

Hazardous heavy metal ions in the environment and removal of Hg from industrial effluents using layered double hydroxides as adsorbents

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Abstract— Environmental pollution is a major concern of current relevance. Contamination with heavy metals is one of the most serious problems in the aquatic environments. Metals are natural trace components of the aquatic environment, but their levels have been increased due to industrial wastes, geochemical structure, agricultural and mining activities. Heavy metals such as As, Cd, Cu, Pb, Ni, Hg, Cr, and Zn are common pollutants and come from different natural and anthropogenic sources. Metals have been reported to affect cellular organelles and induce toxicity & carcinogenicity. This manuscript focuses on heavy and toxic metals in the environment, their sources, their harmful effects on terrestrial and aquatic life of this planet and the usage of various adsorbent materials for their removal. Layered double hydroxides are promising adsorbent materials for the removal of heavy and toxic metals from the waste water.

Keywords—*Environmental pollution, heavy/toxic metal ions, layered double hydroxides, sorption*

I. 1. INTRODUCTION

As a consequence of industrialization, mankind has witnessed various environmental issues in the society. This industrialization has not only blessed the mankind with development and prosperity but eventually disturbed the ecosystem. One of the impacts is visible, in form of water pollution. In the present study heavy metal contamination of water bodies has been discussed. Effluents from large number of industries viz., electroplating, leather, tannery, textile, pigment & dyes, paint, wood processing, petroleum refining, photographic film production etc., contains significant amount of heavy and toxic metals in their wastewater.

II. RELATED WORK

The conventional methods of treatment of heavy metal contamination includes chemical precipitation[1], chemical oxidation[2], ion exchange[3], membrane separation[4], reverse osmosis[5], electro dialysis[6] etc. These methods are costly, energy intensive and often associated with generation of toxic byproducts. Thus, the adsorption has been investigated as a cost effective method of removal of heavy metals from wastewater [7-10].

A variety of low cost adsorbents have been employed for preventing heavy metal pollution of wastewater. These adsorbents include materials of natural origin like zeolites, clay, peat moss and chitin are found to be an effective agent for removal of toxic heavy metals like Pb, Cd, Zn, Cu, Ni, Hg, Cr etc. [11-16].

III. METHODOLOGY

In the present study, layered double hydroxides are employed as an effective adsorbents for the successful removal of mercury from the waste Layered double hydroxides (LDH) forms an important class of inorganic materials owing to their applications in the wide area of current research. Layered double hydroxides are obtained by partial isomorphous substitution of divalent metal ions by trivalent metal ions in the structure of mineral brucite, $Mg(OH)_2$. Their chemical composition can be expressed by the general formula $MII_{1-x}MIII_x(OH)_2An \ x/nyH_2O$, where MII and MIII are divalent and trivalent metal cations and An^- is an n-valent anion. These compounds have a layered crystal structure composed of positively charged hydroxide layers $[MII_{1-x}MIII_x(OH)_2]^{x+}$ and interlayers containing anions and water molecules. The value of x represents a portion of trivalent metal cations substituted in hydroxide layers and usually corresponds to $0.20 < x < 0.33$ [17-20].

Layered double hydroxides exhibit anion-exchange properties, i.e., anions in the interlayers may be exchanged for the other ones. At temperatures of approximately 300 – 500 °C, layered double hydroxides are decomposed to form mixed oxides of MII and MIII metals. In Rehydration of these mixed oxides takes place in an aqueous solution containing the anion to be intercalated, resulting in the reconstruction of the layered LDH structure along with the intercalation of anions from the solution into interlayers [20]. This unique property of layered double hydroxides can be employed for preparation of compounds intercalated with various anions or in removal of anions from solutions. The often used group name “hydrotalcite-like compounds” is related to the mineral hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$). There are some other natural minerals and a great number of synthetic compounds with an analogous layered crystal structure combining various MII and MIII metal cations in hydroxide layers and various anions intercalated in the interlayers.

IV. RESULTS AND DISCUSSION

Heavy and toxic metals in the environment.

The term “heavy metal” refers to any metal and metalloid element that has a relatively high density ranging from 3.5 to 7 g cm⁻³ and is toxic or poisonous at low concentrations, and includes mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), zinc (Zn), nickel (Ni), copper (Cu) and lead (Pb). Although “heavy metals” is a general term defined in the literature, it is widely documented and frequently applied to the widespread pollutants of soils and water bodies [21]. These metals are found widely in the earth's crust and are non-biodegradable in nature. They enter into the human body via air, water and food. A small number have an essential role in the metabolism of humans and animals in very trace amounts but their higher concentration may cause toxicity and health hazards. The hazardous nature of heavy metals has been recognized because of their bio accumulative nature in biotic systems. They can enter into the environment through mining activities, industrial discharge and from household applications, into nearby bodies of water.

Sources of heavy metals

Heavy metals differ widely in their chemical properties, and are used extensively in electronics, machines and the artifacts of everyday life, as well as in high-tech applications. As a result they are able to enter into the aquatic and food chains of humans and animals from a variety of anthropogenic sources as well as from the natural geochemical weathering of soil and rocks. The main sources of contamination include mining wastes, landfill leaches, municipal wastewater, urban runoff and industrial wastewaters, particularly from the electroplating, electronic and metal-finishing industries. With increasing generation of metals from technologies activities, the problem of waste disposal has become one of paramount importance. Many aquatic environments face metal

concentrations that exceed water quality criteria designed to protect the environment, animals and humans. The problems are exacerbated because metals have a tendency to be transported with sediments, are persistent in the environment and can bioaccumulate in the food chain. Some of the oldest cases of environmental pollution in the world are due to heavy metal use, for example, Cu, Hg and Pb mining, smelting and utilization by ancient civilizations, such as the Romans and the Phoenicians.

The heavy metals are among the most common pollutants found in wastewater. These metals pose a toxicity threat to human beings and animals even at low concentration. Lead is extremely toxic and shows toxicity to the nervous system, kidneys and reproductive system. Exposure to lead causes irreversible brain damage and encephalopathic symptoms [22]. Cadmium is used widely in electroplating industries, solders, batteries, television sets, ceramics, photography, insecticides, electronics, metal-finishing industries and metallurgical activities. It can be introduced into the environment by metal-ore refining, cadmium containing pigments, alloys and electronic compounds, cadmium containing phosphate fertilizers, detergents and refined petroleum products. Rechargeable batteries with nickel–cadmium compounds are also sources of cadmium [28–30]. Cadmium exposure causes renal dysfunction, bone degeneration, liver and blood damage. It has been reported that there is sufficient evidence for the carcinogenicity of cadmium [23].

Copper, as an essential trace element, is required by biological systems for the activation of some enzymes during photosynthesis but at higher concentrations it shows harmful effects on the human body. High-level exposure of copper dust causes nose, eyes and mouth irritation and may cause nausea and diarrhea. Continuous exposure may lead to kidney damage and even death. Copper is also toxic to a variety of aquatic organisms even at very low concentrations. Mining, metallurgy and industrial applications are the major sources of copper exposure in the environment.

Zinc is also an essential element in our diet. Too much zinc, however, can also be damaging to health. Zinc toxicity in large amounts causes nausea and vomiting in children. A higher concentration of zinc may cause anemia and cholesterol problems in human beings. Mining and metallurgical processing of zinc ores and its industrial application are the major sources of zinc in the air, soil and water. It also comes from the burning of coal.

Nickel occurs naturally in soils and volcanic rocks. Nickel and its salts are used in several industrial applications such as in electroplating, automobile and aircraft parts, batteries, coins, spark plugs, cosmetics and stainless steel, and is used extensively in the production of nickel–cadmium batteries on an industrial scale. It enters into the water bodies naturally by

weathering of rocks and soils and through the leaching of the minerals [24]. The water soluble salts of nickel are the major problems of contamination in aquatic systems [25]. Paint formulation and enamelling industries discharges nickel containing effluents to the nearby bodies of water [26]. Nickel is also found in cigarettes, as a volatile compound commonly known as nickel carbonyl [27].

Arsenic is found naturally in the deposits of earth's crust worldwide. The word arsenic is taken from Zarnikh in Persian literature, which means yellow orpiment [28]. It was first isolated as an element by Albert Magnus in 1250 AD. Arsenic exists in powdery amorphous and crystalline forms in the ores. In certain areas the concentration of arsenic may be higher than its normal dose and creates severe health hazards to human beings and animals. It enters the environment through the natural weathering of rocks and anthropogenic activities, mining and smelting processes, pesticide use and coal combustion. The toxicity of arsenic as a result of the contamination of groundwater bodies and surface waters is of great concern. Arsenic exists as arsenate, As(V), and arsenite, As(III), in most of the groundwater [29-32]. Adsorption and solution pH commonly controls the mobility of arsenic in the aqueous environment [33-37]. Metal oxides of Fe, Al and Mn play a role in the adsorption of arsenic in aquatic bodies [38-40]. Arsenic has been found naturally at high concentration in groundwater in countries such as India, Bangladesh, Taiwan, Brazil and Chile. Its high concentration in drinking water causes toxic effects on humans and animals.

Clays have been widely used for the removal of heavy metals from aqueous solutions due to their outstanding properties [41,42]. Heavy metals can be removed by ion exchange or a complexation reaction at the surface of clays. During the past few years, surface modifications of natural clays with reagents containing metal binding groups have been explored [42-44]. Several modification techniques such as intercalation of organic molecules into the interlayer space and grafting of organic moieties have been applied [45,46]. Organic-modified clays based on montmorillonite were prepared by embedding ammonium organic derivatives with different chelating functionalities for heavy metal removal [47]. Montmorillonite intercalated with poly-hydroxyl Fe(III) complexes was used for the sorption of Cd(II) [48]. Sodium dodecyl sulphate modified iron pillared montmorillonite has been successfully applied for the removal of aqueous Cu(II) and Co(II) [49]. Smectite intercalated with a non-ionic surfactant shows a good performance for the removal of

heavy metals [50]. Through the grafting of inorganic and organic components, natural clay can be functionalized to obtain a better sorption capacity [51,52]. Heavy metals have been removed through the grafting of amino or mercapto by reaction with the silanol groups onto the surface of clays [53,54]. Synthesis of layered magnesium organosilicates for the removal of heavy metals has been carried out with different organosiloxanes [55]. Sepiolite can be grafted with organic moieties due to its high content of silanol groups. Liang et al have functionalized the sepiolite by nanotexturization in aqueous sepiolite gel and surface grafting in toluene with mercaptopropyltrimethoxysilane. The sorption of Pb(II) and Cd(II) were studied and it was found that the surface modification can obviously increase the sorption capacities for Pb(II) and Cd(II).

LDH materials appear in nature and can be easily synthesized in the laboratory. In nature they are formed from the weathering of basalts or precipitation in saline solution. All natural LDH minerals have a structure similar to hydrotalcite, which has the formula $[Mg_6Al_2(OH)_{16}]CO_3 \cdot 4H_2O$. LDHs have been prepared using many combinations of divalent to trivalent cations including Mg, Al, Zn, Ni, Cr, Fe, Cu, Ga and Ca [56-60]. A number of synthetic techniques has been successfully employed in the preparation of LDHs. There are a number of methods used to synthesize LDHs including coprecipitation methods, hydrothermal synthesis, urea hydrolysis methods, sol-gel methods, ion-exchange methods and rehydration methods.

LDHs have been investigated intensively for anion-exchange properties due to recent interest in developing the use of anionic clays for environmental remediation. The main characteristic that has been studied is to clearly characterize the adsorption properties of the materials under vigorous solid-liquid interface conditions. The effect of sorbent composition, surface and bulk adsorption and concentration of adsorption site have been assessed. The adsorption capacity is significantly affected by the nature of the counter anion of the LDHs layer. LDHs can be used as precipitating agents of heavy metal cations for the decontamination of wastewater. Mn^{2+} , Fe^{2+} and Cu^{2+} cations have been removed by synthetic hydrotalcite-like compounds, with zaccagnaite and hydrotalcite thin films being used for the remediation of aqueous wastes containing hazardous metal ions [61].

Mercury as a pollutant in environment.

Mercury is a metallic element that occurs naturally in the environment. Physical state Dense, silver-white metal; liquid at normal temperatures and pressures vapour pressure 0.16 Pa at 20 °C

Stability Carbon–mercury bond in organic mercury compounds is chemically stable Major uses and sources in drinking-water naturally occurring mercury has been widely distributed by natural processes such as volcanic activity. The use of mercury in industrial processes significantly increased following the industrial revolution of the 19th century. Mercury is or has been used for the cathode in the electrolytic production of chlorine and caustic soda, in electrical appliances (lamps, arc rectifiers, mercury cells), in industrial and control instruments (switches, thermometers, barometers), in laboratory apparatus and as a raw material for various mercury compounds. The latter are used as fungicides, antiseptics, preservatives, pharmaceuticals, electrodes and reagents. However, mercury's industrial uses are decreasing because of environmental concerns and environmental legislation in many countries. Mercury has also been widely used in dental amalgams. A less well characterized use is in ethnic and folk remedies, some of which can give rise to significant exposure of individuals

Mercury, liquid metal has been widely distributed in the environment by natural processes such as volcanic activity. The industrial revolution took place in 19th century increased usage of mercury in industrial processes significantly. Mercury is or has been used for the cathode in the electrolytic production of chlorine and caustic soda, in electrical appliances (lamps, arc rectifiers, mercury cells), in industrial and control instruments (switches, thermometers, barometers), in laboratory apparatus and as a raw material for various mercury compounds. The latter are used as fungicides, antiseptics, preservatives, pharmaceuticals, electrodes and reagents. However, mercury's industrial uses are decreasing because of environmental concerns and environmental legislation in many countries. Mercury has also been widely used in dental amalgams.

The solubility of mercury compounds in water varies, elemental mercury vapour is insoluble, mercury (II) chloride is readily soluble, mercury (I) chloride is much less soluble and mercury sulphide has a very low solubility. Methylation of inorganic mercury is an important process in water and occurs in both fresh water and seawater. Bacteria (*Pseudomonas* spp.) isolated from mucous material on the

surface of fish and soil were able to methylate mercury under aerobic conditions. Some anaerobic bacteria that possess methane synthetase are also capable of mercury methylation (Wood & Wang, 1983). Once methylmercury is released from microbes, it enters the food-chain as a consequence of rapid diffusion and tight binding to proteins in aquatic biota.

Mercury levels in air are in the range 2–10 ng/m³. Levels of mercury in rainwater are in the range 5–100 ng/litre, but mean levels as low as 1 ng/litre have been reported. Naturally occurring levels of mercury in groundwater and surface water are less than 0.5 µg/litre, although local mineral deposits may produce higher levels in groundwater.

Food is the main source of mercury in non-occupationally exposed populations. Fish and fish products account for most of the organic mercury in food. The average daily intake of mercury from food is in the range 2–20 µg, but may be much higher in regions where ambient waters have become contaminated with mercury and where fish constitute a high proportion of the diet (Galal-Gorchev, 1991). {Food Addit Contam. 1991 Nov-Dec;8(6):793-806.

The use of dental amalgams for repair work has been widespread and is considered to be an important source of exposure for those with amalgam dental work. 2.5 Estimated total exposure and relative contribution of drinking-water. On the assumption of an ambient air level of 10 ng/m³, the average daily intake of inorganic mercury by inhalation would amount to about 0.2 µg. If a level in drinking water of 0.5 µg/litre is assumed, the average daily intake of inorganic mercury from this source would amount to about 1 µg. The average daily intake of mercury from food is in the range 2–20 µg. Mercury in drinking-water is considered to be a minor source of exposure to mercury except in circumstances of significant pollution.

About 7–8% of ingested mercury in food is absorbed; absorption from water may be 15% or less, depending on the compound. About 80% of inhaled metallic mercury vapour is retained by the body, whereas liquid metallic mercury is poorly absorbed via the gastrointestinal tract. Inhaled aerosols of inorganic mercury are deposited in the respiratory tract and absorbed to an extent depending on particle size. The extent of transport of inorganic mercury across the intestinal tract is probably dependent on its solubility, ease of dissociation in the gastrointestinal tract and intestinal pH (Friberg & Nordberg, 1973; Endo et al., 1990). Nutritional status with regard to essential divalent

cations such as Cu^{2+} and Zn^{2+} may also influence gastrointestinal absorption. Inorganic mercury compounds are rapidly accumulated in the kidney, the main target organ for these compounds. The biological half-time is very long, probably years, in both animals and humans. Mercury salts are excreted via the kidney, liver, intestinal mucosa, sweat glands, salivary glands and milk; the most important routes are via the urine and faeces.

The samples Mg-Al-NO₃ and Mg-Al-EDTA are characterized by powder X-ray Diffractometry. The PXRD pattern shows the following broad reflections for planes (003), (006) and (110). The corresponding interlayer spacings 'd' are calculated and listed in the table.

Table 1: Interlayer spacing of the samples

Sample name	d(003) (Å)	d(006) (Å)	d(110) (Å)
Mg-Al-NO ₃ -LDH	7.77	3.86	1.55
Mg-Al-EDTA-LDH	14.98	7.38	1.56

The PXRD pattern of Mg-Al-NO₃ and Mg-Al-EDTA is represented in a table 1. The prepared intercalated compound in (b) is different from that of the precursor sample with nitrate anion in the interlayer (a), but both are characteristic of a layered phase with the basal diffractions mainly due to planes of (003) and (006). These patterns also indicate that the intercalation of EDTA in Mg-Al-NO₃ gives rise to an increase in basal spacing from $d=7.77$ Å to $d=14.98$ Å. The subtraction of 4.8 Å as the hydroxide-layer thickness, from the $d=14.4$ Å gives 10.18 Å as interlayer space occupied by EDTA. On the other hand, the values for Mg-Al-NO₃ decrease slightly from Mg-Al-EDTA which agrees with the reported classical values for Mg-Al-EDTA [18]. This suggests that the ligand is probably accommodated in the interlayer space of the LDHs. To confirm the chelation of metal cations in the interlayer, the PXRD patterns of the products Mg-Al-EDTA-M were obtained, but no significant change in the basal spacing of the adsorbent material was observed (PXRD not shown). In addition, the basal spacing is very similar to that found in previous reports [19]. The results suggest that the M-EDTA complexes are formed and

accommodated into the interlayer without apparent deformations.

The sorption experiments of Hg on Mg-Al-EDTA were carried out suspending duplicate samples of 0.1 g of Mg-Al-EDTA in 50 ml of aqueous solution of chromium chloride salt at various concentrations of 0.1-20 mg shaken in a thermostatic water bath at 20, 30, 40, and 50°C for 5, 10, 15, 20, 25 and 30 min. The pH was varied in the range of 3-8. It was determined for the optimum initial pH, contact time and concentration of metal salts. The supernatants were separated to determine the amount of metal Hg by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS). This amount was determined from the difference between initial and final concentration of the metal ion in the supernatant solutions. Metal solutions without adsorbent (blank samples) were also shaken under the same experimental conditions.

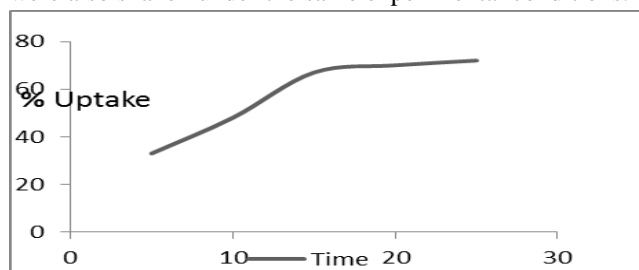


Fig. 1 % Mercury uptake by Mg-Al-EDTA LDH with time (min)

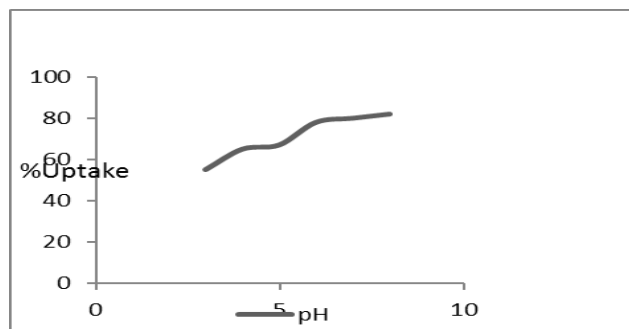


Fig. 2. % Mercury uptake by Mg-Al-EDTA LDH with pH.

The Percent uptake (%) = $\frac{\text{conc. of Hg in the solid phase}}{\text{conc. of Hg in aqueous phase}} \times 100$. Effect of initial metal concentration was investigated using initial Hg concentration varied from 0.1 to 20 mg/100 ml. In experiments concerning the effect of adsorbent dose, a range of solid material samples (0.5, 1, 2, and 5 g) were used. For contact time experiments, the same procedure above was followed, with the difference that the phases were separated after a

determined period of contact time. The temperature was optimized at 35°C for all adsorption experiments.

The Hg ion uptake was affected by pH of the solution as the pH increases the uptake increases reaching a maximum of 82% and 80%, respectively at pH 8.0 and pH 7. The sorption capacities of metal ions at the optimal temperature of 35°C are, 50%, 65%, 67%, 78%, 80% and 82% at pH 2, 3, 4, 5, 6, 7 and 8 respectively. The capacity is relatively constant for pH 6-7. Thus, the optimum pH was chosen to be 7 to avoid any false uptake at pH 8 or above due to the formation of metal hydroxides. This order of uptake clearly shows the pH dependent and the sorption increases with increasing pH value of solution as expected trend for heavy metal ions. The effect of contact time between adsorbent and a Hg solution with an initial concentration of 100 mg/L, 1g of solid material and pH 6.5 at 30°C is presented in Figure 3.

V. CONCLUSION AND FUTURE SCOPE

Layered double hydroxides are good adsorbent materials for the effective removal of heavy and toxic metal ions. EDTA intercalated Mg-Al-LDH is successfully used for the removal of the toxic metal mercury from the laboratory effluents.

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