Separation and determination of the environmental toxic metals using polymer anchored Azomethine complexes

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ABSTRACT
The effects of Environmental Toxic Metals on human health have long been known and the literature dealing with the subject is immense. The analysis of pollutants by using suitable complexing agent is centered on the development of sensitive technique for detection, determination and remove of contaminants from polluted air, water and land. In view of the importance of Azomethine compounds in pharmaceutical as well as industry, the immobilized polymeric reagents for various analytical analysis, the studies mainly focused on the synthesis of new polymeric reagents for anchoring different Azomethine ligands to polymer matrix. The new polymeric reagents by linking Azomethines to different polymers (Polymer Anchored Azomethines) will be used for Extraction of toxic metal ions (Inorganic pollutants) present in Industrial effluents. The nature and amount can be understood in environmental trace chemistry of pollutants by employing advanced instrumental methods.
1. INTRODUCTION

A structural study of polymer anchored complexes seems interesting and useful in view of the numerous applications. Anchoring chelating ligands to insoluble polymer matrix and the reaction of these chelating resins with metal ions, metal complexes provides an easy route for the syntheses of immobilized coordination compounds [1-6]. The Azomethines are important class of ligands which have played a significant role in coordination chemistry and applications of these coordination compounds in various fields [2,7-10] such as Medicinal, Pharmaceutical, Agriculture and Industry. Although a large number of non-Azomethine ligands like diethyl dithio carbamate [10], Oxime [11], β - diketones etc [12-18] have been immobilized to polymer support, only a few Azomethine have been anchored to polymer matrix [2,4,12,19,20].

The polymer supported reagents are also found important as catalyst, for organic synthesis, trace analysis and environmental applications [21]. For example ion selective polymer is especially important because of their ability to retain immobilized catalysts, when used as catalyst from their ability to extract targeted metal ions (usually toxic or precious) in the environment or other aqueous media. Representative examples, include amination of chloromethyl polystyrene with 1,3- diaminopropane to yield stable resin to complex gold from cyanide solutions [22], polymers with dihydroxyl amine acid groups for uranyl ion extraction [23], polymeric 8- hydroxyl quinoline for high copper affinity [24], a supported quinaidic acid resin for the extraction of cadmium [25]. A poly (vinyl benzaldoxime) for selective complexation of ferric [26] (oligomeric sulfide ) for high selectivity of mercuric and silver salts [27] and immobilized crown ethers for selective complexation of palladium, gold, silver, mercury salts [28]

Phosphorous based ion exchange resins are often prepared by chemical modification of styrene divinyl benzene copolymers with monophosphate ligands, their complexes have very stability constants with metal ions. For example methylene diphosphate ligands with polymeric matrix finds applications for the retention and recovery of metal ions from aqueous solution [29] therefore they may useful as new series of ion exchange resins with high metal ion affinity. Many toxic metals are present in the polluted water samples. The industrial waste water contains heavy metals are major pollutants. The waste water contains organic, inorganic metals. Thus may possess a major significant danger to human health. Zinc introduced into water is either remains in dissolved form, which is often used for drinking purposes, so they may be injurious to humans and animals. Many methods have been proposed for their removal forms industrial effluents. The literature survey revealed that there is very little work carried out on the synthesis of di vanillin Schiff base polymer and it is used to remove water soluble Zn(lll) ions. Therefore this investigation has been taken up to go insight in this field and make use of them for environmental pollution analysis and cleaning purpose in industries as well as waste water treatment.

2. MATERIALS AND METHODS

2.1. Materials

4-Morpholinoaniline and vanillin are purchased from sigma- Aldrich. Diethyl ether, methanol, Metal salts were purchased from Merck. Analytical grade solvents and chemicals were used throughout the analysis. The IR spectra were record In KBr medium and FTIR Affinity –I techniques on a shimadzu spectrometer in wave number region 4000-400 Cm⁻¹, UV spectra were record in Annamacharya pharmacy college, Rajampet, Kadapa. The NMR spectra of the ligand and metal complex were recorded on AV-400 M-HZ NMR spectrometer in IICT, Hyderabad in CDCl3 solvents at room temperature.

2.2. Methods

The Polluted water was purified in to different methods. Among all methods ionic exchange method is one of the best method. Impurities like heavy metal and anions are removed by using polymer exchange resins. Schiff base polymers are used for exchange of heavy metals present in the water. The work on the synthesis of various Azomethines, preparation of metal complexes with metals like Cadmium, Lead, Thallium, Copper, Indium, Palladium, Iron, Manganese, Cobalt having high stability constants which are soluble in water have been carried out. In order to remove these ions waste water and industrial effluents, these should be linked to some polymer matrix for easy separation as insoluble polymeric metal complexes.

Azomethines having reactive functional groups OH, NH₂. The ligand and sodium acetate were dissolved separately in ethanol. It was added slowly in to polymer matrix solution. The above solution was stirred at 70°C for 6 h. The resultant functionalized polymer beads were washed with ethanol, and dried.
2.2.1. Method of preparation of Azomethine polymer
Schiff base polymer prepared, Equimolar concentrations of 4-Morpholinoaniline and diVanillin were mixed individually in 50 ml of methanol and refluxed on a water bath with constant stirring for about 4 hours. After completion of the reaction, pale yellow substance was obtained. The solid product was filtered off and washed with methanol and distilled water. The crude product was purified by recrystallization in ethanol and the pure Di vanillin Schiff base polymer (DVSP) was obtained. The preparation of the Schiff base polymer equation were represented in Fig-1

![Fig:1 synthesis of di vanillin Schiff base polymer](image1)

2.2.2. Extraction of metal ion in the polluted sample
The functionalized polymer was kept in contact with 100 ml of ethanol. It was added to the polluted water and stirred at 70°C for 6 h. The crude product was purified by re crystallization in ethanol. The Azomethines as well as the polymers complex will be analyzed by spectroscopic techniques like UV, IR and NMR spectra. The developed new polymeric reagents will be used for extracting the various metal ions present in the waste water and industrial effluents. The metal ions present in the complex can be understood by Electro Analytical Techniques like Polarography, Cyclic Voltammetry. The polymer Schiff base Zn(II) metal complex structure represented in the Fig-2.

![Fig:2 Divanillin Schiff base polymer Zn(II) Complex](image2)
2.2.3. Recommended procedure for the removal of metal ions
A stock solution of zinc sulphate used in this study was prepared by dissolving an accurate quantity of zinc sulphate into 100 ml. The polymerized Schiff base was added to zinc sulphate solution and reflected for 6 h. The mixture was cooled a precipitate was formed, which was collected by filtration. The compound was recrystallized with ethanol. The complex was analyzed by using UV, NMR and IR spectroscopy. This data was nearly same that of the above analyzed polluted sample data.

3. RESULTS
The synthesized di vanillin Schiff base polymer was represented in Fig-1 and di vanillin Schiff base polymer anchored Zn(II) complex structure was represented in Fig – II. The analyzed data from polluted sample was represented in the Table-I. The IR, UV and NMR specters of polymer Schiff base and polymer anchored Zn(II) discussion was given below.

<table>
<thead>
<tr>
<th>Inorganic pollutant</th>
<th>Source</th>
<th>Specification limits</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Automobile Exhaust, Battering, Mixing etc</td>
<td>0.1 ppm</td>
<td>Loss of appetite constipation Abdominal pain</td>
</tr>
<tr>
<td>Cd</td>
<td>Soil around steel &amp; Iron works</td>
<td>0.01mg / L</td>
<td>Liver &amp; Kidney damage, acute Gastritis.</td>
</tr>
<tr>
<td>Zn</td>
<td>Steel works, edible Oils</td>
<td>5 mg/ L</td>
<td>Dizziness Diarrhea</td>
</tr>
<tr>
<td>As</td>
<td>Paper Industry &amp; Cotton growing</td>
<td>0.05ppm</td>
<td>Cramps, paralysis Leukemia</td>
</tr>
<tr>
<td>Cr</td>
<td>Metal plating &amp; Wood preservative</td>
<td>0.05 mg / L</td>
<td>Respiratory cancer</td>
</tr>
<tr>
<td>Cu</td>
<td>Mining, Metal plating</td>
<td>1.5 ppm</td>
<td>Essential Trace Elements, Toxic to plants</td>
</tr>
<tr>
<td>Mn</td>
<td>Mining Wastes</td>
<td>0.05 mg / L</td>
<td>Highly Toxic</td>
</tr>
</tbody>
</table>

4. DISCUSSION
The synthesized Di vanillin Schiff base polymer was yellow in color and melting point 172-174°C. The Schiff base polymer was insoluble in water. Infrared spectra of diVanillin Schiff base polymer and polymer anchored Zn(II) complexes were recorded with FTIR Affinity-1 techniques on a shimadzu spectrometer in wave number region 4000-400 cm⁻¹ using KBr pellets. The IR spectra of polymer Schiff base Zn(II) complex was compared with the ligand indicate the interaction of coordination sits with the metal ion. The FTIR spectra of the polymer Schiff base ligand gave a strong band at 1635 cm⁻¹, due to the formation of Schiff base. This band was shifted to a 1624 cm⁻¹ in the metal complex, indicating Azomethine of nitrogen was involved in the bond formation with metal. The new band was obtained the 737 cm⁻¹ region, indicating the formation metal –nitrogen bond. In the polymer Schiff base Zn(II) another new band was obtain the 619 cm⁻¹, indicating formation of a metal –oxygen bond. The ¹H NMR of polymer Schiff base and polymer Schiff base Zn(II) complex was measured in CDCl₃ as solvents. The ¹H NMR of polymer Schiff base ligand δ (ppm): 8.38 (s,1H, CH=N, Azomethine),6.93-7.19(Ar-H, aromatic protons), 3.87 ( S, 3H, -OCH₃), 5.94 ( S 1H,-OH). The ¹H NMR of polymer Schiff base Zn(II) complex δ (ppm) : 8.65 (s,1H, CH=N, Azomethine),6.98-7.30 (Ar-H, aromatic protons), 3.95 ( S, 3H, -OCH₃). The polymer Schiff base Zn(II) complex was diamagnetic as expected for d¹⁰ systems. The electronic spectrum shows no bands, and the complex may be assigned a tetrahedral geometry. The polymer anchored complex was insoluble in common organic solvents.

5. CONCLUSION
In view of the importance of Azomethine compounds in pharmaceutical as well as industry, the immobilized polymeric reagents for various analytical analysis, this work has been taken up to synthesize new polymeric reagent, by anchoring different Azomethine ligands to polymer matrix for the analysis of metal ions in the industrial effluents, for water analysis and treatment of polluted water to use for environmental pollution control measures. The literature survey revealed that there is little work carried out on the synthesis of polymeric Azomethine ligands. Polymer Schiff base system seems to have very efficient and economical for removing toxic metals from industrial waste water.
SUMMARY OF RESEARCH
The synthesized polymer Schiff base ligand was developed as a reagent for removal of Zn(II) form solution. The remove of Zinc from the waste water increases with increasing contact time. The relative increase in the extent of removal of metal ion from the waste water up to some extent of time after the removal of metal ion from the waste water was constant. Hence the optimum time of reflux was fixed. This polymer Schiff base and metal complex was further useful for bacterial activities.

FUTURE ISSUES
This method was the most important advantage method to removing of metal ions in the waste water up to the maximum.

DISCLOSURE STATEMENT
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REFERENCE
13. Bumagin NA, Potkin VI. Functionalized isoxazole and isothiazole ligands: design, synthesis, palladium complexes,


17. Shigehisa, Akine, Takanori, Wenkuri Dong, Sayuri Masubuchi, Nabeshima Tatsuya. Oxime-Based Salen-Type Tetradentate Ligands with High Stability against Imine Metathesis Reaction; The journal of organic chemistry, 2005,70, 1704-1711.


21. Sumitha Roy, Chatterjee T, Manirul Islam. SK. Polymer anchored Cu(II) complex: an efficient and recyclable catalytic system for the one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles starting from anilines in water. Green chemistry journal; 2013,9.


28. Ronald L. Bruening, Bryon J. Tarbet, Krzysztof E. Krakowiak, Merlin L. Bruening, Reed M. Izatt, and Jerald S. Bradshaw ; Quantitation of cation binding by silica gel bound thiamacrocycles and the design of highly selective concentration and purification columns for palladium(II), gold(III), silver(I), and mercury(II); Analytical chemistry, 1991, 63, 1014–1017.

29. Bruening R.L., Tarbet, B.J., Krakowiak, K.E., Brucning, M.LIzatt, RM., Bradshaw, Quantitation of cation binding by silica gel bound thiamacrocycles and the design of highly selective concentration and purification columns for palladium(II), gold(III), silver(I), and mercury(II); Analytical chemistry (ACS journal) 1991,63, 1014-1017.