Original Research Paper

Extraction and Spectrophotometric Estimation of Fe^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} From Industrial Effluents Using Synthetic Supramolecular Ligand

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ABSTRACT

Increased water pollution due to toxic heavy metals is becoming a serious threat which has been faced by the entire world in the last few decades. To overcome this problem a suitable complex ligand was designed for removal of Fe^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} from the effluents. The work incorporated the synthesis of (4Z)-4-((2Z)-2-(2,5-dihydro-2,3-dimethyl-5-oxo-1-phenyl-1H-pyrazol-4-ylimino) ethylidene amino)-1,2-dihydro-1,5-dimethyl-2-phenylpyrazol-3-one (Supramolecular Ligand) by the condensation method and confirmed by FTIR and 1HNMR spectroscopic methods. The batch extraction experiments designed to examine the effect of various experimental parameters on the extraction efficiency of the heavy metals. The experimental results depicted that up to 30 min time for supramolecular ligand is enough for the significant extraction of all the metals under study. The pH level, slightly acidic to the neutral condition is favourable for maximum extraction of metals. The percent extraction at optimized conditions of time and pH were found to be 98.29, 96.63, 96.95 and 95.64% for Fe^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} respectively. The extraction efficiency was governed by chloroform as a solvent. Simple to synthesize, faster extraction of metals, slightly acidic to neutral pH conditions for extraction are the characteristic features of the compound which governs its applicability.

INTRODUCTION

Water, being a limited resource, an increase in water pollution due to metal ions and other pollutants is of great concern throughout the world (Jethave et al. 2017). The different pollutants responsible for water pollution are organic dyes, inorganic oxyacids and heavy metals etc. Amongst these, heavy metals are considered as more dangerous because even trace quantity in water is considered as carcinogenic (Li et al. 2011, Tang et al. 2008). Though the metals play a vital role in human metabolism and photosynthesis, an excess of these metals in living organisms is responsible for genetic and metabolic diseases (Fraga 2005). Heavy metals have widespread applications in different industrial units, viz. paint, fertilizer, metal industry and electroplating industries (Hua et al. 2012). Particularly in developing countries like India, the local communities have often encountered hazardous effects of pollutants (Himadri et al. 2014).

Different methods like solid-phase extraction and liquid-liquid extraction, adsorption, co-precipitation, and ion exchange have been applied for the removal of heavy metals from water. (Oliva et al. 2002, Saracoglu et al. 2003, Okamoto et al. 2000, Jethave & Fegade 2018, Fegade et al. 2018, Kondalkar et al. 2018). Amongst these, liquid-liquid

extraction is considered more effective because it is a simple, low cost, highly selective and has more removal efficiency. Till now, diverse complexing agents have been synthesized for metal extraction (Sarode et al. 2015, Costa et al. 2013). The aim of the present study is to synthesize a suitable chelating agent for liquid-liquid extraction of Fe^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} from effluents. For this purpose, a supramolecular ligand was synthesized by a simple condensation reaction between 2 moles of 4-amino antipyrine and one mole of glyoxal in methanol. This chelating agent was characterized by NMR, FTIR and mass spectroscopy. The effect of various analytical parameters such as time, pH, concentrations, stripping agents and the presence of other ions on the extraction efficiency was examined. The experimental sets carried out to optimize the above parameters for removal of Fe^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} from industrial wastewater. The remaining concentration of these metals in the reaction mixture was estimated by atomic absorption spectrophotometer.

MATERIALS AND METHODS

All chemicals and reagents used for the experiment and preparation of ligand were of analytical grade and procured from Sigma Aldrich and applied without further purification. Milli-Q water was used at every stage of the experiment.
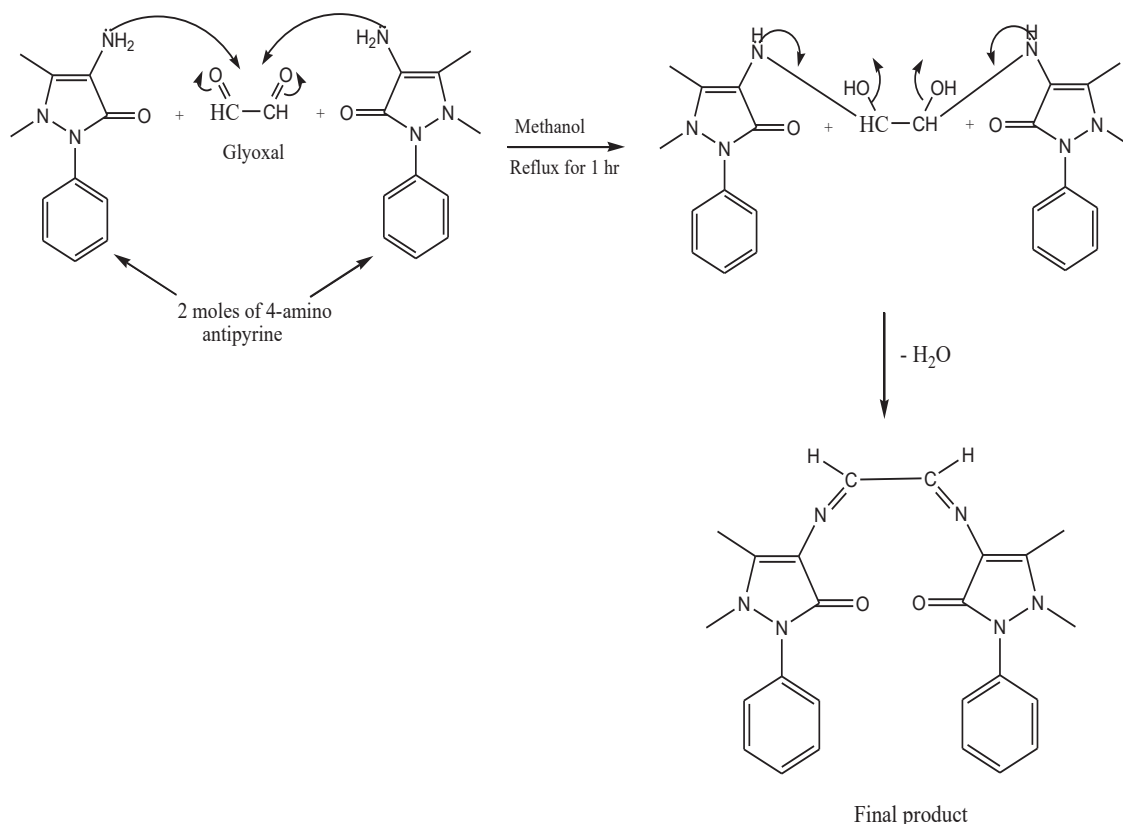
Fig. 1: Possible mechanism of the formation for supramolecular ligand compound.

Digital pH-meter (India, EQUIP-TRONICS model EQ 610) was used for pH determination. Concentration of chromium was estimated using AAS. FTIR spectrum (in the range of 500-4000 cm^{-1}) of the ligand was obtained using FTIR spectrophotometer (Germany, Model: Bruker). H^{1}NMR was recorded on (Germany, Model: Bruker Advance) 400MHz.

Batch Extraction Experiment for Metal Removal

Optimization of diverse analytical parameters on extraction efficiency for metals was carried out by conducting experiments at various experimental parameters. For the choice of solvent, the extraction experiments were performed on different solvents like chloroform, N-butanol, ethyl acetate, toluene and N-hexane. In these experiments, the solvent was optimized based on contact time for chromium extraction at a various time interval. Suitable pH for maximum extraction of chromium was determined by running the experiments at a particular pH range from 2 to 10, provided other optimized variables kept constant. The percent metals extracted (% E) was calculated by applying an Eq. 1.

% E = (concentration of metals after extraction/
total concentration of metals) × 100   …(1)

RESULTS AND DISCUSSION

Synthesis of the Ligand Compound

The 0.2 moles of 4-amino antipyrine were poured in a 100 mL round bottom flask containing 25 mL methanol and the mixture was homogeneously mixed by a magnetic stirring. To these solutions, 0.1 moles of glyoxal was added drop-wise and the reaction solution was refluxed for 1 hr till the yellow residue was obtained and then filtered by a Whatman filter paper. The obtained yellow residue washed with distilled water several times to remove unreacted compounds and impurity forms. The obtained compound was stored in a bottle for characterization and batch extraction purpose. The possible mechanism for the ligand synthesis proposed in Fig. 1.

Characterization of the Compound

The formations of the compound were confirmed by various structural elucidation techniques like FTIR and ^{1}HNMR and presented in Fig. 2 and 3 respectively. FTIR spectrum of the compound showed stretching frequency at 1557 cm^{-1} which indicates the presence of NH$_2$ which in term indicates the
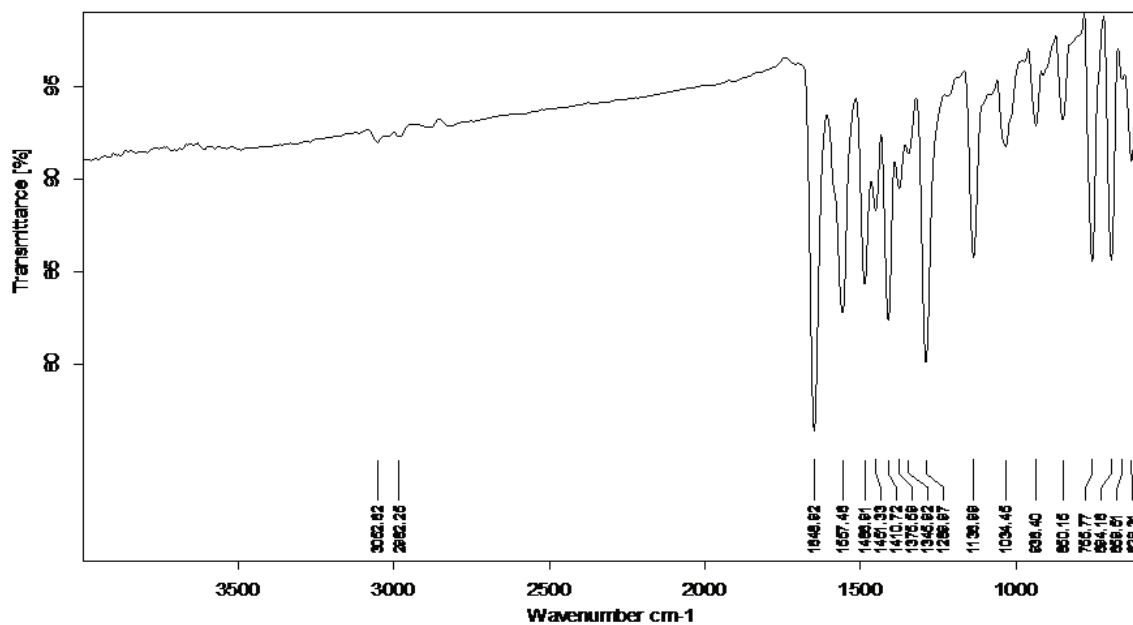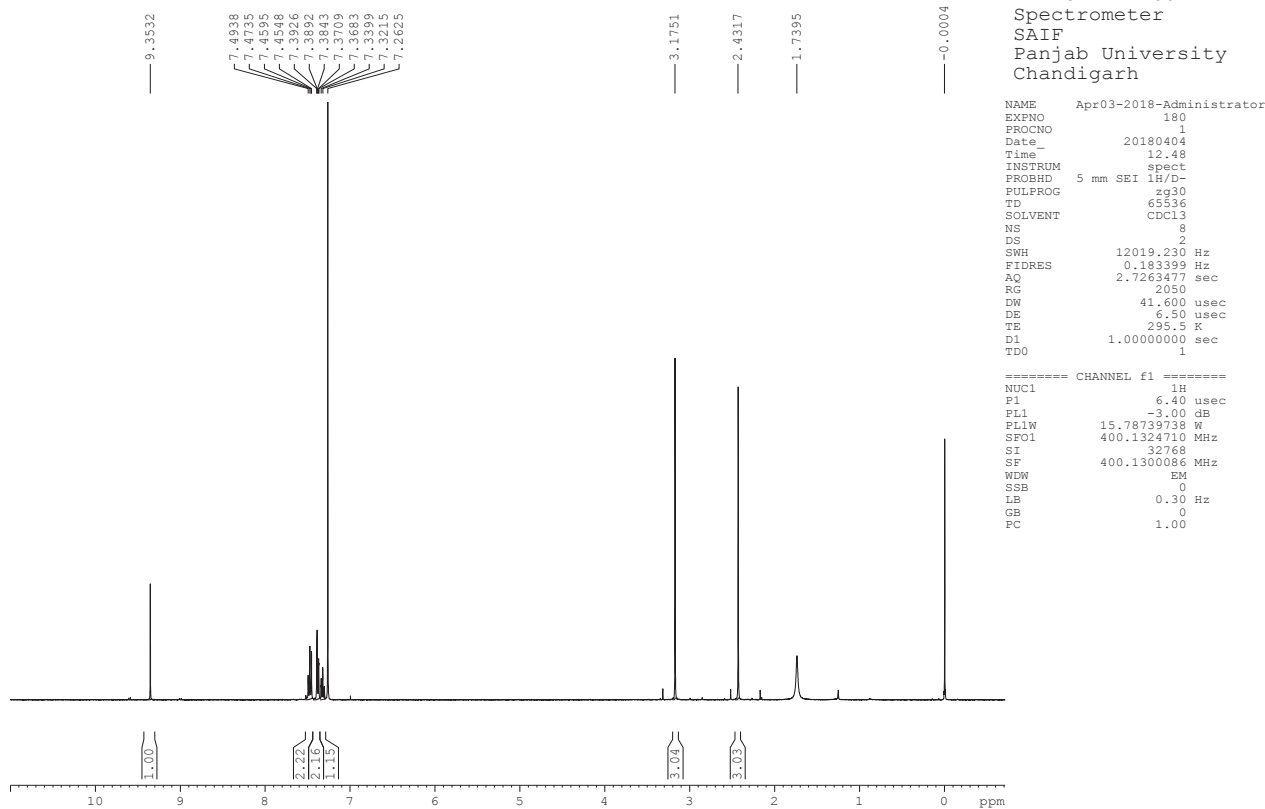
Fig. 2: FTIR spectrum of the supramolecular ligand.

SDP-1

BRUKER
AVANCE II 400 NMR
Spectrometer
SAIF
Panjab University
Chandigarh

NAME	Apr03-2018-Administrator
EXPNO	180
PROCNO	1
Date_	20180404
Time	12.48
INSTRUM	spect
PROBHD	5 mm SEI 1H/D-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	2050
DW	41.600 usec
DE	6.50 usec
TE	295.5 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	6.40 usec
PL1	-3.00 dB
PL1W	15.78739738 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1300086 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Fig. 3: H^{1}NMR spectrum of the supramolecular ligand.

formation of a compound. The different IR frequencies with functional groups are summarized in Table 1. The ^{1}HNMR spectrum of the compound shows a peak near 7.5 which is assigned to $\sim N = C - C = N \sim$ (with H, H above the two central carbons). This peak confirms the formation of the compound. The ^{1}HNMR peaks with functional groups are summarized in Table 2. Both FTIR and ^{1}HNMR characterization showed the formation of the compound.

Selection of A Suitable Solvent for Metal Extraction

Solvent selection is an important part of liquid-liquid extraction. Stability of a complex formed between ligand and metal is highly dependent on the polarity of a solvent (In et al. 2008). Five different solvents were used for extraction of metals by supramolecular ligand, viz., chloroform, N-butanol, ethyl acetate, toluene and N-hexane. The obtained results from the experiment are illustrated in Fig. 4 and showed that chloroform is a suitable solvent for the extraction of metals. The percent extraction of Fe^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} using chloroform found to be 86%, 61%, 66% and 44% respectively. The extraction of the above metals using other solvents was less as compared to chloroform (Sarode et al. 2012). In liquid-liquid extraction, replacement of solvent molecules by either ligand or cation is highly favourable (Nezhadali et al. 2007). This condition seems to have fulfilled by chloroform. So, chloroform is selected as a solvent for further extraction experiment.

Effect of Extraction Time

The definite time required for ligand molecules and cation to dissolve into an organic phase altogether affects the overall extraction (Dadfarnia et al. 2010). The effect of contact time on percent extraction efficiency of the ligand was observed by conducting extraction experiments at a different time interval from 5 to 40 min. The obtained results are portrayed in Fig. 5 and show that the prominent extraction efficiency for metals is noted up to 25 min and after that, no significant extraction was observed. The optimized condition of contact time of 20 min was elaborated for Fe^{+3} and Pb^{+2} while in case of Cd^{+2} and Zn^{+2} it was found to be 25 and 30 min, respectively. The percent extraction at an optimized time was noted as 85.34, 60.21, 64.12 and 43.67% for metals Fe^{+3}, Pb^{+2}, Cd^{+2} and Zn^{+2} respectively.

Optimization of pH for the Extraction of Metals

As pH of the solvent controls the stability of the complex formed between ligand and cation, it is a prime variable in the liquid-liquid extraction (Ramo et al. 2000). The effect of solution pH on the extraction efficiency of metals was observed at 0.5 to 9. The results of various experiments depicted that acidic to neutral pH condition is favourable for metal extraction (Fig. 6). In complex formation, ligand behaves like Lewis base and donate its lone pair of an electron to a metal cation to form a complex. In the case of supramolecular ligand, nitrogen and oxygen are the donor atoms and at suitable pH facilitates the formation of a complex by donating a lone pair of electrons.

Table 1: FTIR frequencies assigned to the functional groups of supramolecular ligand.

Sr. No.	FTIR frequencies (cm^{-1})	Functional groups
1.	3062	=C-H
2.	2982	-C-H
3.	1648	C=O
4.	1557	C=N
5.	1486, 1410, 1375 and 1345	CH$_3$ bending
6.	755, 694, 659 and 629	C-H monosubstituted benzene derivative

Table 2: Assignment of H^{1}NMR chemical shifts to the functional groups of supramolecular ligand.

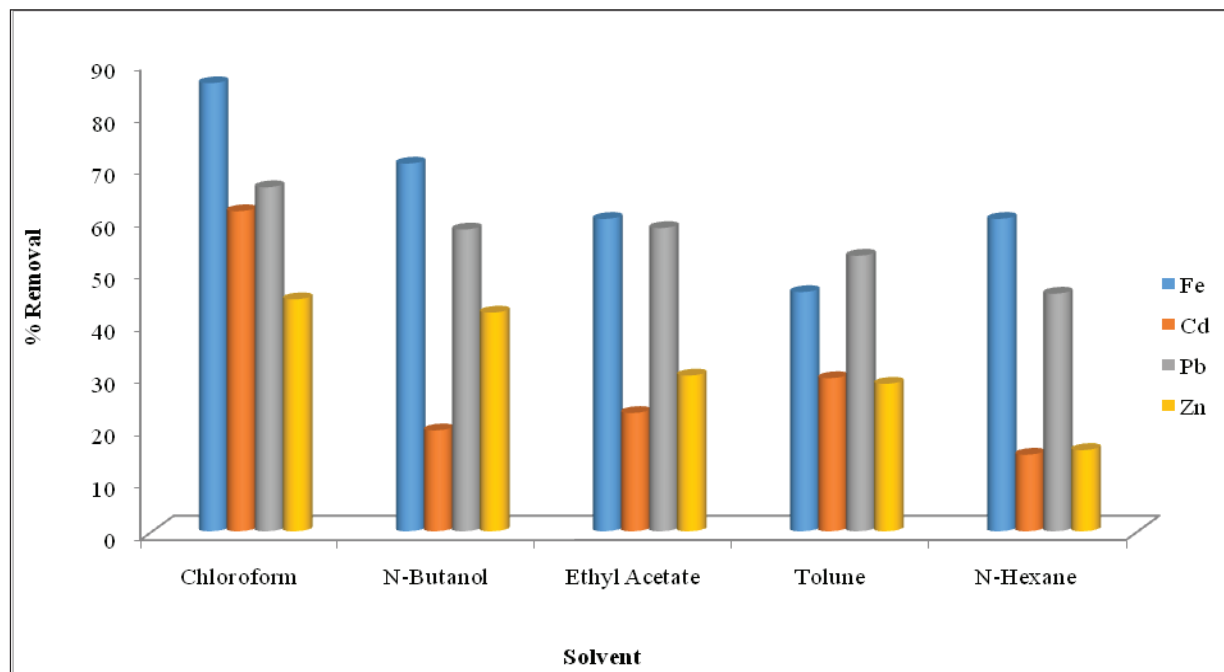| Sr. No.	Chemical shifts (d)	Functional groups
1.	7.49	$\sim N = C - C = N \sim$ (H, H above central carbons)
2.	7.45-7.26	Aromatic C-H
3.	2.43	N-CH$_3$
4.	1.73	CH$_3$-C=C-

Fig. 4: Effect of different solvents on % extraction of heavy metals using supramolecular ligand.
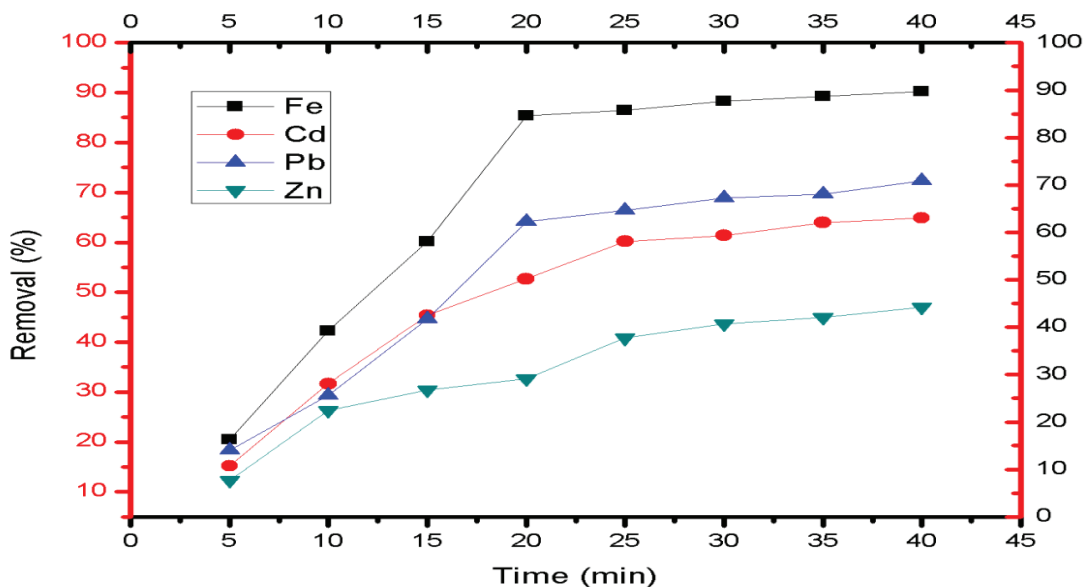

Fig. 5: Optimization of contact time for the extraction of metals using supramolecular ligand.

Effect of Stripping Agents

The recovery of metal ions from organic phase is an important step in liquid-liquid extraction. Generally, acids with different molar concentrations being used for recovery of metals are called as stripping agents. In the present study, three acids, viz. HCl, HNO_3, and H_2SO_4 with molar concentrations from 0.001 to 5 M were used for the recovery of the metals. The results of the experiment (Fig. 7) suggest that 1M HCl showed most metal recovery as compared to other acids. 81.88, 78.93, 81.73 and 80.34% of metal recovery was achieved by using 1M HCl for Fe^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} respectively.
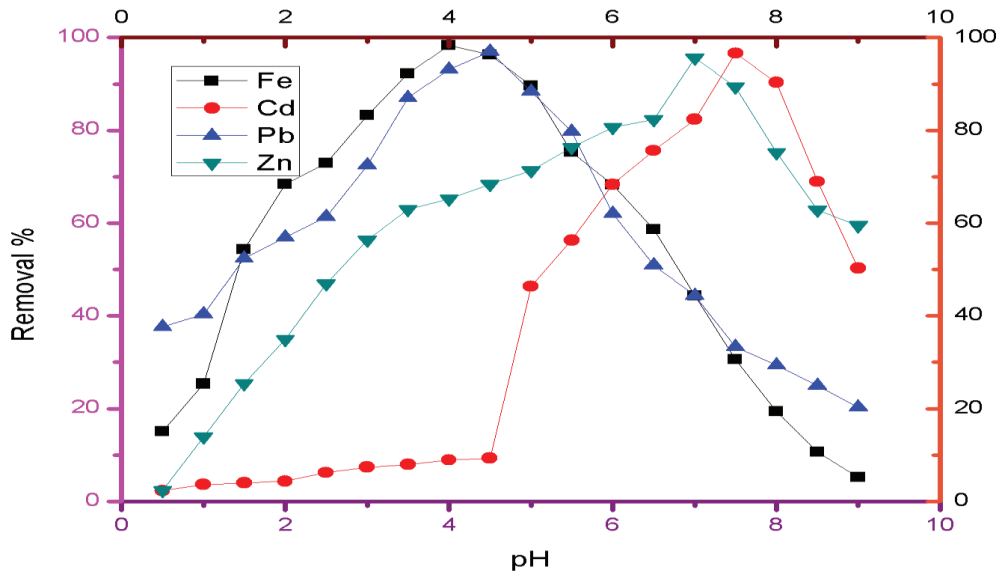
Fig. 6: Optimization of pH to achieve maximum extraction of metals using supramolecular ligand.
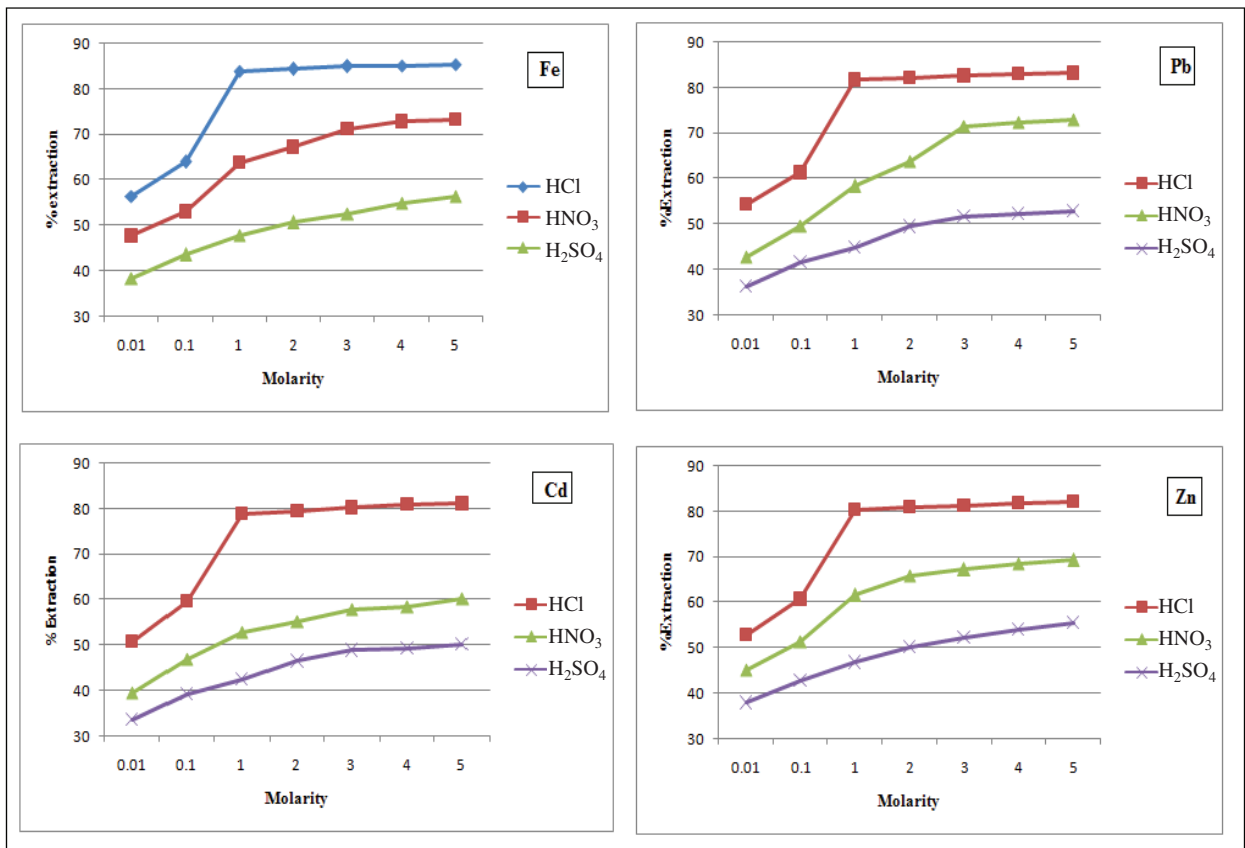

Fig. 7: Effect of the stripping agents on extraction efficiency of supramolecular ligand at different acid concentrations.

Table 3: Application of supramolecular ligand for heavy metals extraction from industrial effluent.

Metal ion	Before extraction (ppm)	After extraction (ppm)	% extraction of metal from industrial effluent
Fe^{+3}	0.3152	0.0004	99.87
Cd^{+2}	0.2398	0.0211024	91.20
Pb^{+2}	0.5856	0.00105408	99.82
Zn^{+2}	0.5043	0.04055176	91.95

Application of Supramolecular Ligand for Industrial Wastewater Samples

Real sample analysis was carried out on samples collected from local metal industry over the optimized condition of time, pH and other variables. The ligand showed impressive extraction efficiency for all four metals over optimized conditions of experimental variables. The reproducibility of the results confirmed by conducting the above experiments five times and mean of the results obtained did not show deviation above 5% from individual results. This shows the reliability and reproducibility of the results. The results of the real sample analysis are summarized in Table 3.

CONCLUSION

In this work, synthesis of a suitable complexing ligand was performed and characterized by FTIR and H^{1}NMR. The extraction efficiency of the compound was tested at various experimental variables such as solvent, time, pH, etc. In addition, the effect of stripping agent on extraction efficiency over industrial samples was observed. The results obtained from batch extraction experiments revealed that chloroform could efficiently remove the metals more than other solvents. 30 min is the time in which the synthesized ligand can significantly extract metals from solvents. It was noted that slightly acidic to neutral pH conditions are favourable for extraction. The significant recovery of the metals can be achieved using 1M HCl. Application of the compound for extraction of metals from real samples at optimized conditions has shown impressive results which signify the applicability of the compound for industrial purpose.

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