Section A-Research paper

A REVIEW OVER THE CAUSAL RELATIONSHIP BETWEEN HYDRO-GEOCHEMISTRY AND BIOACCUMULATION IN SPECIAL REFERENCE TO COALFIELDS.

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Abstract

The coalfields are the major industrial setups in any of the developing country. The studies have revealed that these setups are frequently reported with the groundwater contaminations, especially in concern to heavy metals. The cases of bioaccumulation of heavy metals have also been evidenced in the same setup with sufficient validation. This clearly implies towards the certain kind of association between the groundwater chemistry and the bioaccumulation. The present article evaluates and reviews the association between the hydro-geochemistry and the bioaccumulation in special concern to the coal fields. The hydro-geochemistry in the coalfield clearly elucidates the chemistry of groundwater and too in special reference to the heavy metals. It also elaborates the process of dissolution and migration of these heavy metals from the geogenic source to the groundwater regime. The AMD is the major reason behind the dissolution and migration of heavy metals in and around the coalfield has been fairly validated by the hydro-geochemical studies. The contaminated groundwater has potential to contaminate the surface soil and water bodies by one way or another. Such migration of the heavy metals form the geogenic sources to the surface entities provides exposure to the dependent biota and accumulates accordingly on consumption. Once the heavy metals enter into the food chain through agricultural products or by animal products, it becomes a trouble for the biotic health. The review clearly indicates the causal relationship between the hydro-geochemistry and the bioaccumulation. The monitoring and mitigation of the cause will ultimately put positive impact on the concerning effects. The groundwater treatments in the coalfields and the phytoremediation are the suggested measures at various levels to check the bioaccumulation.

Keywords - *Hydro-geochemistry, Bioaccumulation, Heavy Metals, Phytoremediation, Coalfields.*

1. INTRODUCTION

In the developing world, the advances have to be paid with an appropriate prize and sometimes unfortunately, it charges the fragile environmental stability (Ali *et al.,* 2019; Gautam *et al.,* 2016). In the regions specially labelled for industries are suffering from many environmental issues like of air, water and soil pollutions. The exponential growth of the population has forced the residential regions much nearer to the affected industrial regions causing direct interactions of residents and pollutants in one way or other (Gheorghe *et al.,* 2017). The accretion of the chemicals in any sort of biota due to the considerable difference in the rate of assimilation and rate of elimination can be termed as bioaccumulation and the heavy metals is the prime bio-accumulating category. The problem of the bioaccumulation of contaminants like of heavy metals is common around the industrial zones involved in heavy metal transactions (Briffa *et al.,* 2020). As a consequence, the residents' dependents on the natural systems of food or water get prone to assimilate the same. In environment, the heavy metals are stubborn on release in natural systems and keep their existence for a long shot like of bioaccumulation in plants through contaminated soil system (Shtangeeva, 1995). A heavy metal, once entered in the food chain, creates multi-faceted physiological problems. These physiological problems may include interruptions in nervous system's function, kidney functions, reproductive functions, etc. Simultaneously, they are also referred as carcinogenic, mutagenic and teratogenic in nature (Malik and Maurya, 2014).

The hydro-geochemistry is an applied geoscience studying the groundwater chemistry in all aspects. The heavy metals are basically migrated from the geological setups to the aqueous systems under certain set of conditions (Ganvir and Guhey, 2021). The hydro-geochemistry elucidates the process and cause behind such migration from the host rocks. At initial instance, the groundwater is contaminated by the heavy metals due to approving hydro-geochemical condition either by natural or anthropogenic cause (Ganvir and Guhey, 2020). Once, the groundwater is contaminated, it remains potential for a considerable span of time creating a possible threat to every entity, which may use it for any purpose like of drinking, domestic, agriculture, etc. (Zhuang *et al.*, 2009). The surficial aqueous systems are the most susceptible systems for such contaminations and as a consequence the fishes are at higher risk of bioaccumulation (Youssef and Tayel, 2004; Malik and Maurya, 2014). The present article represents a brief review over the hydro-geochemical courses and their effects in favour of bioaccumulation in special concern to heavy metals.

2. METHODOLOGY

To get an accurate understand about the causal relationships between the hydro-geochemistry and the bioaccumulation, a detailed literature survey has been done by considering selective but competent works. The individual endeavours of hydro-geochemistry were correlated with the corresponding reports of the bioaccumulations to verify the cause and effect association. The principle of convergence of evidence was used on the secondary data to deduce a fruitful interpretation. The overall coverage was specially oriented to the regions of mines and that too of coal mines where the heavy metal contaminations are frequently reported.

3. HYDRO-GEOCHEMISTRY: GENERAL

The study of the groundwater chemistry is termed as hydro-geochemistry and is considered as a prime domain in the contamination studies of aqueous systems. Basically, the chemistry of the groundwater is attributed to the corresponding geological setup (Satapathy *et al.*, 2009). The host rocks containing groundwater are termed as aquifers, which are usually drilled (deep aquifer) or dug (shallow aquifer) for groundwater exploitation. The rock-water interaction in the aquifer is the prime controlling mechanism of the groundwater chemistry. In general, the groundwater in the aquifer assimilates usual ions and provides no harmful issues otherwise. In certain cases like of hydro-geochemical or hydrological disruptions, external influence (enhanced weathering and dissolution), etc. the natural chemical equilibrium among the host rock and the groundwater gets disturbed and as a result contamination occurs (Ganvir and Guhey, 2022).

The chemistry of the groundwater primarily includes major ions and trace metals. The major ions implies for major anions and major cations (Peddiwar *et al.*, 2022). The major anions includes bicarbonates (HCO_3^-), Carbonates (CO_3^{2-}), Sulphate (SO_4^{2-}), Chlorine (Cl^-) and Nitrate (NO_3^-) and the major cations includes Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^+) and Potassium (K^+). These all ions are basically leached out from the host rocks through rock-water interaction (Michael, 2014). The common graphical methods to study the hydro-geochemistry are the Piper plots, Gibbs Plots, Stiff's plot, etc. These plots converges the data and aids in interpreting the groundwater chemistry with much ease. The common geogenic sources of the ions are as follows:

- **Ca^{2+}:** Minerals like Feldspar, Pyroxene, Calcite, etc. and rocks like Limestone, etc.
- **Mg^{2+}:** Minerals like Orthoclase, Microcline, Biotite, Dolomite, etc.
- **Na^+ and K^+:** Minerals like Feldspar, Clay minerals, etc.
- **HCO_3^- and CO_3^{2-}:** Minerals like Calcite, rock like Limestone, etc.
- **SO_4^{2-}:** Mineral like Pyrite, Chalcopyrite, Galena, etc.
- **Cl^- and NO_3^-:** Solution of the NaCl from associated rocks.

4. HYDRO-GEOCHEMISTRY: HEAVY METALS

The chemistry of groundwater also includes, trace metals like Aluminium (Al), Arsenic (As), Cadmium (Cd), Chromium (Cr), Iron (Fe), Nickel (Ni), Lead (Pb), Zinc (Zn), etc. The trace metals are the stable entities in geological setup but on leaching from the host rock under favourable circumstance pose a serious threat to the groundwater system (Scokart *et al.*, 1983). The common geogenic sources of some common trace metals are as follows:

- **Al:** Mineral like Feldspar.
- **Cd:** Minerals like Sphalerite, Carboniferous strata.
- **Fe:** Mineral Pyrite, rocks like Laterite, Iron rich stratums, etc.
- **Ni:** Minerals associated with Laterite, Limonites, Pentlandite, etc.
- **Pb:** Mineral Galena
- **As:** Minerals like Arsenopyrite, Realgar, Orpiment, Arsenolite, etc.

4.1 Dissolution of the Heavy Metals: General

In the geological setup, the heavy metals are usually occurs in a complex compounds as a minor or in the ore bodies of concern metal as major. The stability of these heavy metals is quite assured in the obvious environment of their occurrence. The rock-water interaction in a typical state does not possess the potential to leach out the heavy metals from the host rock in an anomalous rate. The exposures of certain set of conditions either due to the natural cause or anthropogenic cause can accelerate the dissolution of these metals in the groundwater through rock-water interaction (Singh *et al.,* 2017). Such processes act as a catalyst in the dissolution of the heavy metals resulting into anomalous concentration of heavy metals in the groundwater. The enhanced acidity of the groundwater is a suitable example for attributing the accelerated dissolution of the heavy metals.

4.2 Dissolution of the Heavy Metals: Coal Fields

In the regions of mines that to especially in the coal mines the Acid Mine Drainage (AMD) is a common scenario (Singh, 1987). During the process of excavation of coal beds, the overburden has to be removed and disposed at some place. The carboniferous stratum and the coal itself have been reported with the existence of sulphur bearing minerals like of Pyrite. The sulphide minerals constituting metals have a tendency to associate together, like sulphide minerals of iron usually associates with sulphides of copper, lead, Nickel, etc. (Duruibe *et al.,* 2007). Such association possess a strong potential of leaching out metal and sulphur containing solutions. On exposure to the outer environment to the otherwise concealed rock stratum containing sulphide setups, immediately interacts with the moister and air producing the sulphuric acid resulting into the formation of AMD (Zipper *et. al.,* 2014). The interaction can be understood by the example of Pyrite mineral (eq. 1).

$$FeS_{2\ (S)} + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{-2} + H^+ \qquad \text{(eq. 1)}$$

The AMD has a potential to drop the pH level of any aqueous system to which it comes in contact with. As a consequence, the dissolving capacity for the metals increases with the proliferation of acidic environment because of dissolving nature of metals in acidic solutions. The groundwater system is no exception and the lowering of the pH level boost the dissolution of heavy metals.

4.3 Migration of the Heavy Metals

Once the groundwater is charged with the heavy metals through enhanced dissolution, they hold their dissolved state for a considerable period of time. The groundwater is a dynamic entity and keeps flowing from one point to another. As the consequence, the dissolved metals too migrate in intra- and inter aquifer system. The real problem arises when such contaminated groundwater is exploited for the usage of drinking, domestic and agricultural purpose. The dissolved heavy metals now enter into the fauna on direct consumption and into the food chain through agricultural use. The soil is first entity which usually gets affected by the heavy metal contamination on irrigation with contaminated water (Gupta *et al.,* 2010). The plants growing on the soil sucks the nutrition from the soil. In the due course, the heavy metals accumulate in the tissues of the plants and enter into the food chain (Jambhulkar and Juwarkar, 2009; Khan *et al.,* 2015).

Apart from the exploitation of the groundwater, the effluent streams are the surface water bodies that are directly recharged by the groundwater. On such condition, if the contaminated groundwater will recharge the stream, the surface water too gets contaminated by the heavy metals. The surface water streams supplies the water to the stagnant bodies like lakes, ponds, etc. Thus the contamination spreads over the surficial aqueous system. The most affected fauna in such contaminated aqueous systems are the fishes. The common fish tissues where the heavy metals bio-accumulates are the gills, liver and muscles (Maurya and Malik, 2019). In the coastal and riverine regions the fishes are a kind of staple food for locals and the consumptions of such fishes would provide the heavy metal exposure to human health (Haseeb-ur-Rehman *et al.,* 2023).

5. BIOACCUMULATION OF HEAVY METALS: COAL FIELDS

Many of the endeavours have reported the evidences of the bioaccumulation of heavy metals in and around the coalfields. The acid mine drainage produced by the rock-water interaction lower the pH level of the surface and groundwater regime. The dumps of the overburden are also the major points of such interactions. Such interactions liberates the otherwise cloaked heavy metals into the environment. The flora and fauna dwelling around the coal fields are at high risk of the bioaccumulation of the heavy metals through the food chain or by direct ingestion. The soil is the one which deteriorates in coal fields due to lower pH and lower nutrients in turn affected the biota (Rai *et al.,* 2011 and Talukdar *et al.,* 2016). The workers Semy and Singh in 2021 have published the work on the bioaccumulation on plants in Coal Mining Affected Forest of Changki, Nagaland. The work clearly elucidates the dumps and tailing of the coal mine has altered the soil quality and ensued to the bioaccumulation in the plants grown over the field. The heavy metal concentration causes significant shifts in the metabolic and physiological activity of the bio-accumulated plants (Dubey, 2011). An endeavour done by the Zainab and other in 2023 has systematically indicated the health risk index of sheep, cow and buffalo dependent of the heavy metal contaminated soil and water near coal mines of Punjab region. A significant increase in the heavy metals concentration were observed in the edible fruits like *Mangifera indica*, *Anacardium occidentale*, *Psidium guajava*, *Artocarpus heterophyllus* and *Syzygium cumini*, which were grown on the over burden dumps of Mahanadi Coalfield region (Maiti *et al.*, 2016). On consumption of such fruits will definitely affect the health of the respective consumer.

It is fairly clear that the mining executions have serious consequences on the ecology, biodiversity and health of the fauna (Chaulya *et al.*, 2011). An initiative to control the factors responsible for the bioaccumulation must be checked. A systematic study over the sources of the heavy metals and their dissolution and migration process are much expected to hinder them at its earliest. The vertical flow systems constituting limestone drains and artificial wetland have been proven efficient in holding the heavy metals at preliminary level (Zipper *et al.*, 2014). On further migration of heavy metals in soil, the phyto-remediation can be engaged by planting the species like *Cynodon dactylon*, *Eulaliopsis binata*, *Croton oblongifolius and Lantana indica*, which has been proven efficient in metal absorption form the soil (Pratap *et al.*, 2022).

CONCLUSION

The aqueous systems are the feeders of nutrients to the majority of flora and fauna. The contaminations of these systems are significantly influential over the biotic dependents. The major cause of the aqueous contamination is the groundwater contaminations. The hydro-geochemistry is the most anticipated study in the water quality endeavours. It elucidates the chemistry of the groundwater and the controlling mechanism. The contaminated groundwater is potential enough to contaminate the surficial entities like soil and surface water bodies. In concern to the coalfields, the AMD is the major cause behind the heavy metal contamination in the groundwater and in turn for the migration too. The heavy metals are the prime attributes for the toxic bioaccumulations. Thus the chemistry of the groundwater can be hold fairly responsible for the bioaccumulation issues around the coalfield. The systematic observation reveals the causal relationship between the hydro-geochemistry and the bioaccumulation. Hence, the remediation of the groundwater contamination at primary level and phytoremediation at post level for the soil is advisable.

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