GREEN SYNTHESIS OF AN AMIDE-BASED CHEMOSENSOR AND ITS APPLICATION FOR DETECTION OF TOXIC METAL IONS

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Ultrasound-assisted synthesis of a chemosensor from benzoyl chloride and diethylenetriamine in acetonitrile was carried out and the product structure was confirmed by UV-VIS and FT-IR spectroscopy. The synthesized chemosensor interacts with metal ions and produces a notable change in colorimetric measurements. It is observed that as the concentration of metallic ions increases, absorbance also increases, thus the chemosensor can be used for quantitative estimation of metal-ion content.

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Introduction

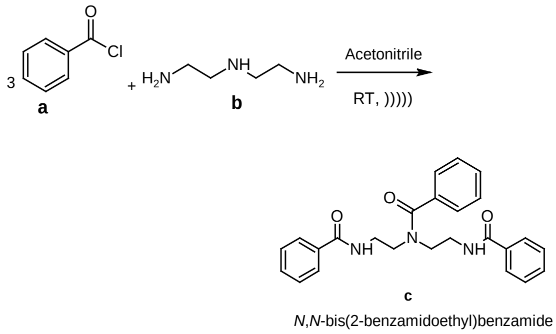
In recent decade increase in industrialization resulted in high pollution of metal ions in the environment which interact with living systems and cause hazardous effects on human health and the environment resulting in toxic cation and poisoning.

Chemosensor is a sensory receptor that shows a detectable change in color and photophysical properties. The ultimate aim of the scientific community is the synthesis of sensitive chemosensor which can be used for the detection of heavy metal ions.[1] The Hg^{2+} is a common, environmentally toxic and hazardous pollutant among the heavy metal ions. Trace amounts of Hg^{2+} in the body can lead neurotoxicity and the mercury ions easily pass through the biological tissues to cause digestive, kidney and especially neurological diseases.[2] The Cu^{2+} ion is an important transitional metal ion which plays a major role in environmental, biological, forensic and chemical fields.[3] Cu^{2+} ion is the third most abundant essential metal ion in the human body transition element after Fe^{3+} and Zn^{2+}.[4] Zinc is the second most abundant transition metal in the human body next to iron and acts as a catalytic co-factor in various metallic-enzymes. Zn^{2+} ions play a vital role in numerous fundamental biological processes such as cellular metabolism, DNA synthesis and neurotransmission.[5] The deficiency of Zn^{2+}ions causes various diseases such as Alzheimer's, Parkinson's diseases, epilepsy regulation disorder in mammalian reproduction, immune system, sense of taste and smell and overall growth of the living body.[6] The zinc is an important constituent in more than 250 metalloenzymes.[7] Cobalt plays a significant role in the metabolism of ferrous and hemoglobin synthesis. The Co^{2+} ions are an important constituent in vitamins.[8] The Co^{2+} shows toxicological effects on human health, including decreased cardiac output, asthma, heart and lung disease.[9] Ni^{2+} is an essential trace ion in organic systems, but the excess accumulation of Ni^{2+} in the body can lead to various diseases such as lung fibrosis, cardiovascular and kidney diseases.[10]

In recent decades, a wide number of efficient chemosensors (ligands) have been developed for the detection of various metal ions in aqueous solution. The type of interaction between chelate and the metal ion is a coordinate bond or host-guest type.[11] Various methods have been used for detection of the metal ions such as rhodamine 6G (R6G) and 8-aminoquinoline (8-AQ) co-modified core/shell Fe_3O_4@SiO_2 nanoparticles used for detection of Hg^{2+} and Zn^{2+}ions in aqueous solution,[12] Rhodamine B chemosensor used for detection of Pb^{2+}in acetonitrile,[13] azadiene-pyrene derivative for Hg^{2+} in aqueous acetonitrile solution,[14] (E)-2-(5-((2-carbamothioylhydrazono)methyl)-6-hydroxy-3-oxo-3*H*-xanthen-9-yl)benzoic acid for the detection of Cd^{2+} ions in aqueous solution,[15] *N*-(1,10-phenanthrolin-5-yl)-2,2-diphenylacetamide for selective detection of Fe^{3+} in an aqueous medium,[16] 8-hydroxyquinoline based graphene oxide for detection of Zn^{2+} in aqueous media,[17] cyclometalated platinum(II) bipyridylacetylide complex for Mg^{2+} in acetonitrile,[18] rhodamine-based compound for Pd^{2+}in pure water,[19] and for highly selective detection of Ag(I) ions.[20]

The syntheses of chemosensors are reported in the literature by various methods from readily available starting materials such as water meditated synthesis of CF_1-CF_3 and use for detection of CN^{-1}.[21] Ultrasound-assisted synthesis of diphenylamine-based Schiff base used in the detection of copper(II) ion in aqueous solution,[22] microwave-assisted synthesis of graphitic carbon nitride quantum dots[23] and photoluminescent carbon dots synthesis using starch (*Tapioca Sago*) via solution method at mild condition[24] and possess great applications in various fields such as environmental,[25] forensic,[26] and the biological sciences.[27]

Herein, we develop an ultrasound-assisted new method for the synthesis of amide-based chemosensor using diethylenediamine and benzoyl chloride. Ultrasound waves accelerate the rate of reaction by cavitation and nebulization phenomenon. The cavitation helps to create a development of implosive collapse of bubbles in a liquid. Nebulization phenomenon helps in the creation of mist from ultrasound passing through a liquid and impinging on a liquid-gas interface.[28]



Materials and methods

All chemicals were purchased from Sigma Aldrich and used without further purification. UV spectrophotometric analysis was carried out using UV-VIS Perkin Elmer, lambda scan-35 system. FT-IR analysis was done on a BRUKER instrument having OPUS software of version 7.0.129.

Procedure for synthesis of amide-based chemo-sensor

In 25 mL round bottom conical flask benzoyl chloride (5.00 mmol), diethylenetriamine (10.00 mmol) and 1-2 mL acetonitrile were taken and kept in ultrasonication bath at room temperature for 10 minutes. The reaction mixture was poured into ice-cold water, and the precipitate of chemosensor was separated by simple filtration. Residue allowed drying at room temperature and dry white crystalline powder compound is used as chemosensor in aqueous ethyl alcohol.

Procedure for preparation of pH 10 buffer solution

For 10 ml: pH 10 buffer was prepared by taking 0.7 g of NH_4Cl, and 5.68 mL NH_3 solution in 10 mL distilled water in a conical flask.

Results and discussion

In the present work, we developed a new method for the synthesis of amide-based chemosensor ((7*E*)-*N*^{1}-benzylidene-*N*^{2}-((*E*)-2-(benzylideneamino)ethyl)ethane-1,2-diamine) using diethylenetriamine and benzoyl chloride under ultrasound irradiation. The absorbance in the UV-VIS analysis of Co(II) ion solution in aqueous ethanol for 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 ppm are illustrated in Figure 2. It was observed that as the concentration of a metal ion in solution was increased, the absorbance was increased. It helps to find out the concentration of a metal ion in an unknown solution by using a standard calibration curve. Mercury (Hg^{2+}), nickel (Ni^{2+}) and copper (Cu^{2+}) show excellent absorbance in the UV-VIS analysis. It was observed that metal ions form stable complexes with chemosensor and show visible color change or change in color intensity of aqueous solution. In UV-VIS analysis, absorbance was increased with respect to concentration and it validates the Lambert-Beer's Law.

The FT-IR spectroscopic technique was used to predict the functional group of chemosensor and metal-complex of chemosensor with the help of stretching frequencies. These results are illustrated in Table 1. The probable interaction of chemosensor with metal ions shows that it forms a stable coordination complex with a metal ion (a predicted structure is given in Figure 1). The synthesized amide-based derivative probably acts as a tridentate ligand showing chromophoric nature with the given metal ions and acts as chemosensor.

Table 1. FT-IR analysis of chemosensor and samples

No.	Sample / Compound	Frequencies, cm^{-1}	Assigned group
1.	Chemosensor	3623, 3750	N-H
		2982	C-H (aromatic)
		1700	C=O
		1647, 1546	C=C (aromatic)
		1280	C-C
		1046	C-N
2.	Chemosensor after reacting with 1% Cu.	2946	C-H
		2876	C-H (Aliphatic)
		1746	C=O
		1656, 1621,1546	C=C (Aromatic)
		3231, 3456	N-H
3.	Chemosensor after reacting with 1% Hg.	2972	C-H (Aliphatic)
		1748	C=O
		1648	C=C (Aromatic)
		1195	C-N
		1317	C-O
		3234-3496	N-H
4.	Chemosensor after reacting with 1% Ni	951	N-Ni^{2+}
		2892	C-H (Aromatic)
		3365	N-H

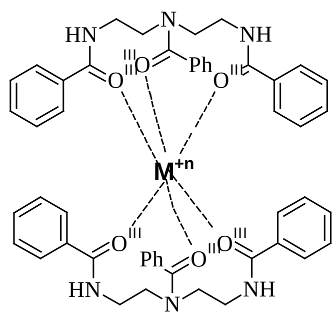


Figure 1. Amide based chemosensor forms coordination complex with metal ions

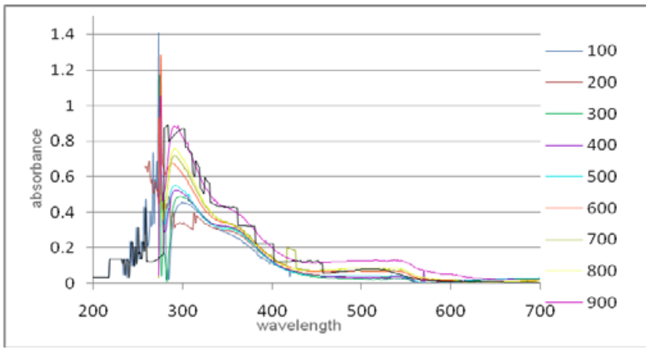


Figure 2. UV analysis of Co^{2+} dilutions with chemosensor (100-1000 ppm)

Conclusion

We developed a simple, efficient and eco-friendly method for the synthesis of amide-based chemosensor from commercially available material. We studied the application of chemosensor for qualitative and quantitative analysis of metal ions in a various extracted solution using UV-VIS spectroscopy techniques. This chemosensor helps in the preliminary analysis and detection of Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} metal ions in aqueous and spiked solutions. This chemosensor has excellent application in forensic chemistry and toxicology to detect the metal poisoning cases.

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