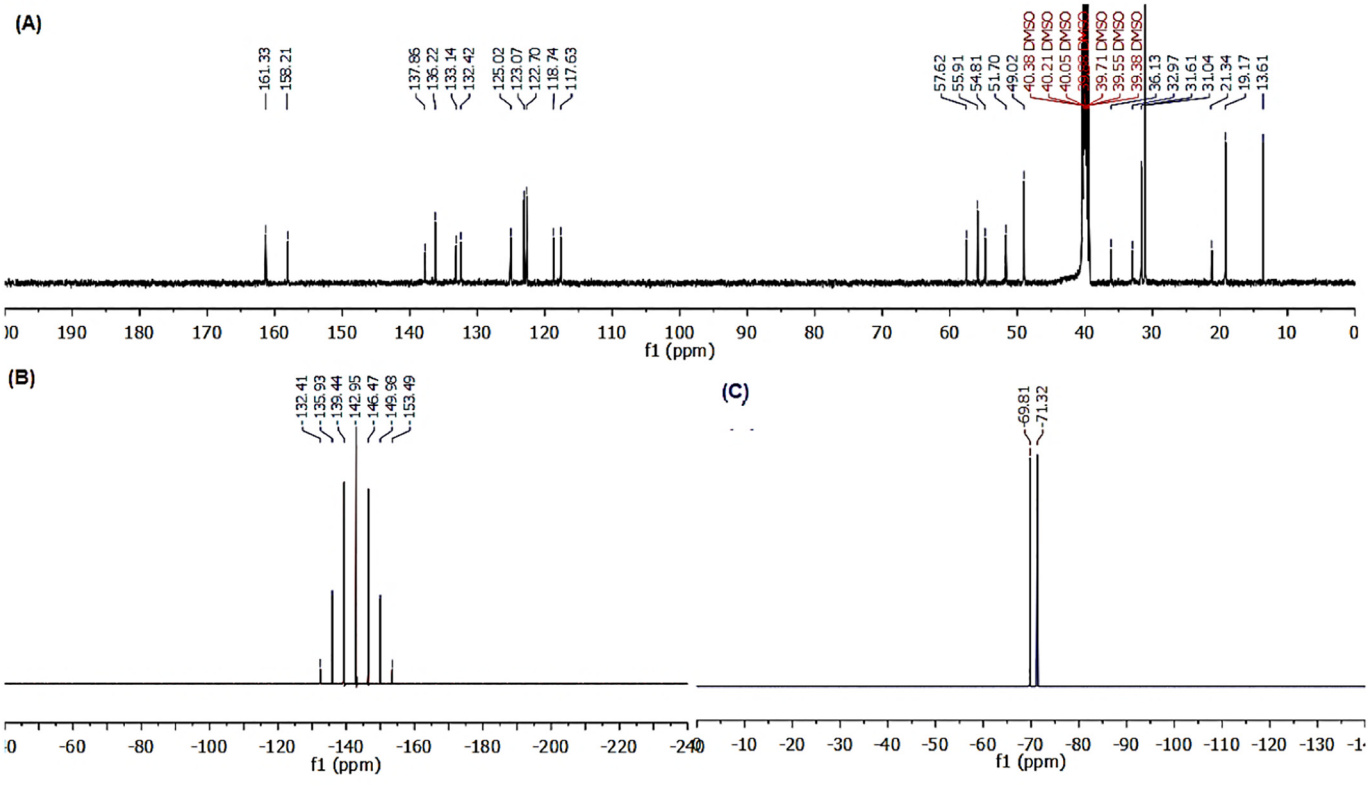
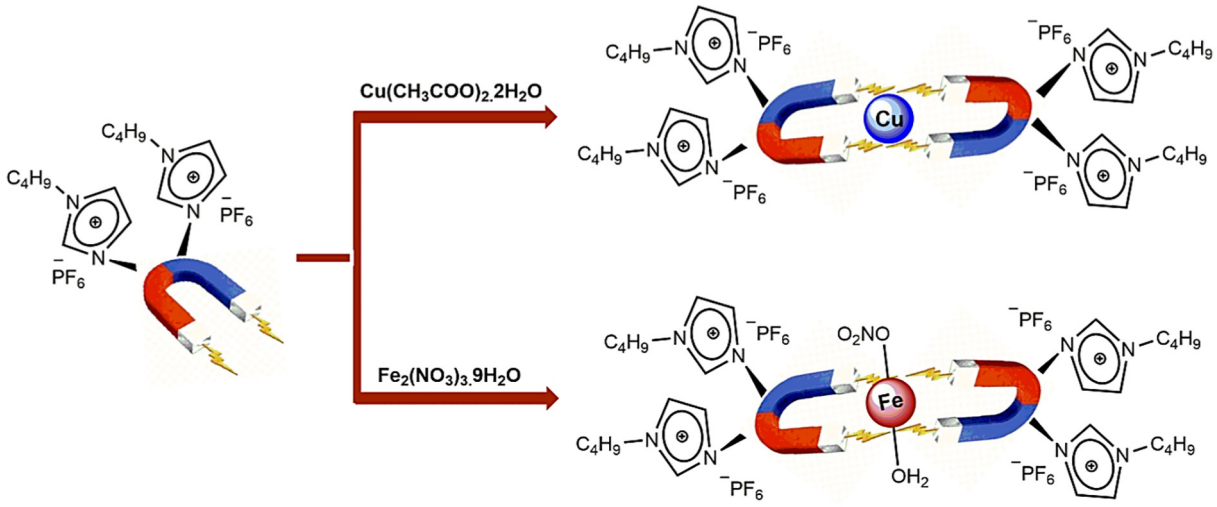


Fig. 2. (**A**) ^{13}C NMR (126 MHz); (**B**) ^{31}P NMR (202 MHz); and (**C**) ^{19}F NMR (471 MHz) spectra of the ABIIL scavenger in d_6-DMSO.



Scheme 2. Scavenging of toxic metal ions (Cu(II) and Fe(III)) by ABIIL and conversion into the corresponding complexes.

Table 1
Removing of the target metal ions by the new scavenger (ABIIL); in comparison with reported ones.[a]

Scavenger	Metal ions	Operating conditions			Uptake (%)	Ref.
		pH	T (°C)	Time (min)		
ABIIL	Cu(II)	**6.4**	**25**	**60**	**96.7**	This work
	Fe(III)	**6.4**	**25**	**60**	**98.9**	This work
HATPS	Cu(II)	6–7	78	120	87.2	[21]
	Fe(III)	6–7	78	120	94.3	[21]
Activated C	Cu(II)	6–7	37	40–60	90.3–95.6	[38]
	Fe(III)	1.5	20	20	53	[39]
Fly ash	Cu(II)	6	40	90	91.4	[38]
GO	Cu(II)	6	20	24 h	94.6	[38]
	Fe(III)	2–3	20	10 h	44.3	[40]
GO-NH_2	Cu(II)	8	25	5	96.6	[41]
	Fe(III)	8	25	5	95.3	[41]
GO/ Fe_2O_3	Cu(II)	5.3	20	24 h	98.9	[38]
Zeolite	Cu(II)	5	65	120	88.1	[42]
	Fe(III)	5	65	120	74.3	[42]
CS	Cu(II)	4.5	20	300	91.2	[38]
	Fe(III)	7	37	180	83.5	[43]
PSCSB	Cu(II)	8	25	150	94.1	[44]
PISCSB	Cu(II)	8	25	30	94.5	[44]

[a] Scavening conditions for ABIIL; ABIIL (0.5×10^{-3})/Metal ion (0.5×10^{-3}) solutions, ethanol (10 mL) containing 100 μL of 0.1 M $NaOH_{aq}$, stirring 60 min/25 °C. GO = Graphene oxide; GO-NH_2 = Amine-functionalized graphene oxide; CS = Chitosan; PSCSB = poly (salicylidene) chitosan Schiff base; PISCSB = poly(ionic-salicylidene) chitosan Schiff base.

3.6. Structural features of the scavenging products

The micro-analytical analysis of the scavenging products (Cu(II)-/Fe (III)-ABIIL) agrees with their proposed molecular formulas, $[Cu(ABIIL)_2]$ and $[Fe(ABIIL)_2(H_2O)(NO_3)]$, (see Experimental section). On the other hand, the structural formulas of these complexes could be deduced based on spectral analysis (IR and UV–Vis). FTIR is essential to predict the ABIIL binding sites with metal ions and the coordination sphere for each metal ion, as well. Synchronous changes in the intensities and/or the positions of the absorption bands recorded in the FTIR spectra of the scavenging products (M-ABIIL) in comparison to those in the spectrum of scavenger (ABIIL) (cf. Fig. S1, ESI); coupled with the emergence of new absorptions bands, confirms the success of chelation of metal ion by ABIIL. Moreover, based on these changes we can propose the most reasonable M-ABIIL chelation mode. For instance, the phenolic (-OH) absorption band (at 3336 cm^{-1} in the spectrum of ABILL) was disappeared in the spectra of complexes, confirming of its deprotonation to form phenolate anion that chelates metal ions. Additionally, shifting in the wavenumber of the C—O peak ($\Delta\nu = -(9–14)$ cm^{-1}) in the spectra of M-ABIIL complexes as compared to the native ABIIL along with the emergence of a weak peak at the rang of 654–547 cm^{-1} (distinctive for M-O stretching vibration), offer more evidence for sharing of the phenolic (OH) group in chelation of metal ions [45,46]. The band due to the azomethine group (-C=N) was negatively

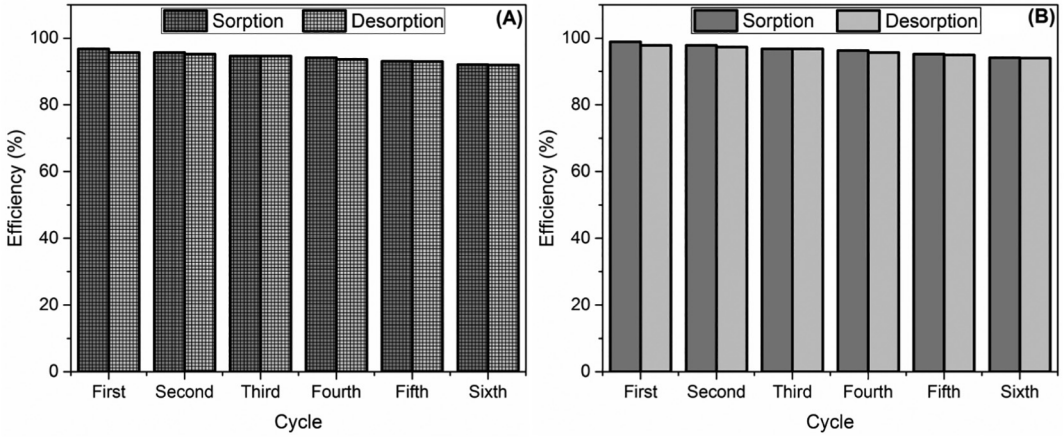


Fig. 3. Scavenging efficiency of the ABIIL for (A) Cu(II) ions and (B) Fe(III) ions after six consecutive scavenging (sorption)–regeneration (desorption) cycles.

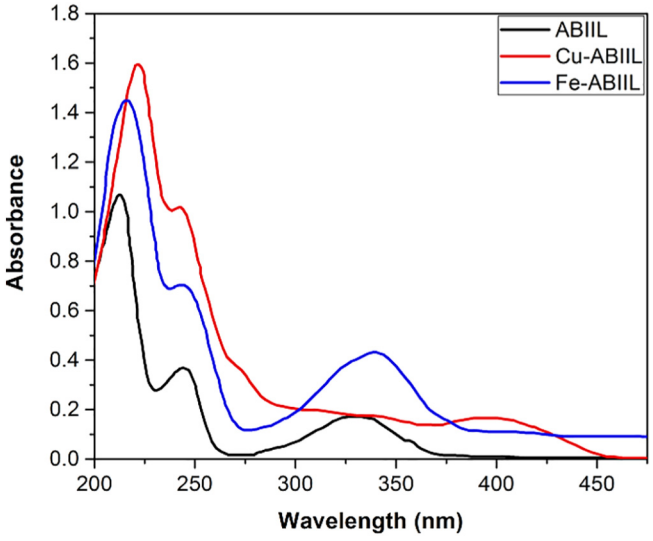


Fig. 4. UV–Vis spectra of ABIIL scavenger and its scavenging products (Cu-ABIIL and Fe-ABIIL).

shifted from 1631 cm^{-1}, in free ligand to 1621 ± 1 cm^{-1} ($\Delta\nu$ = −11 cm^{-1}), in complexes, as indicative of the coordination of the azomethinic N atom with metal ions [21,46]. This is consistent with the growth of a new absorption band at the rang of 465–442 cm^{-1} assignable for M–N vibration. Thus, ABIIL act as a monoanionic bidentate (NO) chelating ligand. The broad band observed at 3453 cm^{-1} in the spectrum of Fe(III)-ABBIL complex, characteristic for the O—H group, emphasizes the involvement of a water molecule in the coordination sphere for Fe(III) ion [21].

The UV–Vis spectra of the solutions of ABIIL scavenger and its metal complexes in DMSO (10^{-3} M) were measured within a wavelength range of 200–500 nm at ambient temperature (Fig. 4). The electronic spectrum of ABIIL is dominated by three main maxima at 337, 249, and 221 nm attributable for the n → π* and π → π* transitions implicated in the azomethine, phenolic, and imidazolium moieties, respectively [47,48]. UV–visible spectroscopy is a very helpful tool in predicting the geometries of complexes on the basis of the identities of d–d transitions. For example, the electronic spectrum of the Cu-ABIIL complex showed a new peak at 397 nm which can be assigned as d → π* metal-ligand charge-transfer (MLCT) transitions (superimposed $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions) that distinctive for the distorted square-planar geometry of Cu(II) complexes [47,49]. The measured magnetic moment for this complex was found to be 1.82 BM which agrees with the presence of odd electron on Cu(II) ion in a square-planar geometry environment [50]. On the other hand, the solution of the Fe-ABIIL complex displayed a characteristic peak at 343 nm due to the spin-forbidden $^6A_{1g} \rightarrow T_{2g}$ transition of a high-spin Fe(III) ion (d^5) in an octahedral field. However, the high-spin octahedral Fe(III) complexes usually show a very weak spin-forbidden d-d transition that hasn't appeared in their UV–Vis spectra. Also, the magnetic moment of the Fe-ABIIL complex (5.62 BM) proposed the high-spin configuration of the Fe(III) ion (d^5 configuration) in an octahedral environment [51].

The stability of the scavenger (ABIIL) and its complexes was checked beneath the physiological conditions (pH = 7.4, T = 36.5–37.5 °C) by storing a solution (10^{-3} M) of each sample in a PBS-DMSO buffer for 72 h; observing the physicochemical changes and recoding the UV–Vis spectra of each stock solution at time intervals (every 24 h). Noteworthy that no physicochemical changes such as color alteration or formation of precipitates as evidence no aggregation of ABIIL or its complexes in their respective solutions. Meanwhile, no significant changes were noticed in the UV–Vis spectra of ABIIL or its complexes during the storing time (Fig. S4, ESI), confirming our earlier suggestion.

3.7. Pharmacological study

3.7.1. Antimicrobial study

To assess the suitability of scavenging products (M-ABIIL complexes) for application as antibiotics, the capacity of these complexes to suppress the growth of common medically-relevant microbes such as *S. aureus* (ATCC-25923) (Gram-positive (G^+) bacterium), *E. coli* (ATCC-25922) (Gram-negative (G^-) bacterium), *A. flavus*, and *C. albicans* (NCIM No. 3100) (fungi) were in vitro investigated in comparison to the native scavenger (ABIIL) and clinical drugs (Antibacterial, Streptomycin (ST), and Tetracyclin (TC); Antifungal, Ketoconazole (KCZ)) (see Fig. 5). It is worth that the scavenging products (Cu(II)-/Fe(III)-ABIIL complexes) are more efficient than the native scavenger (ABIIL) in suppressing the growth of all tested microbial species; with efficacies higher than the clinical drugs, as revealed from the values of ZOIs (Fig. 5). Notably, *S. aureus* is more susceptible to the biocidal effects of the M-ABIIL complexes than *E. coli* (Fig. 5, left). Where the MIC values of Cu(II)-/Fe(III) complexes against *S. aureus* and *E. coli* are 25.4/18.9 μg/mL and 41.2/23.1 μg/mL, respectively (*i.e* the activity of the scavenging products against G^+-bacterium is 1.3–1.6 times higher than G^--bacterium). This, in turn, means Fe-ABIIL is more potent than Cu-ABIIL in fighting the tested bacterial pathogens; with efficacies higher and clinical drugs, streptomycin ($MIC_{S.\ aureus/\ E.\ coli}$ = 50.6/27.5 μg/mL) and tetracycline ($MIC_{S.\ aureus/\ E.\ coli}$ = 37.5/43.2 μg/mL). The promoted antibacterial performance of scavenging products (M-ABIIL) in comparison to the native scavenger (ABIIL) could be explained

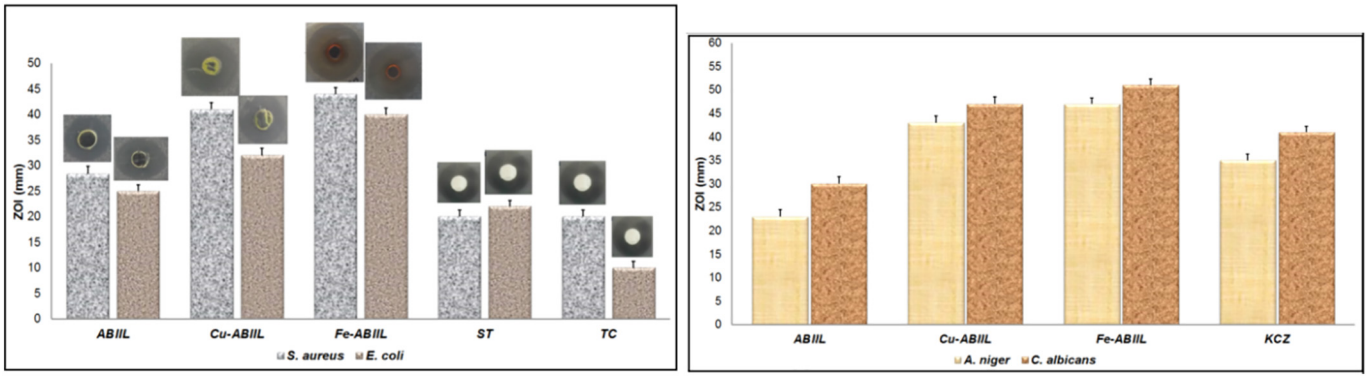


Fig. 5. Graph of the zone of inhibition (ZOI, mm) for the native scavenger (ABIIL) and scavenging products (Cu-/Fe-ABIIL complexes) against different medically relevant microbial pathogens. Insets are the micrographs for ZOI of tested compounds against bacterial strains.

based on the chelation theory [52] and Overtone's concept [53]. Generally, the chelating ligands can form highly stable five-/six-membered metallocyclic rings (chelate rings) upon binding to the metal ions. This metallocyclic ring offer template for the delocalization of p-electrons of metal ion, therefore, reduces its polarity and increases the lipophilicity of the whole complex to a larger extent. This increased lipophilicity promotes the penetration of the metal complex into the phospholipid membrane of the microbial cell, causing either collapse of the permeability barrier [54] or inducing malfunction in metal-binding sites of enzymes of this cell [55]. Meanwhile, as the size and/or the number of metallocyclic rings increases; the polarity of metal ion decreases and the lipophilic character of complex increases, which in turn enhances the interaction between complex and the lipid layer in the outer membrane of the microbial cell [56].

As shown in Fig. 6, ABIIL can form two highly stable six-membered metallocyclic rings which significantly diminishes the polarity of Cu (II) and Fe(III) ions and greatly elevates the lipophilic character of their respective complexes, increasing the mutual interactions between complexes and the outer lipid layer of the microbial cell wall to a larger extent. This may lead to a breakdown of the permeability barrier of the cell, resulting in malfunction of normal biological processes of microbial cells. Several structural features can be proposed as the potential reasons for the preferable antimicrobial activity of Fe-ABIIL complex as compared to Cu(II) complex such as; (i) The octahedral geometry and charge distribution around the Fe-ABIIL complex are more compatible with those around pores of the bacterial cell-wall, making it more able to penetrate this wall and induce more toxic reaction within the pores [57]. (ii) Releasing of Fe(III) ions from the Fe-ABIIL complex inside the microbial cell which can highly interact with DNA, more than Cu(II) ions, disordering its functions and replication [58,59]. (iii) Apart from this, the mode of action of the Fe-ABIIL complex may also invoke H-bonding through additional H-bond donor/acceptor (HBD/ HBA) sites (H_2O, ONO_2), absent in the Cu-ABIIL complex, with the active centers of biomolecules in the microbial cell, resulting in dysfunction in their biological processes [60].

As shown in Fig. 5 (right), the M- ABIIL complexes displayed slightly higher fungicidal activity than their bactericidal efficacy, as revealed from the values of their respective inhibition zones against *A. flavus* and *C. albicans*. Plus, the MIC values (μg/mL) for Fe-ABIIL against microbial species were found to be: 18.9, *S. aureus*; 23.1, *E. coli*; 19.5, *A. flavus*; and 16.8, *C. albicans*.

3.7.2. Cytotoxicity study

The cytotoxic impacts of scavenging products (Cu-ABIIL and Fe-ABIIL) toward two human cell lines (Colon carcinoma cells, HTC116; Normal cells, HeLa) were in vitro assessed as compared to a clinical anticancer drug (Vinblastine, VB) using MTT assay. The cell viability ratio (Fig. 7) and the half-maximal inhibitory concentration (IC_{50}) were used as cytotoxicity indices. Generally, the scavenging products are more cytotoxic than the clinical drug (VB) toward cancer cell lines (HTC116), whereas they are less cytotoxic to the normal human cells (HeLa), as shown in Fig. 7. Just to name a few, remediation of HTC116 and HeLa cell lines with Fe-ABIIL complex (50.0 μg/mL) can reduce their viabilities ratio of HTC116 and HeLa cells by 91.97% and 37.54%, respectively. Whereas, if such treatments were performed using VB, the reduction in cell viability ratios was 87.74% and 51.39%, for HTC116 and HeLa cells respectively. Thus, Fe-ABIIL complex is more active and better safe as anti-colon cancer agent (IC_{50} values: 3.40 ± 0.53 μg/mL toward HCT116; 85.66 ± 1.44 μg/mL against HeLa) than the clinical anticancer drug (VB) (IC_{50} values: 3.79 ± 1.01 μg/mL and 57.12 ± 1.95 μg/mL for HCT116 and HeLa cell lines, respectively).

Again, Fe-ABIIL complex (IC_{50} = 3.40 ± 0.53 μg/mL) exhibit better anticancer activity than Cu(II) complex against HCT116 cells (IC_{50} = 3.58 ± 0.77 μg/mL), and this enhanced cytotoxicity could be ascribed to the same reasons (complex geometry, Fe(III)-DNA interactions, additional HBA and HBD sites) of the promoted antimicrobial activity of Fe-ABIIL complex in comparison to Cu-ABIIL (see Antimicrobial Study section).

4. Conclusion

Aminoethyl-butylimidazolium hexafluorophosphate and salicylalde hyde-butylimidazolium hexafluorophosphate were used as key starting materials for fabrication of a new task-specific ionic liquid (ABIIL) based on bis-(butylimidazolium hexafluorophosphate) supported an azome thine group. The microanalytical and spectral results confirm the

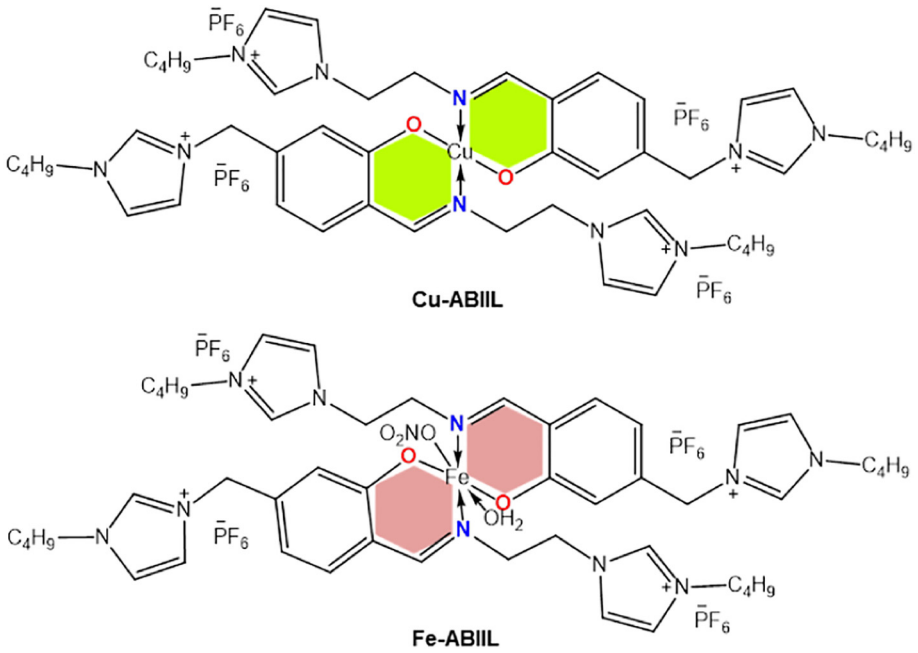


Fig. 6. The proposed structural formula of the scavenging products, [Cu(II)(ABIIL)$_2$] (Cu-ABIIL) and [Fe(II)(ABIIL)$_2$(ONO_2)H_2O] (Fe-ABIIL), showing the differences in their structural features and additional H-bonding active sites in Fe-ABIIL (HBD/HBA, H_2O; HBA, ONO_2).

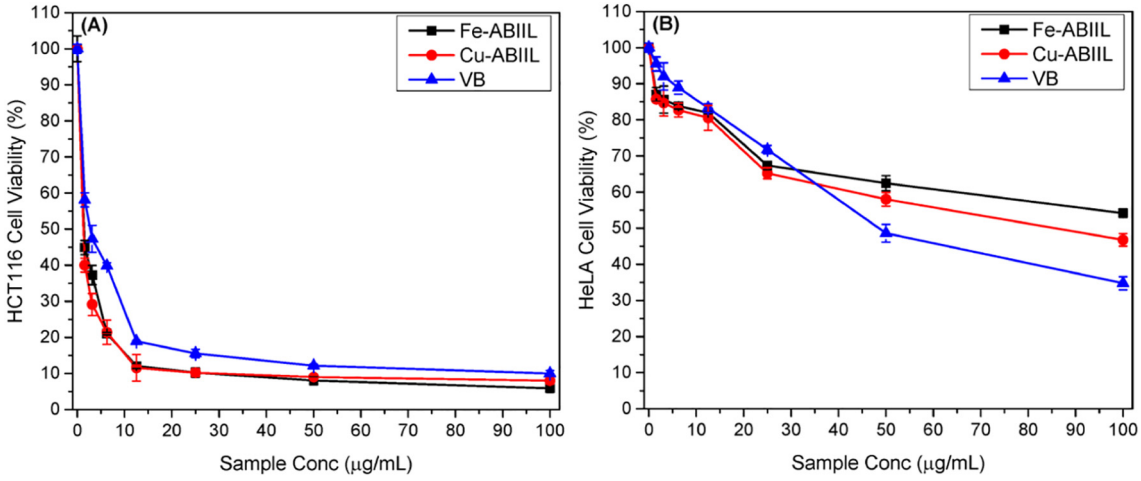


Fig. 7. Cell viability of two human cell lines (**A**) Colon carcinoma cells (HTC116); (**B**) Normal cells (HeLa) after 24 h of treatment with serial concentrations of scavenging products (Cu-ABIIL and Fe-ABIIL) and a clinical anticancer drug (Vinblastine, VB).

successful formation of ABIIL. The resultant material (ABIIL) exhibited excellent solubility in aqueous-ethanolic media, which was useful for extracting of heavy metal ions (HMIs) aqueous-ethanol. The new scavenger (ABIIL) displayed excellent scavenging efficiency for tested HMIs, as it can uptake up to 98.9% and 96.7% of Fe(III) and Cu(II) ions, respectively, from aqueous-ethanolic effluents. Besides, it could be easily regenerated and reused without a significant loss of its efficiency even after six consecutive scavenging–regeneration cycles. The physicochemical features, FTIR, and UV–vis spectral results of the scavenging products indicated that the removal process occurs by the chelation of the anionic form of ABIIL with HMIs. Where the pH-potentiometric studies revealed that ABIIL behaves as a monobasic bidentate (N,O) ligand. The new chelating ionic liquid (ABIIL) underwent a color-change from pale yellow to a yellowish-green and reddish-brown when bound Cu(II) and Fe(III) ions, respectively, to form scavenging products (Cu-/Fe-ABIIL). The pharmacological assessment for the scavenging outputs (M-ABIIL) showed that they have excellent and broad-spectrum antimicrobial activity, with slightly better effectiveness as fungicides than act as bactericides. For instance, the MIC values (μg/mL) for Fe-ABIIL against microbial species were found to be:16.8, *C. albicans* (fungi) < 18.9, *S. aureus* (G^+ bacterium) < 19.5, *A. flavus* (fungi) < 23.1, *E. coli* (G^- bacterium). Additionally, these complexes possessed more cytotoxic effects than the clinical drug (Vinblastine, VB) toward colon cancer cells (HTC116), whereas they are less cytotoxic than VB to normal human cells (HeLa). Thus, ABIIL has great potential not only for removing toxic Cu(II) and Fe(III) ions from aqueous environments, but also to convert them into promising safe pharmacological nominates for chemotherapeutic applications. Therefore, ABIIL may offer an ideal scavenger for the remediation cupric- and ferric-polluted wastewater produced from many industrial processes, before discharging into the aquatic environment, and consequently averted the environment and human the serious impacts of Cu(II) and Fe(III) ions. Based on these promising findings, still, work on the remaining issues for these ionic liquid-based complexes is continuing and will be presented in future reports.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2020.114525.

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