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Detection of Heavy Metal Ions in Water by Rhodamine Sensors: A Review on the Modern Approach

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ABSTRACT

Heavy metals are non-biodegradable, omnipresent and can pose a high risk to the environment and human life. They are required in trace amounts but when present in relatively higher concentrations, they can lead to toxicity in humans, plants and animals. Chemosensors offer a favourable approach to detect these metal ions as they are highly selective and easy to handle. This review discusses different derivatives of rhodamine B dye that are found to sense Cu^{2+} and Hg^{2+} in various water samples by calorimetric and fluorometric methods.

Key Words: Heavy metals, Chemosensors, Rhodamine

INTRODUCTION

Sensing of ions through molecular recognition is an interesting and active research area because of its important role in the biological and industrial processes, medicine,

catalysis, environmental and human sciences (1, 2). The increasing use of ions as industrial raw materials, fertilizers and mining raises environmental concern too (3, 4). There are several spectroscopic techniques such as Atomic Emission (AES), Atomic Absorption (AAS), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and other analytical techniques like Flow Injection Analysis and several chromatographic and electrochemical methods which can detect the ions (5, 6). However, majority of these methods are complicated, time consuming and expensive. On the contrary, chemosensors are low in cost, non-destructive, simple, highly selectivity and can detect ions via simply recording change in colour. Their ability to provide reliable data (both qualitative and quantitative) for a range of analytes (7, 8) makes them a very useful tool.

Heavy metals are also known as **"**high density chemical components which are highly toxic" (9). Their atomic weight varies between 63.5 to 200.6 g mol^{-1} and their specific gravity is greater than 5 g cm^{-3} (10, 11). Heavy metals pose a serious risk to human health and the environment because of their ubiquitous presence and the fact that they are non-biodegradable (12, 13,14). A major toxic effect of heavy metals is their ability to form bonds with the thiol group in proteins (15). The living organisms require heavy metals such as cobalt, zinc, copper, manganese, etc., in low amounts and when they accumulate in the biosphere and their concentration build up, they become toxic (16). The other metals like lead, arsenic, cadmium, chromium and mercury are hazardous even when present in trace amounts (17). For these reasons, they are considered as *"Environmental health hazards"* and are ranked among top ten in the listings of *"Agency for Toxic Substances and Disease Registry Priority List of Hazardous Substances"*. Several international agencies like World Health Organization (WHO), Centre for Disease Control (CDC), Joint Food and Agricultural Organization (FAO)/WHO Expert Committee on Food Additives (JECFA), and International Agency for Research on Cancer (IARC) are working to account for the heavy metal ion toxicity (18-20).

In this review, we have tried to highlight the several mechanisms such as inhibition of enzymes, causing of oxidative stress leading to generation of free radicals which in turn cause lipid peroxidation, damage to DNA etc. through which heavy metal ions exert their toxic effects on living organisms.

CHEMOSENSORS FOR IONS

Ions and Lewis acid based chromogenic hosts

These chemosensors have the coordination sites, which on binding to the guest, cause change in colour as shown by the signalling unit. The change in colour is imputing to deprotonation. The organic base causes the colour change by itself, and also accelerates the proton dissociation of the chromophore induced by the ions. Then through conjugation intramolecular charge transfer occurs which leads to change in colour. Other than the coordination aspects, the colour change happens due to reaction between the chromogenic hosts and the ions and such chromogenic ion sensors can be referred as chromo-reactants.

Non-metal based chromogenic hosts

Non-metal chromogenic host-based ion sensors use hydrogen bond or electrostatic interactions. Neutral ligands donate electron pairs to the metal and neutral receptors donate H-bonds to the ions.

SOURCES AND TOXICITY RANGE OF HEAVY METAL CONTAMINATION

Main sources of heavy metals are automobiles, industrial emissions, radiations and various cosmetic products. Here, we have focused on the Cu^{2+} and Hg^{2+} ions and their detection by rhodamine sensors by colorimetric and fluorometric methods. The WHO limits, sources and side effects are given in Figure-I.

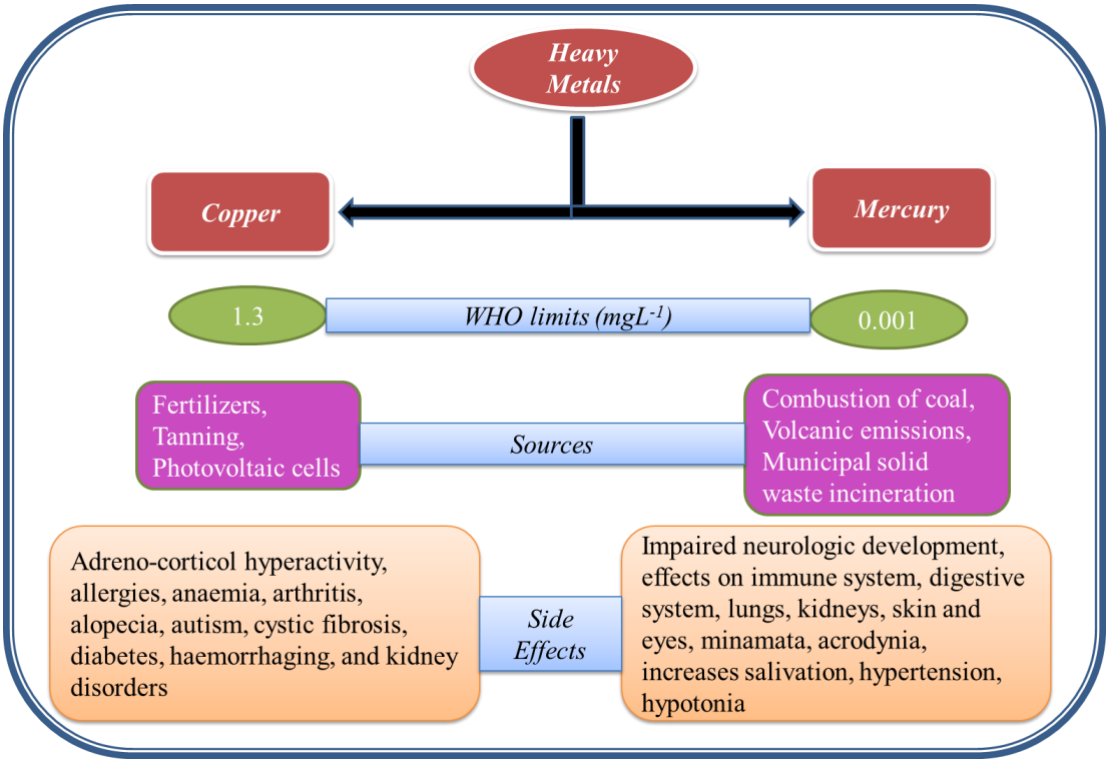

Figure-I Limits, sources and effects of heavy metal ions (Cu^{2+} and Hg^{2+}) (21, 22)

TOXICITY MECHANISM OF HEAVY METALS ON HUMAN CELLS

Disruption of several cellular functions is the basis of toxicity caused by the heavy metals in humans (Figure-II). Heavy metals are excreted from the body through liver, kidney or spleen, but they are usually stored for extended period in these organs as proteins with cysteine content (e.g. metallothionein) tend to bind them and hence reduce their rate of elimination from the body. This causes change in cellular functioning, leading to organ damage.

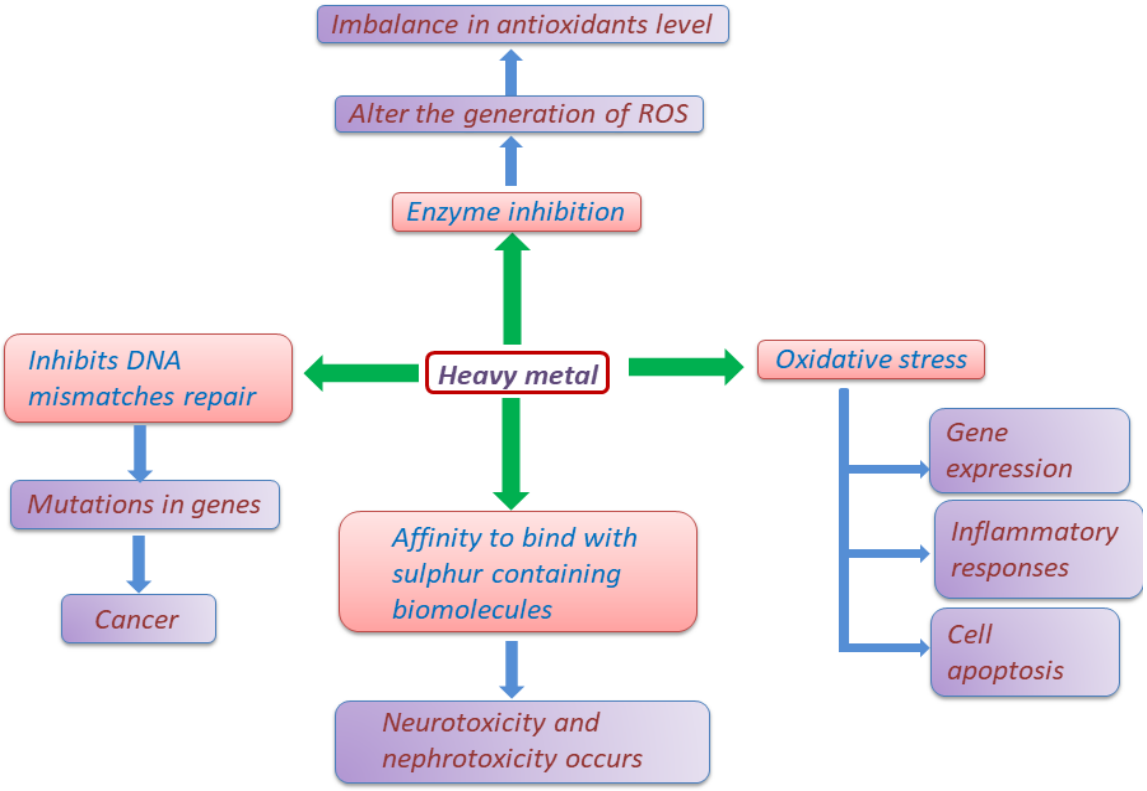

Figure-II Figure showing the effects of heavy metal on humans

RHODAMINE SENSORS

Detection of Copper (Cu^{2+}) ions by Rhodamine B sensor

Copper ions are the cofactor for many metalloenzymes and critical for their catalytic activity. They also play important role in the transcriptional events (23, 24). Hence, development of sensors (fluorescent/colorimetric) for Cu^{2+} ions has received more attention. Perturbation in intracellular copper ion homeostasis also causes oxidative stress and can play a role in several neurodegenerative disorders such as Alzheimer's, Parkinson's, Menkes' to name a few (25). So the identification of Cu^{2+} can help understand its pathological and physiological roles (26). So far, cogent progress has been made in the development of Cu^{2+}-chemosensors that are highly sensitive (27). However, because of the inherent paramagnetic property of Cu^{2+}, fluorescence quenching has been observed in most of these chemosensors (28). Developing their improvised version has been a daunting task as yet.

Wang et al. reported an "Off On" rhodamine-based chemosensor N-(2,4-dinitrophenyl) rhodamine B-hydrazide (DNPRH), which is ultrasensitive and shows selective fluorescent and colorimetric response to Cu^{2+} ions. The medium used for the recognition of Cu^{2+} ions is ethanol and water in 3:1 ratio and Na_2HPO_4-citric acid buffer at pH 7.0 (29) (Figure-III).

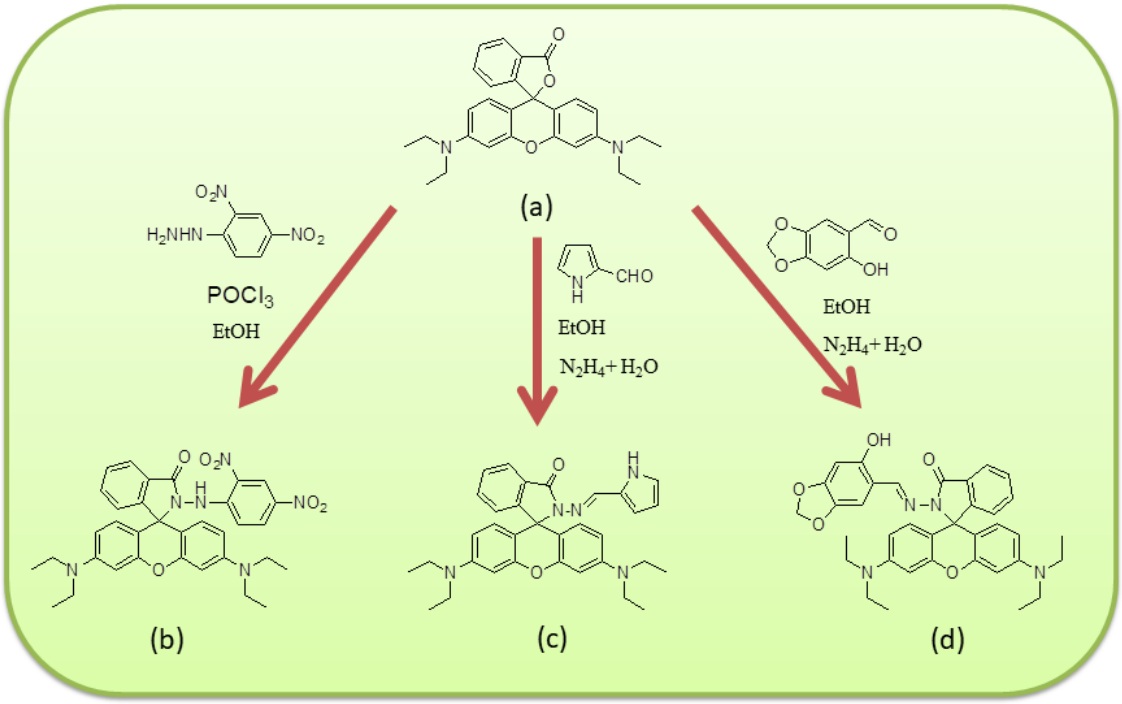

Figure-III Synthesis of chemosensors

(b) DNPRH, (c) R1, (d) RhS from Rhodamine B (a)

N-(2,4-dinitrophenyl)-rhodamine B hydrazide (DNPRH)'s selective reaction with Cu^{2+}

The most important property of chemosensors is their selectivity in binding to the target metal. The binding properties of DNPRH were investigated in the presence of several metal ions by fluorescence and UV-visible measurements. To begin with, they confirmed the stability of DNPRH in ethanol. They also observed absorption spectrum to remain the same when the the solution was stored under refrigerating conditions for about a week. Further, DNPRH solution was colourless and did not emit fluorescence, suggesting it to exist in spiro-cyclic form. On addition of two equivalent of Cu^{2+}, pink colour was seen to be formed immediately with a λ_{max}

of 556 nm and a small absorption peak at 423 nm. At 578 nm was observed fluorescence intensity enhancement, which could be due to a ring-opened structure formed on binding of Cu^{2+} ions (Figure-IV). However, similar pattern were not observed on equivalent addition of K^{+}, Mg^{2+}, Na^{+}, Ag^{+}, Ca^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, Cr^{3+}, except for Fe^{3+} and Fe^{2+} under similar conditions; only negligible absorption and fluorescence spectra change was seen. And when Cu^{2+}were added to the same solution (containing the above mentioned competitive metal ions), the fluorescence intensity got remarkably increased, thereby strongly suggesting the fluorescent selectivity of DNPRH for Cu^{2+} ions.

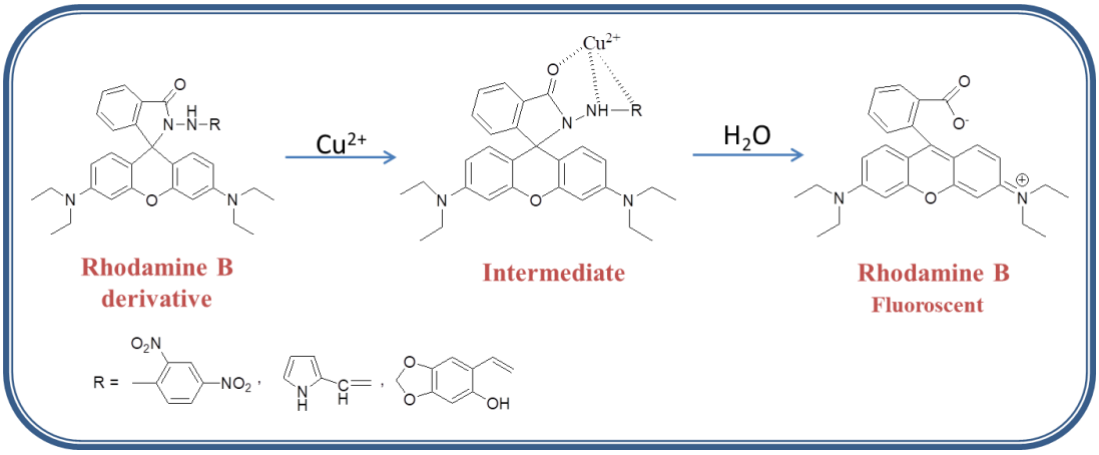

Figure-IV Binding mechanism of Cu^{2+} with different chemosensors

In another study, a new rhodamine derivative containing a pyrrole unit as the chromogenic and fluorogenic sensor for the Cu^{2+}ions has been reported (30). In comparison to the other metal ions, this probe displayed significant increase in the absorbance intensity as well as in fluorescence intensity for Cu^{2+} ions under the physiological conditions. The buffer used in the study was HEPES/acetonitrile. Similarly, a novel sensitive fluorescent RhS sensor (based on rhodamine B derivative) selective for Cu^{2+} ions has been reported by Zhang et al. (31).

Detection of Mercury (Hg^{2+}) ions by Rhodamine B sensor

Mercury is known to be a toxic pollutant that causes a serious threat to the human health. Detecting the levels of Hg^{2+} in water samples is critical since mercury-contaminated water is the prime source of exposure for humans. Mercury is one of

the most toxic heavy metals and is easily absorbed through our skin, causing extensive damage to the endocrine and nervous systems in humans.

A novel fluorescent chemosensor RBHA has been developed by Zhang et.al (32) for the selective detection of Hg^{2+} ions in water. They have used glyoxylic acid additionally to increase the water-solubility (32). Figure-V describes the sensing mechanism of Hg^{2+} promoted hydrolysis of rhodamine-glyoxylic acid conjugate based on MALDI-TOF-MS analysis .

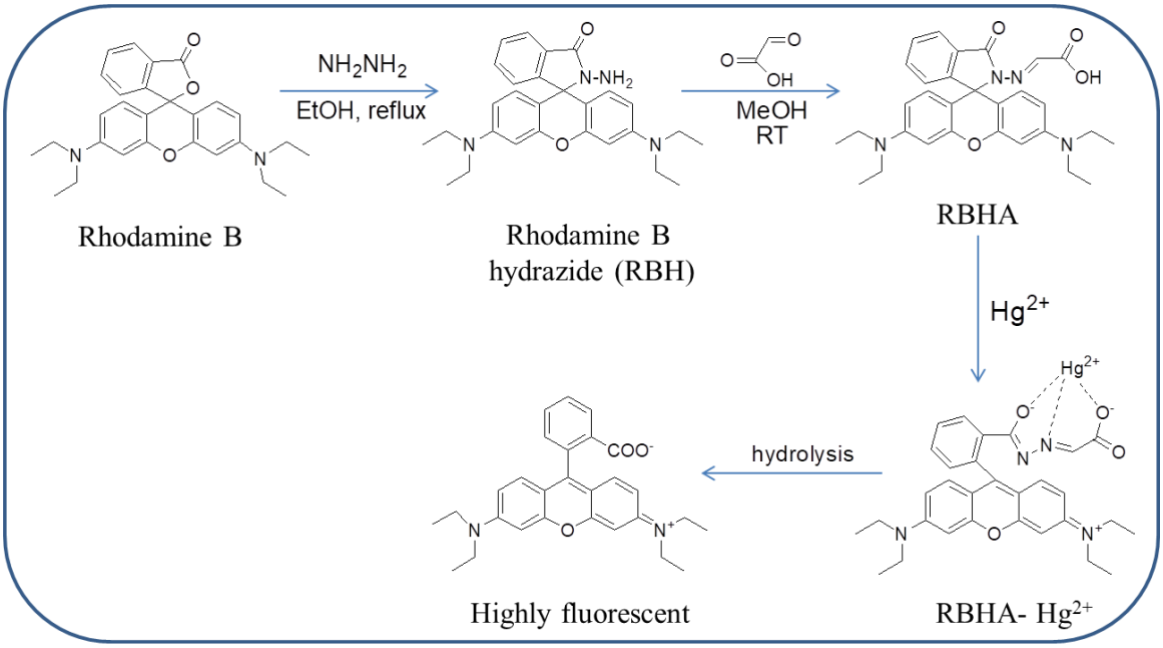

Figure-V Synthesis of chemosensor RBHA and Hg^{2+} driven hydrolysis reaction of the chemosensor

In another study (depicted in Figure VI), Wang et al. synthesized a new chemosensor (**Scheme-I**) of rhodamine for the detection of mercury ions by using lawesson's reagent (33). The chemosensor L1 was greatly selective for the detection of Hg^{2+} ions and the other metals present in the sample did not interfere with this recognition. The sensing mechanism of Hg^{2+} ions is explained in **Scheme-II**.

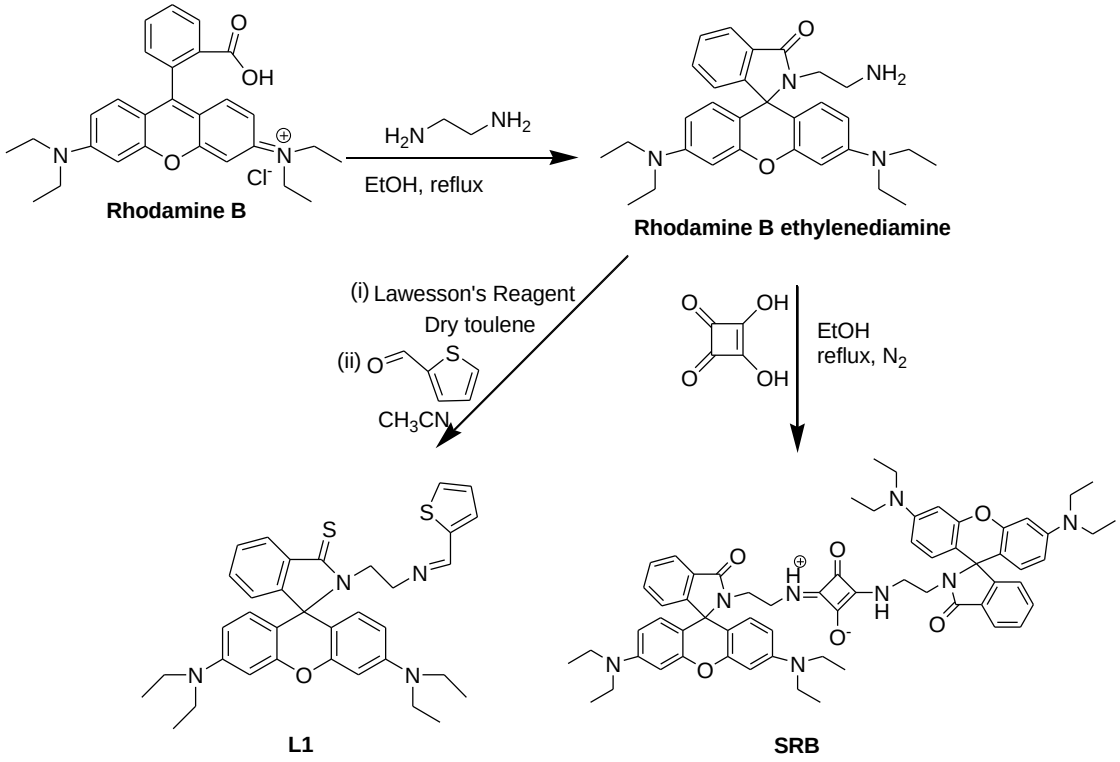

Figure-VI. **Scheme-I:** Synthetic route of compounds L1 and SRB.

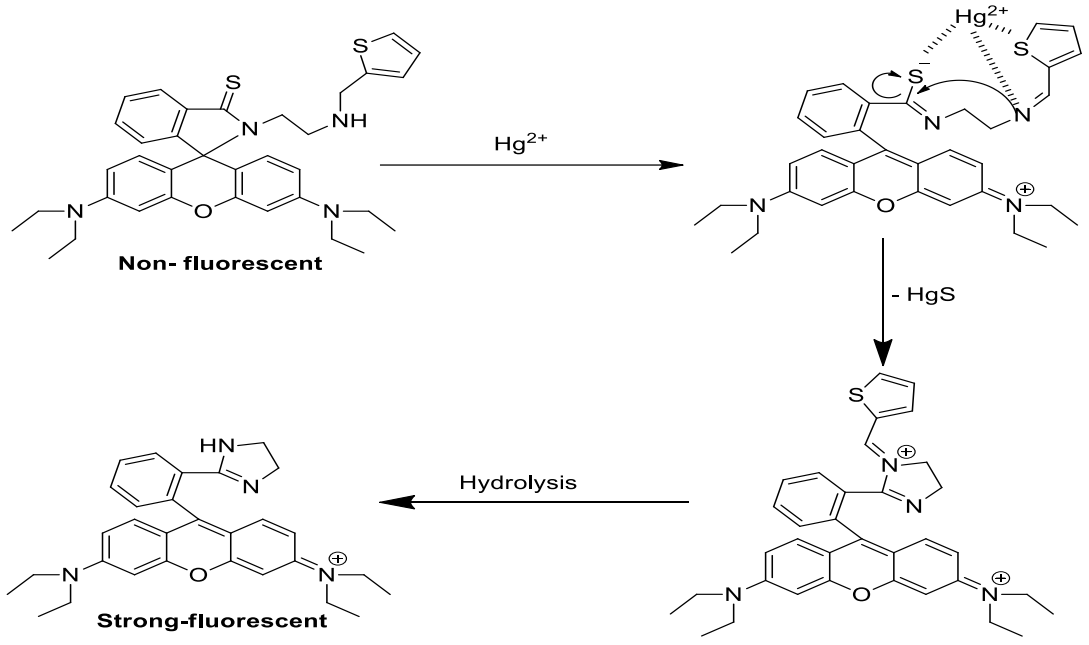

Figure-VI. **Scheme II:** The proposed mechanism of chemosensor L1 with Hg^{2+}

Squaraines are an important class of organic dyes that absorb strongly in the visible to near-infrared (NIR) region. Being electrophilic, these dyes react with nucleophiles, such as CN^- ions and -SH groups (34, 35). Although, squaraine dyes based chemosensors have been reported earlier, in majority of these studies, chelation of Hg^{2+} ions was seen (36-38). Therefore, new approaches to improvise the design and synthetic procedures for chemosensors based on the squaraine chromophore are required.

CONCLUSIONS

This review investigates the chemo-sensing properties of Rhodamine B based sensors. They are found to be effective, exceedingly sensitive and selective and their cost of production is affordable and can be recycled also. The distinct colour and fluorescence changes make Rhodamine B derivatives extremely useful for the sensing of ions through fluorescence or naked-eye detection. The complexation of the various ions like Cu^{2+} and Hg^{2+} ion opens the spiro-lactam ring of rhodamine based moieties, which results in change in the UV–Vis absorption pattern and also causes increase in the fluorescence intensity. Rhodamine based sensors moieties are also useful for the detection of heavy metal ions in water samples.

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