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Lead: Toxicological Profile, Pollution Aspects and Remedial Solutions

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Abstract

Water quality is the keen concern all over the world. As water resources get contaminated naturally or artificially, at last they affect our health as well as economic and social development of the nations. Among the prominent chemical pollutants, lead alone has threatened health of billions due to deterioration in water quality. Thus, safe water for drinking becomes a major worried issue of UNICEF as a major stakeholder in sustaining water quality with responsibility to improve and sustain quality of water through its programs around the world. The mitigation of contaminations through effective techniques is the common global effort toward remediation of pollutions. This chapter has investigated viability of ordinary organic waste and natural polymeric material like chitin, chitosan, and doped bio-composite adsorbents for the mitigation of Pb^{2+} ions from water. The relatively higher adsorption potential of synthesized composites is studied for removing excessive lead concentration from water as tested in batch and column mode. Certain exchangeable metal ions such as Na^+ , Ca^{2+} , and Mg^{2+} aid to form solid precipitate, which is effective in Pb^{2+} retention and facilitate its adsorption. Certain pilot domestic units provide simple, efficient, and feasible options for removal of Pb^{2+} ions from water.

Keywords: lead(II), chitosan, biocomposite, adsorption, diffusion, thermodynamic parameter, batch/column modes

1. Introduction

The need of pure and safe water to the society is a precondition for health and development along with a basic human right as very well cited in the slogan below:

*Water is abundant, besides inexpensive, Yet pure Water is fewer,
While good health, needs to drink it in safe, pure and upmost care!*

Yet, millions of people throughout developing world denied this fundamental fact/right. Water borne diseases may arise through insufficient safe water supplies coupled with poor sanitation, and hygiene causes about 4 million death/year including children [1]. International communities are doing lots of attempts in this sense. Billion people do not have access to improve water sources and are not able to get pure and safe water for drinking as well as for other purposes. In fact, the magnitude of water quality problem is even larger than being projected. The existing

improved sources in developing countries do not provide water of adequate quality for drinking and other purposes.

In 2006, UNICEF has drawn global strategy to distinguish growing importance of ensuring safe drinking water, sanitation, and hygiene strategies for the decade 2006–2015 in its special programs [1–3]. In many Asian countries, the tube well water is viable for extensive toxic and hazardous contaminations such as arsenic, fluoride, and lead [1, 2]. Even today more than half of the world population depends on ground water being a vital source for drinking as it contributes 97% of global freshwater. In a number of geographical regions, ground water is a vital source for drinking due to the fact that it contributes single largest supply for serving drinking water. Especially in India, almost 80% ground water is needed for rural domestic need and 50% needed for urban population. Thus, clean ground water supply is most essential to serve the basic and critical necessities for various utility purposes. Over the years, the availability of pure and safe waters for drinking and other functions has been great concern for better environment [3, 4].

Efficient synthetic purification/treatment processes are used to remove detrimental chemical/biological pollutants along with suspended solids from water and to provide pure and safe water for multiple consumptions such as drinking, therapeutics, pharmaceuticals, chemical, and industrial uses. Throughout the world many, water treatments are almost remains same as mention below:

- i. physical processes like filtration, sedimentation, and distillation;
- ii. biological methods such as slow sand filter/bioactive carbon; and
- iii. chemical techniques, viz. coagulation flocculation, chlorination, and UV radiations.

Ground water is purer and safer than surface water due to earth covering that works as a natural filter, which is the major source for domestic purposes in the developing country like India [2, 5]. In fact, few decades back, water seems to be odorless, free from turbidity, and good from the esthetic point of view and considered to be pure and unpolluted. The concept of water pollution has now changed as even clear water may be latently polluted. As well, surface water is also contaminated by effluents from industries, municipalities, and other places. The contamination of hazardous anions like fluoride in particular and other anions such as nitrate, sulfate, and phosphate in ground water is a wide spread phenomenon causing health problem. The available domestic water purification processes are seldom suitable for rural people due to high cost and maintenance. This creates a great gap between developed water purification technology and its anticipated application [1–4, 6, 7].

Heavy metals such as Zn, Cu, As, Hg, Cr, Ni, Cd, and Pb cause severe problem for humans and aquatic ecosystems if discharged in water through industries and other sources due to particular toxic, hazardous, and carcinogenic nature as well as accumulations in the body based on relative chemical and physiological characteristics [1–4, 6, 8]. The removal of heavy metals from water is seriously needed because of the imposed environmental pollution and ecological degradation. The adsorption process is widely used for the removal of heavy metals from wastewater because of its low cost, availability, and eco-friendly nature. Both commercial adsorbents and bio-adsorbents are used for the removal of heavy metals from wastewater, with high removal capacity. This chapter compiles information on different adsorbents used for Pb^{2+} removal and provides information on the commercially available. Innovative processes and technologies are involved for lessening toxicity so as to cater demands of environmental standards being developed for the treatment of heavy metal polluted wastewater.

Toxic heavy metal removal from domestic wastes, sewage, and industrial outlets is a challenging task, especially in waste effluents. Various methodologies are being investigated as and when for the mitigation of such heavy metal pollution in water [1–4, 6, 8]. The heavy metals including lead, cadmium, and mercury are removed from industrial wastewater by means of assorted techniques namely physicochemical precipitation, electrochemical reduction, ion exchangers, reverse osmosis, cementation, electrodialysis, electrowinning, electrocoagulation, membrane separation, and adsorption. However, technical applications, plant easiness, and cost are vital parameters to choose utmost appropriate treatments for the mitigation of heavy metal pollution from water [4]. Physicochemical adsorption is quite a cheap and capable method for retention of heavy metals from industrial effluents due to its easy, successful, and profitable features. Heavy metal pollution subsists in wastes of a number of industries, such as metal plating, mining, tanneries, chloralkali, radiator built-up, smelting, alloy-making printed circuit board making, and storage batteries. Assorted metals such as tin, lead, and nickel metal-based solder plates shown familiar resistant over plated if applied for solderable applications as metal plating are recommended, as deposited inter-metallic formations ensuing diffusion barrier viable as good solder base for soldering applications. Most of the aforesaid industries discharged huge wastewater contaminated with lead and deemed utmost hazardous to man-health and environment conditions [1–4, 6].

Lead gets absorbed or accumulated in living species and subsequently penetrates in human systems through food chains/cycles. Ingested lead beyond its stringent/permitted level results in serious health disorders. Thus, it is compulsory to treat Pb^{2+} contaminations prior to its discharge into the environment [6, 8]. In fact, heavy metal lead is soft, malleable, bluish gray color being picky interested due to innate toxicity and extensive existence in the atmosphere. Lead is the most toxic metal considered as a priority pollutant as an industrial pollutant, which enters in an environment via soil, air, and water/wastewater. Lead is a systemic poison very toxic in nature because it causes anemia, kidney malfunction, brain tissue damage, and death in severe poisoning [9]. Lead pollution dispersed over the soil and ground water through natural sources and industrial effluents. Certain processing industries, such as acid-battery making, metal plating and finishing, ammunition, anti-knocking agent-tetraethyl-lead synthesis, ceramic/glass industries, and environmental clearout practices, dispersed lead polluted water, which is the foremost lead pollution sources. Alternatively, high lead concentration in the atmosphere also results in enduring health risks to all the elements of ecosystem.

As recommended by the WHO, the maximum tolerable limit of lead metal in drinking water is 0.05 mg/L, while Environmental Protection Agency allows the permissible limit for Pb^{2+} in wastewater as 50 ppb (part per billion). However, industrial wastewaters own Pb^{2+} ion with the amount ranging between 200 and 500 mg/L, which is a lot more than that of water quality standards. Maximum contamination/limiting level concentration and types of heavy metals as discharged are recognized by the USEPA as mentioned in **Table 1**.

1.1 Precedence pollutants in water

The introduction of contaminants into the environment causes pollution, which is the unfavorable alterations of our surroundings. This pollution can be in the form of chemical substances or energy such as noise, heat, and light [6]. Thus, the pollutants can be naturally occurring substances or energies; however, things are considered contaminants if they exist excess of natural levels. All such pollutants that enter the atmosphere by any known or unknown sources surely create harms or discomfort to humans and other living organisms of the planet. Many water

Entry	Heavy metal	Maximum contamination level (ppm)	Potential toxicity profiles
1	Lead	0.005	Damage/fatal to brain, kidney diseases, circulatory and nervous system disorders, death in severe contamination
2	Arsenic	0.050	Skin manifestations, visceral cancers, vascular disease
3	Cadmium	0.01	Kidney damage, renal disorder, human carcinogen
4	Chromium (VI)	0.05	Headache, diarrhea, nausea, vomiting, carcinogenic, respiratory tract problems
5	Copper	0.25	Wilson disease, insomnia, vomiting, hematemesis, hypotension, melena, coma, jaundice, pigmentation of skin, gastrointestinal distress, damage liver kidney
6	Nickel	0.20	Dermatitis, nausea, chronic asthma, coughing, human carcinogen
7	Mercury	0.00003	Rheumatoid arthritis, diseases of the kidneys, circulatory system, and nervous system

Table 1.
Maximum contamination/limiting level (MCL) concentration and types of heavy metals being discharged as recognized by the USEPA standards [1–4, 6].

pollutants may get discharged through domestic, industrial, and agricultural wastes due to human activities or domestic sources. In past years, water with odorless, colorless, and free from turbidity was considered as good, pure, and unpolluted from the esthetic point of view [1–4, 6]. But this entire concept of water pollution was changed. Now even if water is colorless and odorless, it can be polluted and may contain microbes as well as dissolved impurities such as toxic metals, organic pollutants, and radioactive materials. Thus, water pollution can be defined as any change in physical, chemical, or biological properties of matter. It is not possible to analysis water quality for all of chemical pollutants that could cause health problems, nor is it indispensable. However, most of these contaminants occur rarely, and many result from human contagion and affect a few water sources. The chemicals that potentially cause serious health problems by over widespread areas include arsenic, fluoride, phosphate, and nitrate (from swage and fertilizers) [1, 8].

Some of these anionic chemical pollutants are more often found in ground water, though surface water can also be impacted. In order to plan new water supply projects, especially to ground water resources, contamination from lead, arsenic, fluoride, phosphate, and nitrate should be given priority [5, 7, 8, 10]. Subsequently, second priority is to be given to metals (principally iron and manganese). The inorganic chemicals are common cause for water to be rejected from the esthetic view and also enhance salinity of water (saltiness or dissolved salt content of water body). The fresh or naturally occurring water has salinity <0.05% as characterized by low concentrations of dissolved salts [6].

1.2 Significant studies of lead removal

The advancement of today was seeded by research years ago, and progress of tomorrow will be the result of today’s planned research. Comprehension of allied literature of past studies is very much indispensable for any investigation work to formulate sound methodology that acts as a guiding source during advancement of research. Chitin and chitosan are the frequently used biomaterials in mitigation of water pollutants [1, 8]. But, low mechanical resistance and high solubility in acid

medium limit their applications in applied conditions, as observed in water treatment. However, such disadvantages can be overcome by preparation of chitin- and chitosan-based biocomposite matrix by doping techniques. The biopolymer-based adsorbent media can be chemically and mechanically stabilized by doping chitosan matrix to alter its solubility and brittleness. Herein, a novel de-fluoridation procedure has been developed, which successfully removed fluoride from water and exhibits greater competitive adsorption capacities than those of commercial activated alumina (even at broad range of pH). The novel aspects of research work were inferred from review of literature and found that this developed Pb^{2+} removal technique of water works by the sorption of fluoride onto bioadsorbents in efficient way in terms of magnitude of crisis, and this research is a small attempt for a big problem.

1.3 Lead properties

Lead is a soft, malleable heavy metal that belongs to the carbon group with symbol Pb (Latin: Plumbum) [1–4, 6]. It is also found in the earth's crust, and the proportion gets increased with time due to radioactive uranium disintegration. Atomic number of lead metal is 82, atomic weight 207.2, melting point 327.5°C , density 11.34 g/cm^3 , and electronic configuration $[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^2$. Metallic lead has a bluish-white color after being freshly cut, but it soon tarnishes to a dull grayish color when exposed to air. Lead metal exists as the natural abundance in four stable isotopic forms namely Pb^{204} , Pb^{206} , Pb^{207} , and Pb^{208} . Metallic lead PbO rarely occurs in nature; nevertheless, the metal exists in two main oxidation states Pb^{2+} and Pb^{4+} with more stable divalent form in the aquatic environment [2]. Three lead oxides are known, that is, lead monoxide (PbO), lead dioxide (PbO_2), and lead tetroxide (Pb_3O_4) also called minium. Lead is found in ore with other heavy metals such as zinc, silver, and copper and is extracted together with these metals. The main lead mineral is galena (PbS) that contains 86.6% lead by weight. However, as a result of human activity in the atmosphere, lead metal exists mainly as cerussite (PbCO_3) and anglesite (PbSO_4) [5, 7, 10].

2. Environmental sources of lead

The presence of lead in water, air, and soil environment even in traces has detrimental effects on plants and animals. The natural sources of lead are soil erosion, volcanic eruptions, sea sprays, and bush fires. The anthropogenic activities dispersed lead compounds throughout the environment. Lead is transferred continuously through air, water, and soil by natural chemical and physical processes such as weathering, runoff, precipitation, dry deposition of dust, and stream/river flow [1–4, 6].

2.1 Air

The ingestion of lead through food and water is much greater than that of urban air. Inhaled lead of about 20–40%, which is derived from the air, is much more readily absorbed [6]. The air released from the combustion of fossil fuels, especially leaded gasoline, and several industrial processes dealing with storage batteries, mining, and ore smelting operations are of major concern regarding lead pollution in the atmosphere. Children are more susceptible to airborne lead poisoning, and lead absorbed in the guts of infants and young children is estimated to be 5–10 times greater than in adults [2, 11]. Faulty removal of lead-based paint, street dirt, and household dust absorbed through the lungs, skin, and intestinal tract is also responsible to airborne lead contamination. Cigarette smoke is also a significant

source of lead exposure due to lead arsenate insecticides sprayed on tobacco. Most of lead ions reside in smoke-ash; however, studies have estimated 20 nanogram of lead per cigarette smoke, leading toxic effects on lungs of smoker.

2.2 Food

Food sources can be contaminated with lead due to spraying of lead arsenate insecticides or lead accumulations during food processing. Exclusively imported pottery such as ceramic cookware possess lead-containing glaze is a common source of lead toxicity. Lead solder used for sealing of food cans, especially the acidic foods such as tomato, okra and orange, grapefruit, or cranberry juices are also key sources of lead intake. Canned juices and canned baby foods such as evaporated milk may contain up to 100 and 200 μg of lead per liter, respectively [12], as high as 300 μg /day total lead uptake through food. Ingestion of peeled lead-based paint pica in children causes poisoning [2, 8, 13].

2.3 Soil

The toxic lead compounds are strongly adsorbed onto the upper layers of soil and do not leach into the subsoil. The average residence time of lead in the atmosphere is about 10 days. The presence of high concentration of lead in the soils results in lead contaminated fruits and vegetables. Particulate pollutants are emitted through leaded paints, leaded gasoline, and lead in pipes that can also contaminate the soil with heavy metal lead/ Pb^{2+} [14].

2.4 Water

The solubility of lead compounds is the highest in soft and acidic water, and it is a function of pH, hardness, and salinity of water sample. Several industries engaged in releasing of industrial wastewater effluents, lead acid batteries, fertilizers, pesticides, and mining waste; metallurgical, chemical, and petrochemical industries are prominent sources of releasing toxic lead in the water stream. Lead rarely occurs in natural water bodies, but the major source of lead in drinking water is from lead-based plumbing materials. The corrosion of such leaded pipes/fixtures enhances lead amount in community water. Old homes constructed before 1986 owing lead pipes, fixtures, and solder are the main contributor to lead in tap water. Other water delivery systems such as lead solder used to join copper pipes, brass in faucets, coolers, and valves are liable for lead content in water. Older submerged pumps used in well water can also contain leaded-brass works. Seawater and river water contain 2–30 ppt and 3–30 ppb of lead content, respectively. Phytoplankton contains 5–10 ppm, freshwater fish 0.5–1000 ppb, and oyster 500 ppb of lead/ Pb^{2+} concentration [15].

3. Control of lead contamination

In India, the Central Pollution Control Board (CPCB) has carried out a major ground water quality survey, and the report recognized about 20 critical sites of ground water pollution in various states of India. CPCB found that industrial effluents are the primary and major cause for ground water pollution [1–4, 6, 11]. The major heavy metal contamination sites including lead metal in Indian scenario have been reported in **Figure 1**. The chemical quality of ground water as monitored by CPCB India showed that the states such as Haryana, UP, Punjab, West Bengal, Tamilnadu, and Telangana own heavy contaminations of lead metals [12, 13].

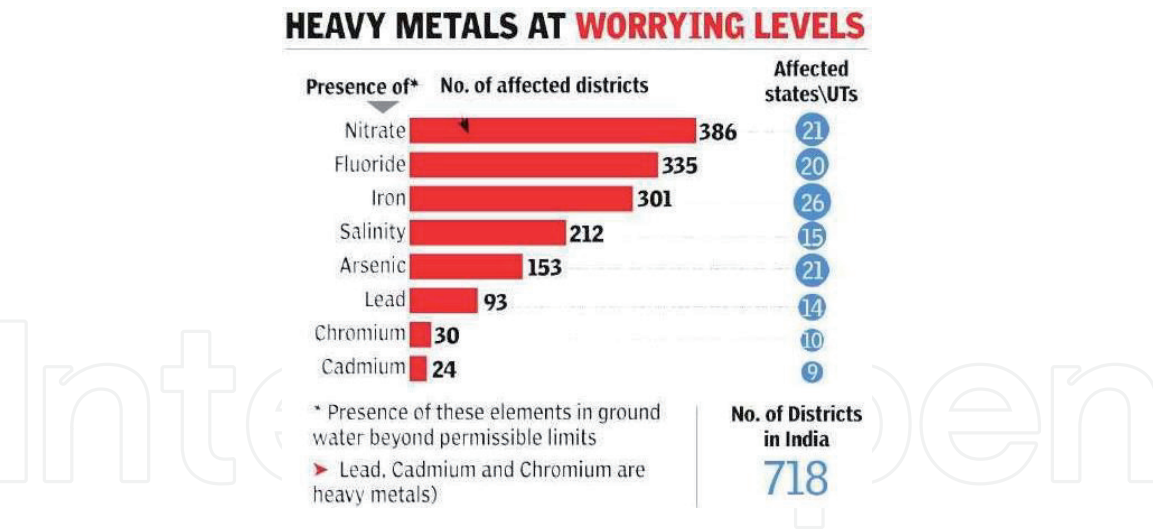


Figure 1.
Heavy metal contaminations in various Indian states. Sources: Timesofindia.indiatimes.com/articleshow/65204273.cms?utm_source=contentofinterest&utm_medium=text&utm_campaign=cppst.

3.1 Regulatory aspects of lead in water

According to the Indian Standard Institution (ISI), the tolerance limit for discharge of lead into drinking water is 0.05 mg/L and land surface water 0.1 mg/L [16]. The World Health Organization (WHO 1995) had proposed safe total lead limit of 50 ppb in drinking water, which was further decreased to 10 ppb [1–4, 6]. The permissible limit of lead ions in drinking water as set by the European Union (EU), the United States Environmental Protection Agency (USEPA), and Guidelines for Canadian Drinking Water Quality in 2012 is 10, 15, and 10 ppb, respectively. However, more recently, an EPA document recommends a zero lead/Pb²⁺ value in national primary drinking water standard [17].

4. Symptoms and health effects of lead

The human body contains around 120 mg of lead, and 10–20% of lead is absorbed by the intestines. The doorway of poisonous lead in human system mainly through contaminated air, food, and water sources manifests overt and detrimental health problems. Lead is a cumulative poison, and it elucidates destructive effects on almost every physiological systems namely musculoskeletal, nervous, cardiovascular, digestive, reproductive, excretory, endocrine, and metabolic system. Lead is highly toxic and carcinogenic even at low concentration [2, 6]. International Agency for Research on Cancer (IARC) classifies inorganic lead compounds as probably carcinogenic to humans (Group-2A). The National Toxicology Program (NTP-2005) of the US Department of Health and Human Services concluded that “Lead and lead compounds are reasonably anticipated to be human carcinogens” [16, 17].

4.1 Effects of lead on children

Children are usually more vulnerable for toxicity of lead due to immature blood-brain barrier and the fact that lead can easily cross blood brain and placental barrier, and thus they readily absorb a larger amount of lead per unit body weight than adults. The serious effects of Pb²⁺ on health of children include encephalopathy, peripheral neuropathy, cognitive impairment, and personality disorders (USEPA, 1986a). If the neuropathy is severe, the lesion gets permanent. Lead

toxicity showed dark blue lead sulfide line at the gingival margin of the person. It is found that the fatal effects of lead (II) are marked by seizure, coma, and death if not treated immediately according to the USEPA studies [2, 8, 18]. Evidence suggests that lead may cause fatigue, irritability, information processing difficulties, memory problems, a reduction in sensory and motor reaction times, decision-making impairment, and lapses in concentration [12]. Lead interferes with heme biosynthesis by changing the activity of three enzymes δ -aminolevulinic acid synthetase (δ -ALAS), δ -aminolevulinic acid dehydratase (δ -ALAD), and ferrochelatase and thus affects the hematological system. The presence of Pb^{2+} ions above 70 mcg/dL in human blood exhibited microcytic and hypochromic anemia being characterized by hemoglobin reduction and basophilic stippling of erythrocytes along with a shortened life span of red blood cells (erythropoiesis) [6, 11, 12]. Increase blood lead level shows decreased intellectual capacity and IQ level of children by four to seven points for every 10 μ g/dL [11]. Attention deficit hyperactivity disorder (ADHD) hearing impairment in child may disrupt peripheral nerve function (ATSDR 2007).

4.2 Effects of lead on adults

Lead toxicity affects renal system as it causes many effects such as aminoaciduria, glycosuria, and hyperphosphaturia, that is, Fanconi-like syndrome [2, 19]. Kidney disease, both acute and chronic nephropathy, is a characteristic of lead toxicity [12]. Lead poisoning inhibits excretion of the waste product urate that causes a tendency for gout, that is, saturnine gout. Occupationally, lead exposed individual tends to have more hypertension than normal people and augmented risk for cardiovascular diseases, myocardial infarction, and strokes [20]. Lead toxicity includes gastrointestinal disturbances – abdominal pain, cramps, constipation, anorexia, and weight loss – immune suppression, and slight liver impairment. In adults, high levels of lead can cause headaches and disorders of mood, thinking, memory, irritability, lethargy, malaise, and paresthesia. There is also some evidence that lead exposure may affect adult's postural balance and peripheral nerve function, which can cause tremors or weakness in fingers, wrists, or ankles [2, 21]. Lead poisoning affects the human male reproductive system by decreasing the sperm count and increasing the abnormal sperm frequencies. Women are more susceptible to lead poisoning than men, and lead toxicity causes menstrual disorder, infertility miscarriages, and stillbirths. Lead inhibits several enzymes required for the synthesis of heme, causing a decrease in blood hemoglobin. Lead interferes with a hormonal form of vitamin D, which affects multiple processes in the body, including cell maturation and skeletal growth. Lead poisoning is also known to cause psychotic behavior such as hyperactivity or schizophrenia.

5. Assorted treatment processes for lead removal

Detrimental heavy metals must be removed from the environment in particular water so as to protect the human beings and the environment [2–4, 6, 22]. To accomplish the increased stringent environmental regulations and maximum permissible limit of contaminant in water, a wide range of treatment technologies such as chemical precipitation, coagulation flocculation, flotation, ion exchange, membrane filtration, electrochemical treatment technologies, adsorption [5, 21], and bio-adsorption are most frequently examined for the mitigation of heavy metals from wastewater [2, 8]. Certain merits and demerits of various physicochemical methods used for the mitigation of Pb^{2+} from wastewater are mentioned in **Table 2**.

Entry	Treatment techniques	Merits	Demerits
1	Physicochemical precipitation	Low-cost, easy operation, high efficiency	Huge sludge/waste formations, addition burden of solid-waste disposal
2	Adsorption	Cheap, simple conditions for operation, wide pH workability, high binding capacity/efficiency	Less selective, create large wastes/secondary pollutants
3	Membrane filtration	Small space requirement, low pressure, high separation selectivity	Highly expensive, membrane fouling
4	Electrodialysis	Elevated separation selectivity, great efficiency	Costly, membrane fetid, needs more energy/power
5	Photo-catalysis	Remove metals, organics, green process, less byproducts	Limited utilities, prolong time

Table 2.
The merits and demerits of various physicochemical methods used for the mitigation of Pb^{+2} from wastewater [2, 22].

The reduction of Pb^{2+} in wastewater to 0.05–0.10 mg/L level is required before its discharge to outlet. Certain frequently used methods for remediation of Pb^{2+} from water are as follows:

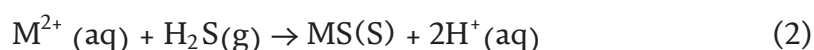
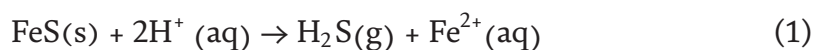
- a. **Precipitation:** It is usual practice use for remediation of Pb^{2+} of ppm level contamination from water. Pb^{2+} salts are insoluble in water and yet get entrapped as precipitates via treatment with certain chemicals such as soda lime, bisulphite, or ion exchangers in a practicable manner. This method uses many chemicals and ultimately generates huge solid wastes and thus poses a burden of sludge disposal. Besides the precipitation, techniques are nonspecific and noneffective for low concentration of Pb^{2+} ions [2].
- b. **Ion exchange:** Ion exchange is another methodology use for the mitigation of Pb^{2+} ions from water. This is quite cheaper than the other known methods; besides ppb levels, Pb^{2+} ion removal can be achieved at large-scale workups. In fact, ion exchangers are natural materials namely certain clays, functionalized porous, gel polymer, zeolite, montmorillonite, and soil humus or some synthesized resins that hold positive/cation as well negative/anion exchanging parts with the other ions in solution owing to a better affinity from the surroundings [5, 7, 8, 10, 18, 23]. Certain artificial matrixes like organic resins are usual for ion exchangers used for the removal of Pb^{2+} ions from water/wastewater. However, such man-made ion exchangers are disadvantageous as nontolerant high level of metal due to matrix fouls [1, 5, 7, 8, 10, 18, 23]. Furthermore, synthetic/natural ion exchangers are non-selective and extremely susceptible to altered pH conditions. Ion-exchange methods have been widely used to remove heavy metals from water due to their many advantages, such as high treatment capacity, high removal efficiency, and fast kinetics [24]. The synthetic resins are most commonly preferred in ion exchange process as they effectively remove the heavy metals from the solution. The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration, and contact time. Charges present of ionic pollutant also controls ion-exchange phenomenon as reveled in purolite C-100 cation exchange resin carried abatement of Ce^{4+} , Fe^{3+} , and Pb^{2+} ions from aqueous solutions. Moreover, natural zeolites have also been widely used due to its low cost to remove heavy metal from aqueous solutions. Many researchers

have demonstrated that zeolites exhibit good cation-exchange capacities for heavy metal ions under different experimental conditions [2–8, 10–12, 23, 25]. Clinoptilolite, natural zeolite, was extensively used to remove Pb^{2+} with an initial concentration of 2072 mg/L, at optimum pH 4, with an adsorption capacity of 0.21–1 meq/g in fixed bed and batch mode operation style. Clinoptilolite was studied for the removal of Pb^{2+} with an initial metal ion concentration of 1036 mg/L, at optimum pH 4, with a removal efficiency of 55% in batch mode experiments [26]. Inadequacies in use of this process are that ion exchange resins must be regenerated once exhausted, which in turn the regeneration eventually causes serious secondary pollution. Ion exchange process is not economical and cannot be used on large scale [5, 7, 8, 10, 18, 23–31].

- c. **Electrowinning:** Electrowinning is also called as electroextraction being frequently used by mining and metallurgical operations for leaching and acid draining. Metal transformation industries employed electrowinning and electrodeposition for amputation and recovery of metal lead ions at insoluble anodes. In electrowinning, metals are electrodeposited from its ores via a leaching route. Electrorefining uses a similar process to remove impurities from a metal as similar to electrorefining used for eliminating impurities from metal. In-bulk conditions, electroplating occurs economically in straightforward purification of metals. In this process, a current is passed through an inert anode via a liquid leach containing lead metal and subsequently deposited at electroplate/cathode [2, 25].
- d. **Electrocoagulation:** Electrocoagulation is an electrochemical process, which uses electrical charges to remove Pb^{2+} from water in an efficient manner, while contaminants are maintained in solution. In this technique after neutralization of Pb^{2+} ions in the solution, the residual coagulant aids destabilization and precipitation of other reverse charges/counter ions. Electrocoagulation is also performed in number of ways such as radio-frequency diathermy or short wave electrolysis. This electrocoagulation is capable to remove Pb^{2+} ions due to the fact that it is hard to take out by filtration or chemical treatments. Various electrocoagulation devices are known with complexity from plain anode and cathode to the larger and more complex device using manageable electrode potentials, passivation, anode consumption, cell redox potentials, ultrasonic, UV ray, and advanced oxidation processes.
- e. **Cementation:** Cementation is a heterogeneous process similar to precipitation technique wherein metal ions like Pb^{2+} are reduced into zero valence at a solid metallic interfaces. This is more commonly used for refining leach solutions. In its solution, Pb^{2+} ions are precipitated in the presence of other solid via electrochemical system as metal with higher oxidation potential bypasses in solution and restore lower oxidation potential metals.
- f. **Chemical precipitation:** Chemical precipitation is an effective and most widely used process in the industry due to its relative simplicity and inexpensive operation [1–4, 6]. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates that can be separated from the water by sedimentation or filtration. Conventional precipitation technique consists of hydroxide precipitation and sulfide precipitation.
- g. **Hydroxide precipitation:** The most widely used hydroxide precipitation technique is relatively simple and low cost with the ease of pH control. The pH

range of 8–11 exhibits the decreased solubility of various metal hydroxides. The coagulants such as alum, iron salts, and organic polymers are used to enhance the removal of heavy metals from wastewater. Lime is the preferred choice of the base used in hydroxide precipitation at industrial settings. To increase lime precipitation, fly ash was used as a seed material. By using fly ash-lime carbonation treatment, the initial concentrations of 100 mg/L of Cd^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , and Pb^{2+} from synthetic effluents can be reduced to 0.08, 0.14, 0.03, and 0.45 mg/L, respectively, at optimum pH 7 with a removal efficiency of 99.37–99.6% [22, 32, 33]. Hydroxide precipitation has some limitations despite of its wide usage. First, it generates large volumes of relatively low-density sludge and consequently poses dewatering and disposal problems. Second, the metal hydroxide precipitation will be inhibited due to the presence of complexing agents in the wastewater, and third, as some metal hydroxides are amphoteric, accordingly in case of mixed metal pollution in water, ideal pH for one metal may put other metals back in solution.

h. Sulfide precipitation: Abatement of toxic heavy metal ions using sulfide precipitation is also an effective process. One of major advantages of sulfide precipitation over hydroxide precipitation is that sulfide precipitates are nonamphoteric and of lower solubility than hydroxide precipitates. Similarly, sulfide sludge demonstrated better thickening and dewatering characteristics than the corresponding sludge of metal hydroxide. The sulfide precipitation process can attain a higher extent of heavy metal removal over a broader pH range than hydroxide precipitation [1–3]. The technique of heavy metal removal by sulfide precipitation involves initial generation of H_2S gas at low $\text{pH} < 3$ (Eq. (1)) and subsequent adsorption at higher pH 3–6 (Eq. (2)) as shown below:



The sulfide precipitation studies revealed that Cu^{2+} , Zn^{2+} , and Pb^{2+} with the initial concentration of 0.018, 1.34, and 2.3 mM get easily precipitated out at optimum pH 3 with a removal efficiency of 100, >94, and >92%, respectively [1–4, 6]. Investigation showed that pyrite and synthetic iron sulfide are used to remove/precipitate out Cu^{2+} , Cd^{2+} , and Pb^{2+} from water/wastewater [3, 4, 6]. The major drawback of use of sulphide precipitation is the evolution of toxic H_2S fumes in acidic conditions. Therefore, this precipitation needs to be carried out in neutral or basic medium. Furthermore, metal sulphide precipitation is likely to form colloidal precipitates that cause troubles in separation either by settling or by filtration processes. Chemical precipitation is appropriate to treat wastewater containing high concentration of heavy metal, and it is ineffective for low metal concentration. It is not economical and can produce large amount of sludge as a secondary pollutant [34].

i. Membrane filtration: Membrane filtration technologies used in heavy metal removal are easy in operation and highly efficient and space saving, but its tribulations such as high cost, complex operation, membrane pollution, and low permeate flux have restricted their use in heavy metal removal. The membrane filtration technique includes ultra-filtration, reverse osmosis, nanofiltration, and electrodialysis [1–8, 10, 23].

j. Ultra-filtration: To obtain high removal efficiency of metal ions, the micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) were suggested. MEUF was first introduced by Scamehorn et al. in the 1980s for the removal of dissolved organic compounds, and multivalent metal ions from aqueous solutions used MEUF to remove Cd^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , and Pb^{2+} from synthetic water using anionic surfactants [5, 7, 8, 10]. Ferella et al. studied MEUF to remove Pb^{2+} and AsO_4^- , with an initial concentration of 4.4 ppm to 7.6 mg/L at optimum pH 7.5 with a removal efficiency of 99 and 19% for Pb^{2+} and AsO_4^- , respectively [5, 7, 8, 10, 23]. The recovery and reuse of exhausted surfactant is necessary; otherwise, it enhances treatment cost and in addition causes secondary pollution due to solid waste/sludge disposal problem. Hence ultra-filtration technique has not attained wide applicability at industrial scale [12].

k. Reverse osmosis: Reverse osmosis (RO) is progressively more popular wastewater treatment alternative in chemical and environmental engineering. In reverse osmosis process, the water is to be purified and allowed to pass through the semi-permeable membrane and at the same time rejecting the contaminants. RO systems are yet to be broadly applied for wastewater treatment. Reverse osmosis alone is not applicable for complete recovery and reuse of fluids. Pretreatment methods namely media filtration, pH adjustment, and use of anti-precipitants are required prior to the reverse osmosis. The main disadvantage of RO is the high power utilization owing to the pumping pressures and the reinstallation of the semi-permeable membranes. Reverse osmosis and electrodialysis use semi-permeable membranes for the removal and revival of Pb^{2+} from water. In this technique, cation and anion membranes from water, which are tied to the electrodes in electrolytic cells under constant electrical supply and subsequent allied ions, get drifted. Treatment characteristics are optimized with respect to Pb^{2+} concentration in the effluents, pH, temperature, and flow volume. Reverse osmosis and electrodialysis (mentioned below) techniques use semi-permeable anionic/anionic membranes which possess certain drawbacks like high cost, generates huge sludge, low retention capacity, and less selectivity and large power usage. Thus, both these techniques are neglected while adsorption method is preferred for the remediation of heavy metal contaminants from water/wastewater [1–8, 10–12, 23].

l. Electrodialysis: Electrodialysis (ED) is another membrane technique used for the separation of ions through membranes from one solution to another under the influence of electric field. This process has been widely used for the treatment of brackish water, industrial effluents, recovery of useful materials from effluents, and salt production [3]. ED is also used as a potential method for wastewater treatment containing heavy metals. The effects of operating parameters on Pb^{2+} mitigation from water have been investigated by ED, and the results revealed that Pb^{2+} separation improved with increasing voltage and temperature [12].

m. Coagulation and flocculation: Coagulation followed by sedimentation and filtration is one of the most significant methods for wastewater treatment, but coagulation method is restricted only to the hydrophobic colloids and suspended particles. Many coagulants such as aluminum, ferrous sulfate, and ferric chloride are widely used for the effective removal of wastewater pollutants. Flocculation is the process by which fine particulates are caused to clump or agglomerate together into flocs. In general, PAC (polyaluminum chloride), polyferric sulfate (PFS) and polyacrylamide (PAM) are widely used

flocculants in wastewater treatment, but practically, they are ineffective in heavy metal removal. The flocculation by humic acid (HA) is also studied. It is also studied to reveal better removal of Pb^{2+} and Zn^{2+} from solution by binding such ions to HA and then coagulating-flocculating with cationic polyelectrolyte polydiallyl dimethyl ammonium chloride (poly-DADMAC). Generally, coagulation-flocculation cannot treat the heavy metal wastewater completely [24]. So, it must be combined with other treatment techniques. Besides, coagulation-flocculation involves chemical utilization and sludge formation as a secondary pollution.

- n. Flotation:** Recently, flotation has found widespread use in heavy metal removal from wastewater due to its several advantages such as high metal selectivity, high removal efficiency, high overflow rates, low operating cost, and more concentrated sludge production [27]. Flotation has been implemented to remove heavy metal from a liquid phase using small air bubble attachment. The main flotation processes are dissolved air flotation (DAF), ion flotation, and precipitation flotation used for metal ion abatement from water. Among these techniques, ion flotation has been proved to be a promising method for the wastewater treatment. The ion flotation is an adsorptive bubble separation techniques based on imparting the ionic metal species hydrophobic by the use of surfactants and removal of these hydrophobic species from wastewater by the passage of air bubbles reported the 100% removal of copper (II) and Pb^{2+} from water at pH 6 and 7, respectively, using ion floatation technique. Despite of several advantages, the shortcoming in use of flotation techniques involves high initial capital cost, high maintenance, and expensive operation [12, 27].
- o. Electrochemical treatment:** Electrochemical wastewater treatment technologies are rapid, well controlled, and capable of producing less sludge. It requires few chemicals and possesses better metal reduction capacity. Electrochemical technologies include electrocoagulation, electroflotation, and electrodeposition. Studies of electroflotation technique revealed more stress on separation of heavy metal ions such as iron, nickel, copper, zinc, lead, and cadmium with maximum removal [1–4, 6, 11]. The quantitative electrodeposition of copper and lead ions onto specially designed palm shell AC electrodes has been reported in the recent investigation studies [1–4, 6]. Nevertheless, the requirement of high initial capital cost and the expensive electricity supply restricts wide usage and application of electrochemical techniques in wastewater treatment [6, 23].
- p. Adsorption:** Adsorption is defined as the process where a solute is removed from the liquid phase through contact with a solid adsorbent, which has a particular affinity for that particular solute [1–4, 6, 10–12]. All adsorption processes mainly depend on the equilibrium and mass transfer rates, which involve the accretion of substances at the interface of liquid-liquid, gas-liquid, gas-solid, or liquid-solid interface. The substance being adsorbed is adsorbate, and adsorbing material is adsorbent. The reverse phenomenon of adsorption is termed as desorption where a solute/pollutant gets released from/through an adsorbent. The process of adsorption can be classified as physical adsorption/physisorption and chemical adsorption/chemisorption, which depends on the forces involved in adsorbate-adsorbent interactions. Adsorption is now recognized as an effective and economic method for the mitigation of wide variety of water pollutant by sorption. Among the aforementioned technologies, adsorption has been preferred due to

its flexible operation and capabilities to generate high quality treated effluent as well as adsorbent by desorption. Several adsorbents such as agricultural wastes, carbon nanotubes, biosorbents, industrial byproducts, natural substances, and activated carbon have been studied for the heavy metal wastewater treatment. Numerous studies for the removal of heavy metal ions from water onto activated carbon are well known due to its high surface area and large micropore/mesopore volumes [1–4, 6, 11, 12, 24, 27–29, 34]. The production of activated carbons from abundantly available agricultural wastes converts unwanted, additional agricultural waste to useful valuable adsorbents. Adsorption capacity of natural materials for metal Pb^{2+} removal from water is shown in **Table 3**.

The activated carbon of agricultural wastes such as coconut coir pith, nutshells, oil palm waste, rice husk, and peanuts is used for the removal of lead metal from water [1–4, 6, 11, 12]. *Eucalyptus camaldulensis* Dehn. bark agricultural waste bagasse was studied for the removal of contaminants from water. Carbon nanotubes are relatively new adsorbents, which show great potential for the removal of heavy metal like lead ions from water. The adsorption of Pb^{2+} ions onto acidified multi-walled carbon nanotubes (MWCNTs) showed the removal capacity of 85 mg/g of adsorbent at NTP conditions [1–4, 6, 11, 12]. The carbon nanotubes (CNTs) that are used as effective adsorbents for Pb^{2+} adsorption at pH 5, contact time 80 min, and agitation speed 50 rpm were found to have maximum adsorption capacity of 102.04 mg/g. Agricultural waste materials that act as a potential adsorbent for sequestering heavy metal ions from aqueous solution were also investigated [5, 7, 8, 10, 23]. In addition, chemically modified plant wastes that act as low cost adsorbents for heavy metal uptake from contaminated water were also reported [25]. Finally, industrial byproducts such as lignin, diatomite, clino-pyrrhotite, aragonite shells, clay, and peat were used to remove Pb^{2+} from water [1, 25, 34]. However, the adsorption efficiency of such industrial wastes is pH dependent and better works only in the pH range from 2 to 6 (mostly acidic), while competitive sorption capacity falls relatively in multicomponent/metal systems.

Entry	Assorted adsorbents	Pb^{2+} adsorption capacity (mg/g)
1	Zeolite, clinoptilolite	1.6
2	Modified zeolite/MMZ	123
3	Clay (HCl-treated)	81.02
4	Poly(methoxyethyl)acrylamide-doped Clay	85.6
5	Calcinated phosphates	155
6	Activated phosphate	4.0
7	Zirconium phosphate	398
8	Almond shells	8.0
9	Palm shell oil	3.4
10	Maize cope and husk	456
11	Ecklonia maxima – marine alga	235
12	Oedogonium species	145
13	Nostoc species	93.5
14	Bacillus – bacterial biomass	467

Table 3.
Adsorption capacity of natural material for Pb^{2+} removal from water [24].

6. Selective adsorbents for lead remediation

Chitosan has an excellent adsorption capacity due to its low chemical and mechanical strength [1–4, 6, 11, 12]; its fullest adsorptive capacities are not met [5, 7, 8, 10]. Thus, several attempts of chitosan modification were carried out in previous research studies. In present research work, the materials namely graphite, iodate, and activated carbon of *Luffa cylindrica* are used for the modification of chitosan by blending/doping or impregnation method. The resultant adsorbents obtained are called graphite-doped chitosan composite (GDCC), iodate-doped chitosan composite (IDCC), and activated carbon of *Luffa cylindrica*-doped chitosan biocomposite (ACLFCS) [5, 7, 10]. The graphite has been selected for the study so as to check the adsorptive potential of chitosan-graphite composite and its prospective applications in wastewater treatment. The deacetylated amino groups in chitosan can be chemically modified easily [5, 7, 8, 10, 23]. Iodine molecule has a characteristic property of donating a new function to the host material. The iodate salt has been selected for modification of chitosan so that to find out whether the new surface chemistry of iodate-doped chitosan composite has an impact on Pb^{2+} removal from water or not. *Luffa cylindrica* is mainly a lignocellulosic material composed of cellulose, hemicelluloses, and lignin (60, 30, and 10% by weight, respectively) belonging to the Cucurbitaceae family.

Agricultural residues are abundant in a number of developing countries such as India, Korea, China, Central America, and Japan. Consequently, these disposed, unconventional, and widely available *Luffa cylindrica* fibers can be transformed into an activated carbon, which is a carbonaceous material that possesses highly developed porosity, a large surface area, relatively high mechanical strength, and a variety of functional groups on its surface [10, 34]. The transformation of agricultural residue into an activated carbon ultimately provides a way to reduce its environmental burden or hazards. The cationic nature of chitosan and the anionic nature of activated carbon of *Luffa cylindrica* can produce a stable, granular biocomposite due to two oppositely charged interactions. The purpose of doping of chitosan with *Luffa cylindrica* activated carbon is to explore the expected synergistic effects achieved through the incorporation of certain functionalities in the resultant biocomposite that could be responsible for the adsorption of Pb^{2+} . The choice of adsorbents for Pb^{2+} removal from water is concerned with its high adsorption efficiency, safety and simplicity for use, ease for maintaining, minimal production of residual mass, low capital cost, and nontoxicity. The synthesized adsorbents such as GDCC, IDCC, and ACLFCS satisfy all such requirements [24, 34]. To the best of our knowledge, there were no published reports on the removal of Pb^{2+} ions from water using GDCC, IDCC, and ACLFCS. In fact, the ability of above synthesized adsorbents to adsorb other heavy metal ions was also not reported. This provided a way for more adsorption studies for Pb^{2+} ions to be conducted by using these synthesized adsorbents. Batch adsorption of Pb^{2+} is studied as a function of various parameters, namely pH, agitation time, adsorbent doses, and initial Pb^{2+} concentration onto specially developed adsorbents like GDCC, IDCC, ACLFCS, raw chitosan, and activated carbon of *Luffa cylindrica* plant [1–4, 6]. Adsorption kinetics and isothermal studies are conducted to know the mechanism of batch adsorption of Pb^{2+} removal from water [1–4, 6, 10].

7. Case studies for Pb^{2+} removal

Chitosan is a natural nitrogenous amino polysaccharide found to be highly selective for the uptake of toxic heavy metal ions from contaminated water resources

[5, 7, 8, 10, 23, 24, 34]. Due to its adsorptive potentiality, it has been popularly used for environmental cleanup or for the mitigation of toxic heavy metal ions from water/wastewater. Despite of its variety of advantages, it possesses some major inadequacies that impose an urge for its modification so as to allow its better fit for the wastewater treatment applications. The present research work dealt with the modification of chitosan by various techniques such as blending, impregnating, and doping it with inorganic/organic materials, and the resultant biocomposites can be effectively utilized for the mitigation of toxic Pb^{2+} from water. This case study used synthesized chitosan-doped composites which were characterizations through advanced techniques like X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier transform infra-red spectroscopy (FTIR), elemental analysis, BET, and BJH pore size distribution for better understanding of adsorption mechanism.

The batch mode Pb^{2+} adsorption was studied as function of different operating parameters such as pH, adsorbent doses, initial Pb^{2+} concentration, and agitation/contact time. The adsorption isothermal studies were conducted by means of Langmuir and Freundlich models.

Adsorption kinetic studies conducted so as to know the time-dependent adsorption behavior of doped bioadsorbents toward the removal of Pb^{2+} from water. The adsorption kinetics revealed the existence of both heterogeneous surface and monolayer coverage of adsorbed Pb^{2+} ions via the pseudo-second-order kinetic process. Amid all biocomposites, iodate-doped composite bioadsorbent has been proved to be an effective adsorbent for the sorption of Pb^{2+} from water [5, 7, 8, 10, 33, 35]. An effective adsorbent dose of iodate-doped bioadsorbent was found to be 0.5 g/L with 99% efficiency achieved in 4 h [18].

The regeneration/desorption studies were done by desorption of exhausted adsorbents by means of several acid/alkali treatments, which provide the information about the respective utility of adsorbents in multifold cycles for batch mode adsorption of Pb^{2+} from water. Various studies demonstrated that the batch adsorption mode is used for the mitigation of Pb^{2+} from water using synthetically modified bioadsorbents namely raw chitosan (CS), GDCC, IDCC, ACLF, and ACLFCS [1–3, 7, 8, 18, 23, 29–31]. Chitosan-modified composites/biocomposites namely GDCC, IDCC, and ACLFCS were synthesized by means of impregnating/doping methodology [1–3, 7, 8, 18, 23, 24, 35]. Characterization studies of all synthesized chitosan composites/biocomposites were carried out by various instrumental techniques such as FTIR, TGA/DSC, XRD, BET surface area, BJH pore size distribution, SEM, and CHNS analysis. FTIR analysis of raw chitosan revealed that the absorption peaks are related to various functionalities namely $-\text{OH}$ group, $-\text{NH}_2$ bending in amide, and $\text{C}=\text{O}$ stretch in amide, and these functional groups were also responsible for Pb^{2+} ion adsorption onto the raw chitosan. Functional groups $-\text{OH}$, $\text{C}=\text{O}$, and $-\text{NH}_2$ were concerned with adsorption performance of Pb^{2+} onto GDCC [18, 24, 34].

Similarly, the functional groups $-\text{OH}$, $\text{C}=\text{O}$, $\text{C}-\text{N}$, iodate, and $-\text{NH}_2$ were responsible for Pb^{2+} adsorption onto IDCC. FTIR analysis of ACLF revealed that the absorption peaks are related to various functional groups namely $-\text{OH}$ group, aromatic $\text{C}-\text{H}$ stretch, aromatic $\text{C}=\text{C}$ stretch, and phenolic $\text{C}-\text{O}$ stretch [27–29]. The responsible and accurate sorption sites for Pb^{2+} adsorption onto synthesized adsorbents were ascertained by changes in FTIR band frequencies of assorted functional groups like $-\text{OH}$ and $-\text{C}=\text{O}$, NH_2 , and $-\text{NH}(\text{C}=\text{O})\text{CH}_3$.

TGA of raw chitosan showed two steps of degradation, initial with 5% weight loss and the second with 46.28% weight loss. At the end of 955°C , total weight loss of raw chitosan was 70%. TGA/DSC analysis of pure graphite showed high thermal stability and displayed only 2.5% weight loss at the end of temperature 955°C . TGA

of GDCC composite exhibited two steps of degradation, and at the end of 954.9°C, the total weight loss was found to be 35%. Thus, with respect to the raw chitosan, the GDCC showed more thermal stability. TGA/DSC analysis of IDCC indicated that this composite is less stable than raw chitosan [29, 30].

Thermogravimetric analysis (TGA) of ACLF revealed the high thermal stability where at the end of 910°C, it exhibited total weight loss of only 25%. XRD analysis of raw chitosan showed the broad diffraction peak at $2\theta = 20^\circ$. XRD pattern of GDCC exhibited that the peaks of both raw CS and powdered graphite indicated the formation of single-phase composite. The peaks were obtained at $2\theta = 26.5^\circ$ corresponding to graphite, and the broad peak at around $2\theta = 20^\circ$ that was due to the chitosan decreased in intensity in GDCC composite, which confirms that graphite is doped onto the surface of raw chitosan [7, 8, 18, 23].

In IDCC, the XRD pattern is slightly broaden and showed a small hump at $2\theta = 25^\circ$ and $2\theta = 34^\circ$. The XRD pattern of IDCC after Pb^{2+} adsorption showed some additional crystalline peaks at $2\theta = 30^\circ$ corresponding to Pb^{2+} ion adsorption. XRD analysis of ACLF showed the amorphous structure with two broad diffraction peaks at $2\theta = 24^\circ$ and $2\theta = 42^\circ$, which were the characteristic peaks of activated carbon. In ACLFCS biocomposite, the XRD pattern shows both the peaks of raw CS corresponding to $2\theta = 19.28^\circ$ and a small hump at $2\theta = 42^\circ$, which was a characteristic peak of ACLF [2]. The result indicates the successful doping and incorporation of ACLF with raw CS. SEM morphology of raw chitosan depicts uneven texture with bumpiness and porous cavities. SEM images of GDCC revealed flaky, smooth, shiny, and porous morphology with small amount of voids or cavities. SEM morphology of IDCC revealed that the bumpiness corresponding to raw chitosan was lost after doping it with iodate [2, 4, 7]. Similarly, in IDCC, the adsorbent surface was highly irregular and porous in nature with large number of round or elliptical shape cavities [7, 8, 18, 23]. SEM morphology of ACLF depicts the porous texture. ACLFCS possesses porous texture with round and elliptical shaped voids that can provide the adsorption sites to the adsorbate. SEM images of lead loaded adsorbent namely raw chitosan (CS), GDCC, IDCC, ACLF, and ACLFCS showed complete change of surface morphology [5, 7, 8, 10, 18, 23, 24, 34].

SEM image of lead loaded raw chitosan, IDCC, ACLF, and ACLFCS revealed surface morphology where the porous structure is quite shallow and not clearly seen.

The adsorption of Pb^{2+} by GDCC adsorbent showed deposition of whitish, sharp, needle-shaped crystalline mass observed onto its proactive surfaces [24]. The BET surface area of raw chitosan (CS), GDCC, IDCC, ACLF, and ACLFCS was found to be 9.923, 3.8, 6.984, 321, and 132 m^2/g , respectively [1–4, 6–8, 18, 23]. The further lower in surface area in IDCC and GDCC with respect to raw chitosan and ACLFCS with respect to ACLF is due to doping of iodate and activated carbon of *Luffa cylindrica*, respectively, with raw chitosan structure. BET surface area of doped chitosan composites namely GDCC, IDCC, and ACLFCS was decreased due to blockage of internal porosities of adsorbents [2, 7, 8, 18, 23]. Adsorptive capacity of adsorbent for the removal of Pb^{2+} from water found increasing with rising surface area as viable for pure physisorption phenomenon [1–3, 5, 7, 8, 10, 18, 23, 25].

The physisorption was the limited phenomenon, while the chemisorption mechanism was mainly observed for all the synthesized bioadsorbents used for Pb^{2+} removal from water [2, 5, 7, 8, 18, 23]. The batch adsorption of Pb^{2+} as a function of pH, doses of adsorbent, initial Pb^{2+} concentration, and contact time has been carried out by using raw CS, GDCC, IDCC, ACLF, and ACLFCS bioadsorbents [1–8, 18, 23]. Maximum adsorption capacity of raw chitosan was found to be at an optimum parameter of pH 6, with 35 mg/L Pb^{2+} ion concentration at an adsorbent dose of

0.9 g/L achieved in contact time of 140 min. By using GDCC adsorbent, the maximum 98% removal of Pb^{2+} was observed at optimum pH 6. Results showed that the maximum adsorbent capacity was at a dose of 1 g/L and equilibrium time achieved at 120 min of contact time for 35 mg/L Pb^{2+} ion concentration. The batch adsorption studies for Pb^{2+} removal from water by using IDCC revealed maximum removal at optimum pH 6 with an adsorbent dose of 0.5 g/L in contact time of 240 min. The regeneration ability of IDCC adsorbent demonstrated 25–30% decreased percentage recovery of Pb^{2+} ions at the end of fourth adsorption-desorption cycle. The maximum adsorption of Pb^{2+} onto ACLF was exhibited at an optimum parameter of pH 5.5, with an adsorbent dose of 0.3 g/L achieved in 12 min of contact time for 35 mg/L Pb^{2+} concentration [2, 7, 8, 18, 23]. Batch adsorption of Pb^{2+} using ACLFCS biocomposite was pH dependent, and maximum 98–99% Pb^{2+} removal occurred at pH 5 in contact time of 15 min and at an optimum dose of 0.1 g/L [2].

The percentage recoveries of metal ions decreased by 28% at the end of fifth adsorption-desorption cycle due to saturation of adsorbent-binding sites [2, 8, 24]. Equilibrium adsorption experiments for all the adsorbents were studied at room temperature and data obtained fitted to Langmuir and Freundlich adsorption isotherm [1–8, 10, 18, 23, 29–31]. The maximum adsorption capacity for raw CS, GDCC, IDCC, ACLF, and ACLFCS was obtained as 8.77, 6.711, 22.22, 101.01, and 111.11 mg/g, respectively [2, 7, 8, 18, 23, 24]. The adsorption kinetics was analyzed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models [7, 8, 18, 23]. The adsorption experimental data better fitted with pseudo-second-order kinetic model for all the adsorbents namely raw CS, GDCC, IDCC, ACLF, and ACLFCS [2, 7, 8, 18, 23, 24]. All these synthetically modified chitosan-doped composite/biocomposite has been proved to be effective and economic adsorbents for the adsorption of Pb^{2+} from water.

8. Conclusions

Various methodologies are being developed for the mitigation of Pb^{2+} from water/wastewater including chemical precipitation, electrochemical reduction, ion exchange, reverse osmosis, membrane separation, and adsorption. All such approaches being developed must be cheaper and more effective with the concern of reducing further/secondary waste generations besides boosting the quality of treatments. Physicochemical adsorption is the preferred treatments seeking for cheap, biocompatible adsorbents get intensified nowadays. A number of techniques have been chosen for the treatment of Pb^{2+} polluted water/wastewater; however, the selected one must focus on certain crucial parameters such as pH, initial Pb^{2+} ion concentration, efficiency, and overall output as compared to other existing technologies besides socioenvironmental impacts and economic parameters such as fund investment and functioning costs. Last but not the least, its technical applicability, plant simplicity, and low cost are also guiding factors that played vital roles in the selection of the most suitable treatments. All such factors are most effective for opting suitable treatment techniques so as to protect the nature/environment.

9. Futuristic research

Following recommendations are made for the future scope:

- the modification of synthesized chitosan-based biocomposite should be investigated by using other techniques such as sol gel and hydrothermal;

- synthesized chitosan-based bioadsorbents are investigated for the removal of other toxic heavy metal ions namely cobalt, mercury, zinc, copper, bismuth, cadmium, chromium, and arsenic;
- bioadsorbents can also be investigated for the adsorption of Pb^{2+} contaminated waters;
- the chitosan-based biocomposite modification can be investigated in order to increase its surface area for effective adsorption of pollutants;
- the competitive removal of Pb^{2+} from water in its combined presence with other toxic heavy metal ions can also be studied;
- batch mitigation of Pb^{2+} onto the synthesized adsorbents at various temperatures may be conducted so as to determine its thermodynamic parameters;
- shelf life of synthesized and regenerated adsorbents also anticipates for investigation; and
- column mode of Pb^{2+} removal from industrial wastewater as futuristic step.

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