

Mini Review

Rhodanese is a possible enzyme marker for cyanide environmental stress on aquatic life

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Rhodanese is a cyanide detoxifying enzyme. The role of man through his anthropogenic activities in and around water bodies have increased in recent times. These have led to constant exposure of water body to cyanide and cyanide compounds with increase to loss of many aquatic lives. There are limited methods employed in quick detection of cyanide in water. The aim of this paper was to present rhodanese, an enzyme, as a possible marker for detecting and monitoring water pollution as a result of environmental stress from anthropogenic activities and constant climatic changes.

Key words: Rhodanese, aquatic life, water body, cyanide, toxicity.

INTRODUCTION

Fish and aquatic invertebrates are particularly sensitive to cyanide exposure. Free cyanide was reported to be the primary toxic agent in the aquatic environment. Environmentally relevant exposures to cyanide ions can cause stress, increase in mortality and place an appreciable metabolic load on fishes and other aquatic organisms (Eisler, 1991). It is now accepted that some human-induced climate change is unavoidable. Potential impacts on water supply have received much attention (Whitehead et al., 2009; Oyedeji et al., 2013), projected changes in air temperature and rainfall could affect river flows and, hence, there is mobility and dilution of contaminants (Whitehead et al., 2009). Increased water temperatures will also affect chemical reaction kinetics and freshwater

ecological status. It has also been reported that increase flow of water will lead to changes in sediment loads that will further result to invasion by alien species stimulating the potential for toxic algal blooms and reducing dissolved oxygen levels (Whitehead et al., 2009). The bacteria rhodanases have potential for effective remediation of cyanide-polluted environments, ultimately leading to improvement of fish and other aquatic organisms in receiving water bodies (Oyedeji et al., 2013).

Anthropogenic sources of cyanide in the environment include certain industrial processes, laboratories, fumigation operations, cyanogenic drugs, fires, cigarette smoking, and chemical warfare. Although, cyanide is ubiquitous in the environment, levels tend to be elevated

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in the vicinity of metal processing operations, electroplaters, gold-mining facilities, oil refineries, power plants, and solid waste combustion (Eisler, 1991). Many chemical forms of cyanide are present in the environment, including free cyanide, metalocyanide complexes, and synthetic organocyanides, also known as nitriles. But only free cyanide (that is, the sum of molecular hydrogen cyanide, HCN, and the cyanide anion, CN⁻) is the primary toxic agent, regardless of origin (Smith et al., 1978; Eisler, 1991).

Fish are the most sensitive aquatic organisms tested. Adverse effects on swimming and reproduction were observed between 5 and 7.2 µg free cyanide per liter; lethal effects usually occurred between 20 and 76 µg/L (Smith et al., 1978; Billard and Roubaud 1985). Biocidal properties of cyanide in aquatic environments were significantly modified by water pH, temperature, and oxygen content; life stage, condition, and species assayed; previous exposure to cyanides; presence of other chemicals; and initial dose tested. Natural sources of cyanide include various species of bacteria, algae, fungi, and higher plants that form and excrete cyanide (Way, 1984). Activities that will increase the concentration of bacteria and other forms of microorganism will affect the water quality that invariably affects the aquatic life. While, the activities around reservoirs, rivers, sea and ocean have been described as those that enhance increase in environmental pollution especially the use of fertilizers and other chemicals by farmers (Okonji et al., 2010), effluent from industries and poor sewage disposal by the locals and also the climatic changes that brings along with it, increase in rain fall and melting of ice which has a concomitant increase in water volume (Okonji et al., 2010). The use of cyanide compounds by the mining industry, coupled with limitations in current analysis and monitoring of these compounds, raises serious concerns regarding public safety and environmental protection at mine sites using cyanide processing (Flynn and Haslem, 1995). There is need for continuous monitoring of pollutants such as cyanides in fresh and marine waters.

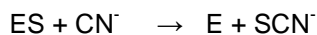
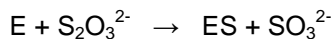
CYANIDE

Cyanide is highly toxic and its ineffective detoxification may result in inhibition of respiration (through iron complexation in cytochrome oxidase), ATP, subcutaneous hemorrhaging, liver necrosis, and hepatic damage in aquatic organisms (Eisler, 1991; Okonji et al., 2011). Cyanides are produced by certain bacteria, fungi, and algae and are found in a number of plants (Eisler, 1991; U.S. Department of Health and Human Services, 2006). The principal detoxification pathway of cyanide is catalysed by a liver mitochondrial enzyme, rhodanese.

RHODANESE

The enzyme rhodanese is ubiquitous in nature (Sorbo,

1951; Aminlari et al., 2002; Okonji et al., 2010). The enzyme is known to be responsible for the biotransformation of cyanide to thiocyanate (Sorbo, 1953; Jarabk and Westley, 1974; Lee et al., 1995). The overall reaction can be described according to the following scheme:



The reaction proceeds by way of double displacement mechanism in which covalent enzyme-sulphur intermediate is formed (Westley, 1981). Rhodanese shows activity in all living organisms, from bacteria to man. It has been studied from variety of sources, which include bacteria, yeast, plants, and animals (Himwich and Saunders, 1948; Jarabak and Westley, 1974; Anosike and Ugochukwu, 1981; Lee et al., 1995; Agboola and Okonji, 2004). The activities of rhodanese enzyme have been detected in different species of fish (Okonji et al., 2010).

ANALYTICAL METHODS

There are very limited numbers of toxicological studies suitable for use in deriving a guideline value. Cyanide can be determined in water by both titrimetric and photometric techniques, methods that are described as been cumbersome. The determination of rhodanese follows spectrophotometric determination of cyanide present in experimental sample. The process is cheap and very fast to achieve. The assay follows the modification of the method described by Sorbo (1953), though; many scientists have come up with different methods with little variations in all the methods described (Lee et al., 1995; Nagahara et al., 1995; Agboola and Okonji, 2004).

PERSPECTIVES

Mining and regulatory documents often state that cyanide in water rapidly breaks down—in the presence of sunlight into largely harmless substances, such as carbon dioxide and nitrate or ammonia. However, cyanide also tends to react readily with many other chemical elements, and is known to form, at a minimum, hundreds of different compounds. Many of these breakdown compounds, while generally less toxic than the original cyanide, are known to be toxic to aquatic organisms. In addition, they may persist in the environment for long periods of time, and there is evidence that some forms of these compounds can be accumulated in plant (Eisler, 1991) and fish tissues (Heming and Blumhagen, 1989). Discussions on toxicity of cyanide and cyanide compounds focuses on fish, since they are the most sensitive species studied (Eisler, 1991), and are impacted by relatively low cyanide concentrations. For example, fish are killed by cyanide concentrations in the microgram per liter range, whereas

bird and mammal deaths generally result from cyanide concentrations in the milligram per liter range (Eisler, 1991). Acute toxicity is described as those concentrations of cyanide that lead to the death of more than 50% of the test population within 96 h (Ingles and Scott, 1987); chronic exposure can be lethal. Chronic toxicity describes the adverse health effects from repeated exposures, often at lower levels, to a substance over a longer time period. In addition, chronic cyanide exposure may affect reproduction, physiology, and levels of activity of many fish species, and may render the fishery resource non-viable (Leduc, 1984; Ruby et al., 1986). Whether the toxic effects of HCN are cumulative, is apparently not known.

CONCLUSION

There are limited methods employed in quick detection of cyanide in water. The use of enzyme in environmental studies is becoming popular especially in area of toxicology. Rhodanese assay is a rather cheap and fast method of determining the presence of cyanide in polluted aquatic environment.

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