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Review Article

THE INTERACTION OF HUMIC SUBSTANCES WITH ORGANIC AND INORGANIC POLLUTANTS: A REVIEW

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ABSTRACT

Pollution of aquatic systems is one of the major problems today that bear a direct impact on human health. Various contaminants released because of various natural and man-made activities degrade the quality of these ecosystems thus makes them unfit for human consumption. In this regard, the potential application of humic substances needs a special mention. Humic substances, comprising of humic acid, fulvic acid and humin, have recently been explored for their unique properties and this article provides an insight into the role of humic substances in pollution control.

INTRODUCTION

The natural ecosystems today are under immense pressure as they are getting increasingly polluted due to increased industrialization and rapidly growing human population. Aquatic ecosystems are no exception as direct discharge of domestic sewage and effluents from industries and factories and indirect addition of various chemicals through agricultural runoff (containing pesticides, herbicides, insecticides, heavy metals, etc), accidental and process spillage, etc has contaminated these natural systems (Khayatzadeh and Abbasi 2010, Solomon 2008), affecting the water quality and thereby reducing its utility. This contamination has adverse effect on the organisms using this system as their habitat, but humans are also bound to get various health related problems. However, in nature, a system exists in the form of humic substances that plays a role in ameliorating the quality of these ecosystems as humic substances have been shown to play an important role in the binding of both organic and inorganic contaminants in natural environment thereby reducing their bioavailability and toxicity to organisms in surface waters, soil solutions, and groundwater (Koopal *et al*. 2001, Koukal *et al* 2003). This applies to different groups of compounds such as herbicides, fungicides, insecticides, nematicides, dioxins and also some pharmaceutical products like estrogenic compounds, that are known to act as possible environmental endocrine disruptors (Rupiasih and Vidyasagar 2008, Pena-Mendez *et al*. 2005, Suffet and MacCarthy 1989, Shin *et al*. 1999, Loffredo *et al*. 2000). This article reviews the role of humic substances in the binding of heavy metals and some organic pollutants.

Action Mechanism of Humic Substance

Humic substances (HS) are natural compounds, which constitute most important pool of transient refractory organic carbon in the geosphere (Rupiasih and Vidyasagar 2008). These compounds are produced in the natural systems during the physical, chemical and microbiological transformation (humification) of biomolecules that is going on along with the decomposition process. These compounds are ubiquitous in nature and represent most of the organic materials of soil, peat, lignites, brown coal, sewage, natural waters and their sediments. About 80% of total carbon in terrestrial ecosystem and 60% of the carbon dissolved in aquatic ecosystem are made up of humic substances and these can be divided into 3 components; alkali soluble Humic and Fulvic acids, and insoluble residue Humin (Pena-Mendez *et al*. 2005). These compounds are known to have extremely complex structure and are primarily composed of carbon, hydrogen, oxygen, nitrogen and sulphur, having a large proportion of more or less condensed aromatic nuclei, with a large number of functional groups such as carboxyls, phenolic and alcoholic hydroxyls, carbonyls and quinine groups fixed on them (Sahu, 2015), that impart these compounds unique biological and physiochemical features (Rupiasih and Vidyasagar 2008). Humic substances cannot be described by unique chemically defined molecular structures, these are operationally defined by a model structure

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constructed on the basis of available compositional, structural, functional and behavioural data and containing the same basic structural units and the same types of reactive functional groups (Senesi, 1993). These unique properties of HS have credited them with so many practical applications in industry, agriculture, environment and biomedicine (Rupiasih and Vidyasagar 2008, Pena-Mendez *et al*. 2005). Out of these, the role of HS in the treatment of pollutants need special mention as the pollution of natural systems is one of the major problems the world is facing today.

In natural aquatic systems, a fraction of humic material either settles down to the bottom being adsorbed strongly to the bottom sediment or remains suspended as particulates and/or dissolved in water. Supra-molecular structure of humic substances has been shown to have abundant micro spaces with statistically average dimension (0.24-0.48 nm) which resemble molecular sieves that ensure efficient sorption of low molecular compounds like organic xenobiotics, herbicides, pesticides, metal ions, etc.(Piccolo 2001). The functional moieties such as carboxylic, phenolic and alcoholic groups interact with free metal ions and hydroxides and it is accomplished by the removal of a proton from either carboxylic acid or hydroxyl functional groups followed by bond formation to the metal. These interactions have been described variously as chelation, complex binding, ion exchange, surface adsorption, coagulation and peptidization reactions (Soleimani *et al* 2010, Meinelt *et al*. 2001). Various other factors like pH, ionic strength and dissolved inorganic species also determine the amount of metal complexation.

However, complexation is not the sole mechanism by which HS may influence bioavailability of metals in natural waters. HS as a part of Dissolved Organic Matter (DOM) may also adsorb to biotic surfaces (e.g., algal surfaces) and block surface sites where toxic metal must adsorb in order to be taken up by the cell (Hwang *et al*. 1995, Koukal *et al*. 2003).

Interaction of Humic Substances with Pollutants

Various organic and inorganic compounds released in natural systems degrade their quality. Out of these, heavy metals constitute a major group of pollutants that has been shown to have a negative effect on each component of ecosystem it interacts with. The heavy metals have variously been used to denote:(I) metals with atomic number 23(i.e. vanadium) onwards except Rb, Y, Cs, Ba, and Fr; (II) metals with density greater than 5; and (III) metals which are toxic to man and other life forms when found in the environment (Khayatzadeh and Abbasi 2010).

An important feature of heavy metal physiology is that many of them are essential for growth such as Copper, iron, manganese and zinc are important for cellular activities however, some others like cadmium, chromium, mercury, nickel, zinc can be toxic when present in sufficient concentration (Fuhrer 1986, Engel *et al*. 1981). The eight most common pollutant heavy metals listed by the Environment Protection Agency (EPA) are: As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn (Khayatzadeh and Abbasi, 2010.).

Heavy metals in surface waters can be of natural or anthropogenic sources, but mostly anthropogenic inputs of some trace metals surpass natural inputs (Koukal *et al*. 2003) as these are released by various industrial and anthropogenic activities in soil and from here, these toxic heavy metals find their way to ground water and surface water and ultimately affects environment quality and human health. Even their interaction with soil makes it unproductive because of phytotoxicity (Misra and Pandey 2005). When present in any ecosystem, these heavy metals produce their harmful effects when they enter cells of organisms. These heavy metals find their way inside cells through the transport systems of nutrient metals that consists of proteins located in the external cell membrane. Various functional groups (eg. Carboxylic, amino, thio and hydroxyl groups) present in these transport proteins interact with metal ions and these are taken to cell's interior where they produce toxic effects by displacing nutrients from their metabolic sites (Koukal *et al* 2003).

Cadmium, belonging to group IIb in the periodic classification of elements, is widely distributed in the aquatic environment and is usually considered as a toxic metal to aquatic plants and animals as well as human beings (Sahu, 2015). Cadmium is toxic to humans when the daily intake is 250 to 300 micrograms and cadmium intoxification is known to produce Itai-Itai disease associated with skeletal deformities and bone loss, kidney damage, and generalized pain. In fishes, cadmium interferes with the ionic and water balance (Hwang *et al*. 1995) and also known to produce skeletal deformities and impaired functioning of kidneys. Survival and growth of Isopods is also effected by cadmium toxicity. Cadmium also impairs plant growth and this inturn effects primary productivity of aquatic ecosystems (Solomon 2008). However, humic substances are considered a major factor in affecting the toxicity of Cadmium in natural water. Hollis *et al* (1996) have shown that the addition of 5-20 mg C/l Dissolved Organic Carbon containing HS to small rainbow trout (*Onchorhynchus mykiss*) results in reduction in cadmium toxicity. Similar results have been obtained by Playle *et al*. who found that in presence of Dissolved organic matter, a reduction was observed in cadmium binding to fish gills (Hollis *et al*. 1996, Playle *et al*. 1993a, Playle *et al*. 1993b.).

Copper belongs to third transition metal series. Though copper has a positive role to play as an integral part of proteins and enzymes in biological systems, it is highly toxic to most aquatic plants, invertebrates and fish, but not acutely toxic to humans (Sahu, 2015). Humic substances are also known to reduce the bioavailablity of copper. Toxic effects caused by copper are mainly because of free cupric ions and complexation with humic substances (forming $CuCO_3$ (aq.) and $Cu_2(OH)_2CO_3$ (s.) at pH 7) leads to reduction in toxicity of copper towards biota. Tubbing *et al* has shown that the presence of HS as a part of DOM can reduce the bioavailability and toxicity for copper (Tubbing *et al*. 1994). Also, it has been shown by Sunda and Lewis that increasing humic content causes decreasing metal toxicity toward phytoplankton as they have demonstrated in case of alga *Pavlova lutheri* (Sunda and Lewis 1978, Giichter *et al*. 1978, Sedlacek *et al*. 1983, Bäckström *et al*. 2003). Identical results have been obtained with cyanobacterium Aphanizomenon floss-aqual as it becomes less sensitive to copper in the presence sediment extract containing humus (Clarke *et al*. 1987, Sunda and Guillard 1976).

Also, survival in case of Amphipods is known to increase by 35-90% relative to control groups in presence of Cd and Ca with humus treatment (Besser *et al*. 2003).

Lead is a member of group IV elements of the periodic classification (Sahu, 2015). Lead contamination of natural water systems has adverse behavioural, physiological, and biochemical effects on humans especially fetuses and children. Lead can cross the placenta thus resulting in miscarriages, stillbirths, and birth defects such as neurological damage. Lead has been found to be toxic to aquatic plants and animals though to a lesser extent. When lead concentrations in algae exceed 500 ppb, enzymes needed for photosynthesis are inhibited (Taub and Frieda 2004) reducing productivity of aquatic ecosystems (Solomon 2008). Application of humus rich soil to lead contaminated soil has also been shown to reduce the availability of lead to biota as has been demonstrated by Zhang *et al*. (Zhang *et al*. 2013).

Similarly, Mercury (Hg) has been classified as a high priority pollutant because of its persistence in environments and toxicity to aquatic and marine organisms and also because of the long range transport of elemental mercury (Hg0) in atmosphere, it is considered as a global pollutant. Dissolved organic matter has been shown to perform photochemical reduction and reduction of Hg(II)in dark (Rocha *et al*., 2000; Gu *et al*., 2011; Zheng *et al*., 2012; Chakraborthy *et al*. 2015). Similar results were also obtained in case of zinc where humic substances, especially fulvic acids were known to play a key role (Du *et al*. 1995, Bäckström *et al*. 2003, Zhang *et al*. 2013). Recently, the idea of phosphate treatment to heavy metal contaminated soil has been proposed as an alternative to soil treatment. Apatite minerals are known to react with many transition and heavy metals and metalloids to rapidly form secondary phosphate precipitates that are stable over a wide range of geochemical conditions. Treatment of hydroxyapatite, phosphate rock or phosphoric acid to contaminated waters and soil has been shown to reduce lead contamination in aqueous and soil solutions as it leads to the formation of pyromorphite having very less solubility (Misra and Pandey 2005, Chaturvedi *et al*. 2006, Seaman *et al*. 2001).

Interaction of Humic Substances with Organic Pollutants

Various organic pollutants are also added to the natural environment due to human activities. this includes chemicals belonging to various classes like various types of pesticides e.g., herbicides, insecticides, fungicides, etc., used in agriculture, organic solvents, detergents and surfactants, polynuclear aromatic hydrocarbons (PAH) released from industries, endocrine disruptor compounds (EDCs) to name a few (Loffredo and Senesi, 2006). These are included in the category of "anthropogenic organic pollutant" (AOP) which may be defined as "any organic chemical that is foreign to the natural ecosystem and may adversely affect, either directly or indirectly, the natural physical, chemical and biological equilibria and processes in the global environment or a portion of it" (Loffredo and Senesi, 2006).

Out of these, Endocrine disruptor compounds (EDCs) needs special mention. These include several organic compounds of natural and anthropogenic origin that are suspected to interfere with the endocrine system of animals and humans by blocking or imitating natural hormones, or by interfering with the synthesis, storage, secretion, transport, catabolism and activity of various natural hormones thereby altering or disrupting the normal functioning of the endocrine system (Lintelmann *et al*., 2003). Although consequences of such interference have not yet completely understood, but recent progress in both epidemiological and toxicological research indicates that exposure to these compounds may have an important role in the aetiology of a many endocrine mediated disorders and may thus interfere with human reproductive function and success. Different classes of herbicides, fungicides, insecticides and nematicides, several industrial chemicals, including PCBs, PAEs, dioxins, and some pharmaceutical products, like estrogenic compounds, have been identified as potential environmental EDCs.

Humic substances in environment have been shown to be able to reduce the toxic effects of these anthropogenic organic compounds by various mechanisms including

- modification of water solubility of AOPs
- exert catalytic activity on some AOP transformations
- act as photosensitizers promoting AOP photodegradation
- adsorb and partition AOPs (Loffredo and Senesi, 2006)

Adsorption is the most important mode of interaction of AOPs with HS and various physical and chemical binding mechanisms i.e., ionic, hydrogen and covalent bonding, charge transfer or electron donor- acceptor mechanisms, dipole-dipole and van der waal's forces, ligand exchange and cation and water bridging are involved (Loffredo and Senesi, 2006).

CONCLUSION

The review on humic substances thus provides an insight about their role in control of both organic and inorganic pollutants in soil and aquatic ecosystem. This field is new and has not been explored in a comprehensive manner. Hence, research in this field needs to be done so as to understand the multiple ways humic substances influence the fate, reactivity and transport of inorganic and organic pollutants in aquatic ecosystems.

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