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Adsorption of Pb(II) from wastewater by natural and synthetic adsorbents

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Abstract: Water pollution is a major concerned to the human health. Most of the global surface water is contaminated with heavy metals, has become a serious problem today. Particularly, Pb is highly toxic and directly associate with health risk such as damage to kidney, liver and central nervous system. In this review article, removal of lead utilizing various adsorption methods is described. Such as, *natural* (*e.g.* shells and peels corncobs, mushrooms, dairy manure, orange, apple, custard apple, peanut, eggshells, banana, eggplant, fish scales algae); *activated carbon* (*e.g.* sugar cane, orange peel, chicken feather fruit seed and bentonite); nano-composite, magnetic nanomaterials, polymer composite; chitosan, cellulose, clay, lignin, calcite, resin and chemicals are presented.

Keywords: Adsorption; Lead; Wastewater; Natural adsorbent; Nanomaterials.

1. Introduction

Most of the living organisms of earth including plants and animals need water. Although the surface of Earth dominates with water, however, the availability of potable water exhaust constantly and major challenge in this century [1-2], (Figure 1). Moreover, vast growth of populations and industrialization in 19th century followed non-sustainable approach while utilizing water sources and thus resulted in "*water pollution*" a popular term. Polluted water could be due to fungi, microbial pathogens and contamination of heavy metals [3-7]. Particularly, the metal salts such as As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, Tl and V are highly toxic and harmful to the living species including humans, aquatic animals and ecosystem [8-12]. Amongst them Pb is a highly toxic metal contaminant and directly dangerous to living organisms in damaging kidney and liver [13]. The maximum contaminant level as per United States Environmental Protection Agency (USEPA) is 0.006 mg/L, which is much more close to mercury.

Naturally occurring Pb minerals are thoroughly exploited in chemical industries, batteries, electroplating, mining, smelting, paint, pigments, dying, leaded glass and other industrial process, which releases a sufficient amount of Pb waste contaminated with soil and water. A few decades before, in 1970s lead was widely used as an additive in gasoline, which discharges 70% of lead in the environment with large concentration directly depositing on soil [14]. The United States Consumer Product Safety Commission banned lead as an additive component with immediate effect. The concentration of lead in these industries is higher than permissible discharge level, however, the later one may contain higher concentrations of lead (40.8 to 319.4 mg/L) [15]. In general, various technologies have been employed to remove heavy metals from contaminated water. Such as, chemical precipitation [16-17], ion exchange [18-19], adsorption [20-21], membrane filtration [22-23], reverse osmosis [24-25], solvent extraction [26], electrodialysis and electrochemical treatment [27-28]. Adsorption process has been attracted to many chemists due to simple design, low cost and no sludge formation over the other existing methods. In this context, there are few reviews clearly presented topics related to wastewater treatment [29-31].

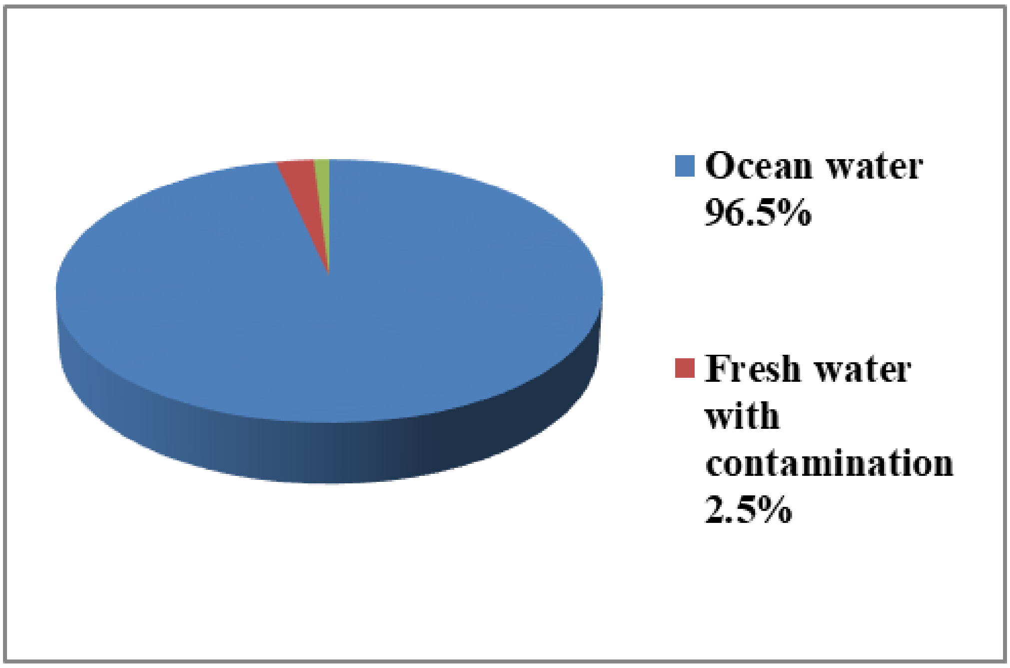


Figure 1. Water % on Earth.

In this review, the methods involving wastewater treatment for the removal of Pb^{+2} ions have been described. Most of the research carried out in developing water treatment method including natural, synthetic materials such as nano-composite, clay, lignin, etc. are presented in subsections of this article.

2. Results

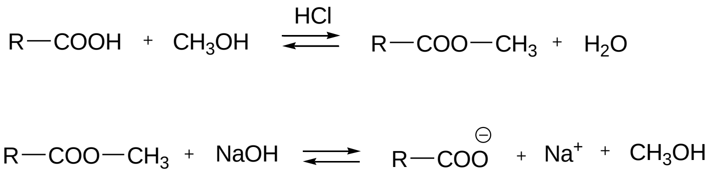
2.1. Methods for removal of Pb^{2+} ions.

2.1.1. Natural source for adsorption.

Nature produced adsorbing materials have been important in water purification due to their non-toxicity and easy availability. Moreover, the utilization of fruits, shells, seeds and other low-cost and waste materials have been implemented in water purification [32]. In this part of section we have focused on highlighting the natural material utilized in the removal of Pb^{2+} ions from water.

Xiao and coworkers developed corncobs as natural adsorbent in the removal of Pb^{+2} ions from wastewater [33]. The corncobs were processed to activate carboxylate ions (COO^-), which act as adsorbent of Pb ions via chelation. A corncobs-based carboxylate ion was prepared by esterification reaction (Scheme 1). Thus, powdered corncobs were dissolved in methanol (633 mL) followed by addition of HCl as catalyst (5.4 mL), [34-35] and this mixture was heated for 48 h at 333 K (Scheme 1). Then the obtained corncob-ester was hydrolyzed using sodium hydroxide to yield the corresponding carboxylate ions (COO^-) at room temperature. The formation of carboxylate ion was confirmed by FTIR, which showed a characteristic peak of

C=O at 1650–1600 cm^{-1} (instead of 1730 cm^{-1}) due to intermolecular hydrogen bonding [36-37]. In order to optimize the adsorption process, they performed various conditions, such as pH, contact time of adsorbent and different metal concentration. Optimized adsorption took place at pH 5, efficiently adsorbed 43.4 mg Pb/g within 60 min. Amongst the corncobs derived adsorbents, corncobs-carboxylate (-COOH) groups showed superior results than the corncobs-esters (-COOR).



Scheme 1. Preparation of carboxylate ion based corncobs.

Later, Vimla and coworkers reported removal of Pb ions by utilizing three different mushrooms as natural adsorbent, namely *oyster mushroom*, *button mushroom* and *milky mushroom* of species *Pleurotus platypus*, *Agaricus bisporus and Calocybe indica*, respectively [38]. Generally, the removal of metal ions is pH dependent. In this study, it was observed that pH 5 was most suited conditions along with the amount of mushroom loaded (4 g/L, 3 g/L 5.5 g/L) and their respective contact time (120, 240 and 180 minutes) to remove Pb^{+2} ions (Table 1). It is important to note that removal of Pb was enhanced with an increase in concentration of bio-adsorbent, due to availability of more adsorption sites, which was constant at 3-5.5 g/l.

Table 1. Mushroom based natural adsorbent.

Mushroom	pH	Lead concentration (mg/l)	Lead adsorption capacity (mg/g)
Pleurotus platypus	5	10-100	27.10
Agaricus bisporus	5	10-100	33.78
Calocybe indica	5	10-100	23.41

Zhang reported dairy manure compost as a natural and efficient biosorbent for the removal of heavy metals, which was found in simulated acid mine drainage [39]. The heavy metals such as Pb > Cu > Zn was investigated using this manure. Adsorption kinetics indicated that the heavy metal ions reached equilibrium within 60 min of adsorption process, indicating rapid adsorption rate. Maximum adsorption of Pb was observed at pH 3.5 and pH 4-5.5 for Cu and Zn, respectively. The author performed regeneration of adsorbed metals using ion exchange process. In order to find the ion exchange process and adsorption pattern, 300 mg of dairy manure compost was mixed with 20 mL of heavy metal solution (1 mmol/L) at pH 4.0 and the release of cations such as Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} and H^{+} was determined and Pb ions 0.113 meq/g adsorbed along with the compost. Regenerated dairy manure compost was efficient for at least three cycles without a significant decrease in adsorption capacity.

Guo and co-workers utilized another natural material; orange peel derived grafted copolymer as biosorption to remove Pb^{2+} in addition to Cd^{2+}, Ni^{2+}, [40]. The synthesis of grafted copolymerization-modified orange peel was carried out by employing Cu-catalyzed cross-linking of orange peel with methyl acrylate followed by hydrolysis of ester [41]. It was observed that the biosorption of grafted peel was 4.2 fold greater (476.1 mg g_{-1}) than the corresponding natural orange peel. Adsorbent peel was recycled and their reusability was also investigated, firstly adsorption and then desorption mechanism by using 0.05 mol L^{-1} HCl as eluent to check feasibility of adsorbent. Recycled adsorbent showed excellent adsorption capacity of Pb^{2+} ions for three consecutive cycles without any deterioration (Table 2). Furthermore, the Langmuir isotherm (equation 1) [42], revealed monolayer and homogeneous adsorbent surface with equal biosorption activation energy. On the other hand Freundlich isotherm (equation 2), [43] indicated multilayer and heterogeneous adsorbent surface with a non-uniform distribution of heat of biosorption.

$$\frac{Ce}{qe} = \frac{1}{q_{max}b} + \frac{Ce}{q_{max}} \quad \text{eq. 1}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{eq. 2}$$

Where, q_{max} = monolayer capacity of the biosorbent (mg g^{-1}); b = biosorption constant (L mg^{-1}); KF and 1/n = Freundlich isotherm constants.

Table 2. Recycled study of adsorbent.

Cycle	Amount of Pb before biosorption (mg L^{-1})	Amount of Pb after biosorption (mg L^{-1})	Biosorption (%)	Recovery (%)
1	50	4.0	92.0	96.7
2	50	3.9	92.2	96.5
3	50	4.2	91.6	95.0

Apple pomace as a natural adsorbent to remove Pb from wastewater has been reported by Pakde and coworkers [44]. The apple pomace was collected from Himachal Pradesh, India and dried at room temperature, crushed and sieved to 0.5 mm pore size. Such pomace contains poly-phenolic (–OH) and carbonyl (–C=O) functional groups, which directly form a coordinate bond with Pb^{+2} ions. In order to optimize adsorption process, a batch process was employed by studying various parameters such as pH, amount of adsorbent and time. Interestingly, the maximum adsorption was observed at pH 4 with the addition of 800 mg adsorbent to remove Pb^{+2} ions. This adsorption process was also investigated by kinetic experiment, it was found that the process follows pseudo-second-order. Langmuir and Freundlich isotherm resulted q_{max} value of 16.39 mg/g and K of 16.14 mg/g, respectively.

Sivakumar *et al*. have been chosen crush of custard apple fruit shell (*Annona squamosal*), as an efficient adsorbent to adsorb Pb^{+2} and Cd^{+2} ions from aqueous solution [45]. It is important to note that the adsorption of Pb ions completed within 30 minutes, 90.93 mg g^{-1} of maximum adsorption at pH 5. Langmuir and Freundlich isotherms revealed that the adsorption process followed pseudo-second order kinetics, spontaneous and endothermic thermodynamically (eq. 3).

$$q_e = \left(\frac{C_0 - C_1}{m}\right) V$$

$$\% \text{ of Removal of Pb(II)} = \frac{C_0 - C_1}{C_0} \text{ X } 100 \quad \text{eq. 3}$$

Where q_e = metal adsorbed (mg/g); C_0 = initial metal concentrations (mg/L); C_1 = final metal concentrations (mg/L); V = volume of solution; m = mass of the adsorbent (g)

Then, the research group of Tasar employed a peanut shell as adsorbent in removal of Pb^{+2} ions from aqueous solution [46]. Peanut shells are agricultural waste, that has been utilized as adsorbent. Shells were dried at ambient temperature then heated to 80 ^{o}C, and grounded to 30-50-mesh size. Furthermore, the powdered sample was analyzed using proximate and chemical analysis, BET, FTIR spectroscopy, which clearly indicated that the presence of hemicellulose, cellulose and lignin as a major component in peanut shell. When the powdered material was subjected for adsorption, it was observed that the maximum adsorption took place at pH 3.5–5.5 (33 mg/g), bioadsorbent 18.4-32.87 mg/g with 1-2 g/L concentration at 20 °C, respectively. Unlike the other reports, here, the peanut shells adsorption showed that the process thermodynamically exothermic and spontaneous. The author claimed that the peanut bio-adsorbent was associated with certain advantages such as low-cost and ecofriendly and could be better alternate over the existing methods.

Later, Bhatt *et al*. reported an extensive adsorption study on eggshells, banana peels and pumpkin to remove Pb^{+2} ions from wastewater [47]. These naturally occurring adsorbents were prepared by thoroughly washing with water followed by drying at 50 °C for 48 hours and further sieved to uniform particle size. In order to optimize the adsorption process, various parameters were investigated using stock solution of lead nitrate (1.598 g of $Pb(NO_3)_2$ dissolved in 1000 mL deionized water). The maximum adsorption was found at pH 7 with strong agitation (100 rpm) to mix natural adsorbent and Pb^{+2} for 90 min. Amongst these screened natural adsorbents, eggshells showed a good capacity to adsorb lead ions, probably negative ions on the surface of shells.

Recently, the research group of Ilavský, Barloková and Newcombe has been utilized Bayoxide E33, granular ferric hydroxide and CFH 0818 to adsorb As, Fe and Sb [48-49]. Inspired by this work, later; Biela *et al*. utilized similar adsorbent to treat Pb^{+2} ions from domestic water [50]. Adsorption study was conducted using Fe-based material; 97.0% adsorption of Pb^{+2} ions was achieved with Bayoxide E33 within 15 minutes. However, the other two adsorbents granular ferric hydroxide and CFH 0818 resulted in 96.1% and 95.3%, respectively. The amount of adsorbed ions was calculated using equation 4.

$$\eta = \frac{C_{RW} - C_F}{C_{RW}} \quad \text{eq. 4}$$

Where, η = contamination removal efficiency; CRW = concentration of contamination in raw water [$mg.l^{-1}$]; CF = concentration of contamination after filtering [$mg.l^{-1}$]

In another instance, Darvanjooghi and co-workers have chosen commercially available eggplant peels as a natural adsorbent to remove Pb^{2+} ions [51]. It is depicted in literature that the peel of eggplant contains cellulose, lignin, and hemicelluloses [52]. In order to prepare adsorbent firstly treated with acid (HCl) to remove lignin followed by base 1M NaOH [53]. During this process the ester in plant material hydrolysed to the corresponding carboxylate (–COOH) and alcohol (-OH) ions, which could be responsible for adsorbing Pb^{+2} ions. The formation of -COOH and –OH was confirmed by FTIR, in which characteristic peaks appeared at 1500 and 1800 cm^{-1} 1740 cm^{-1} and 1631 cm^{-1}. Then, the processed eggplant 100-1200 µm (0.2 g/L) was subjected to the batch adsorption study by using water sample with 70-ppm Pb^{+2} ions. It was concluded that the Pb ions adsorbed at pH> 4 and 25 °C in 110 minutes. The investigation of thermodynamic parameters such as temperature, equilibrium constant (K), standard- enthalpy, -entropy and -free energy changes revealed the reaction is pseudo-second-order kinetics.

Magsi and co-workers utilized fish scales to remove Pb and other transition metal ions such as Cd, Cr, Cu and As from water [54]. Detection of these heavy metals was performed by atomic absorption spectrophotometer. Bio-adsorbent was prepared by treating fish scales with 15% HNO_3 followed by drying and grinded to 140 mesh size. The obtained powder form of scale showed the presence of hydroxyl group (-OH), confirmed by FTIR. Batch adsorption process was conducted using column by maintaining flow rate 1 liter per 120 minutes, it was found that 20 g of powdered fish scale adsorbed 99% of Pb^{+2} ions from wastewater.

Very recently, Kumar *et al*. reported micro-algae biomass for the treatment of municipal wastewater using bioreactor [55]. Flouty and co-workers reported for the first time, application of algal mass in removal Pb^{+2} ions from the aqueous medium [56]. The algae cyanobacterium *Aphanizomenon ovalisporum* was isolated from the Litany River, Lebanon, which is also known to produce toxin *cylindrospermopsin* [57]. Furthermore, amine, phosphate, carboxyl and carbonyl functional groups were detected in FTIR analysis. Interestingly, the elemental analysis showed presence of C = 66.15%, N = 14.58% and O = 16.79%, respectively, however after adsorption the % of N and O substantially increased due to adsorption chelated metal ions. It was observed that the optimum conditions involved pH (7.5), time (75 min) and bioadsorbent cyanobacterium (0.7 g L–1), which is efficient in the removal of 87.59% of Pb^{+2} ions. Adsorption of metal ions (Cu and Pb) was determined using Taguchi's method [58-59]. Previously, Zolfaghari also utilized Taguchi's method in optimizing experimental conditions for adsorption of Pb^{+2} and Hg^{+2} ions, such method is advantageous due to low-cost, short time to study [60].

2.1.2. Carbon.

Abdelhafez and Li together developed sugar cane and orange peel as adsorbent material [61]. The pyrolysis of sugarcane and orange peel at 500 °C resulted in the corresponding carbon, which has been utilized in the removal of Pb^{+2} ions from aqueous medium. Characterization of carbon adsorbent was studied using Boehm titration, [62-63] and infrared spectroscopy. FTIR data obtained for samples showed presence of –COOH, -OH and –C=O groups, appearing characteristic peaks at 1637.27 cm^{-1}, 1384.85 cm^{-1} and 1101.43 cm^{-1}. Such functional groups chelated with Pb^{+2} ions during the course of adsorption process. Under the optimized conditions (pH 5, 25 °C) readily prepared carbons of sugar cane and orange peel adsorbed 86.96 mg/g (30 min) and 27.86 mg/g (15 min) of Pb^{+2} ions, respectively. In addition, they also investigated recycling of adsorbent using the desorption technique, thus the adsorbent was treated with 1M HNO_3. Mostly this method was effective for two cycles without any deterioration.

Fly ash is a by-product of coal combustion, which was sufficiently discarded in United States. Earlier, Nascimento, [64] Roman-Zamorano, [65] and Zheng, [66] has been studied conversion of fly ash into Zeolites or respective molecular sieves. Now, Brooks and coworkers reported alkali fly ash-based adsorbent to adsorb Pb ions using permeable reactive barriers [67]. Such a reactive barrier technique has been utilized for adsorption of Cd and Cr, respectively [68]. The carbon adsorbent was prepared by mixing fly ash and aluminum powder followed by additions of sodium hydroxide, sodium silicate and water, which was cooled to room temperature to produce different size pellets. Employing these pellets the adsorption study was conducted with water sample containing 1000 ppm of Pb^{+2} ions, interestingly, the process efficiently ions and reduced to 0.6 ppm. It is important to note that the Pb ion treated was very close to domestic water permissible limit of such metal contamination.

Jande and coworkers described activated carbon derived from chicken feather as adsorbent to remove Pb^{+2} ions [69]. The preparation of such activated carbon was performed by charring chicken feathers at 400 ºC in a horizontal tube furnace, followed by their treatment with KOH under nitrogen atmosphere. It is stated that the KOH treated carbon effectively enhance in surface area, which was determined Brunauer, Emmett and Teller (BET) surface area. For example, before KOH treatment carbon pore size was 642 $m^2 g^{-1}$ and after KOH treatment substantially increased to 1,642 $m^2 g^{-1}$ with pore size 3.2 to 3.8 nm. Activated carbon prepared at 800 °C, showed good adsorbent and 81% of Pb^{+2} ions was removed from $Pb(NO_3)_2$ solution.

Shrestha and coworkers have attempted the removal of Pb contaminated wastewater, using another type of activated carbon, generally, found in Nepal fruit seed *Lapsi* (*Choerospondias axillaris*) [70]. In order to prepare activated carbon as adsorbent, firstly Lapsi seeds were thoroughly washed with water then dried at room temperature and further crushed into powder form. After obtaining powder, it was separated into two forms based on their size. One part was treated with conc. H_2SO_4 and another part with 1:1 mixture of H_2SO_4: HNO_3, considered as carbon-1 and carbon-2, respectively. Characterization of these carbons was carried out by using Boehm titration method [71-72], and FTIR spectroscopy. It was observed that these carbons (1 and 2) obtained from lapsi seed showed presence of functional groups, such as carboxylic, lactonic, phenolic, which are probably responsible for adsorbing Pb^{+2} ions. The authors stated that the adsorption process is pH dependent and found that pH 5 was suitable to remove maximum Pb^{+2} ions. The kinetic study conducted using Langmuir and Freundlich adsorption isotherm, which indicated that Langmuir isotherm equilibrium was better than Freundlich isotherm.

Yarkandi reported that the American bentonite and activated carbon as adsorbent in the removal of Pb^{+2} ions from aqueous solution [73]. Amongst them, bentonite a naturally occurring material was efficient than activated carbon to adsorb Pb^{+2} ions from wastewater. It was also observed that initial adsorption of Pb^{+2} ions decreased with an increase in metal ion concentration. Performing an experiment using both materials further proved this phenomenon. Adsorption was carried out employing 100 mg/L Pb concentration and adsorbent dose was 0.5 g/250 mL at 25 °C. In case of activated carbon, a Pb^{+2} ion was efficiently adsorbed at pH 1-5.5, on the other hand, bentonite reduced efficiency up to pH 4. It is stated that the negative ions onsurface of the clay decrease at higher pH and thus affected adsorbtion of Pb^{+2} ions. Theoretical isotherm models such as Langmuir and Freundich has been analyzed and showed that the adsorption followed pseudo-second order kinetic path. The thermodynamic parameters such as $\Delta G°$, $\Delta S°$ and $\Delta H°$ for the adsorption process was found to be endothermic.

2.1.3. Nanomaterials.

Zahoor and coworkers reported magnetic carbon nanocomposites as adsorbent to remove Pb^{+2} and As, Cr, Cu, Pb, and Zn ions [74]. The nanocomposite was prepared from watermelon peel, which was treated with $FeCl_3.6H_2O$ (10% w/v) and alcohol for 24 h. Formation of nano-composite was characterized by various methods, for example FTIR showed typical peak appeared at 580 cm^{-1} and 400 cm^{-1} correspond to magnetite structure. Since the nano-composite associate with magnetic properties, the separation of adsorbent and metal smoothly took place. In addition their process efficiently adsorbed Pb^{+2} ions at pH 1-10, however, the decline was noted at higher pH.

Babu *et al*. reported another nano material approach for adsorption of Pb^{2+} ions along with Cd^{2+} and Cu^{2+} [75]. Preparation of chromium doped nickel nano oxide was carried out by mixing $(NiNO_2)_2 \cdot 6H_2O$, glycine and water. The resulting gel layer was then transferred to porcelain dish at 500 °C. The obtained powder was ground in a mortar and characterized by SEM and TEM, which showed 10 nm of nanoparticles. Under the optimized conditions adsorption of Pb^{2+} ions was investigated, which resulted 0.15 g of nanoparticles are efficiently adsorbed metal ions at pH 9 within 45 min. In addition with Langmuir and Freundlich isotherm, the other kinetic models such as, Dubinin- Radushkevich and Temkin isotherm revealed that the adsorption process follows pseudo-second-order kinetics.

Gusain and Ray together developed a molybdenum sulfide based multiwalled carbon nanocomposite as adsorbing material to remove Pb^{+2} ions from industrial wastewater [76]. In order to synthesize specified nano-composite it was performed three step sequence; (i) oxidation of pristine multi-walled carbon nanotubes using 3:1 mixture of H_2SO_4:HNO_3 (ii) oxidized nanotubes were then subjected to O-silylation using mercaptopropyltriethoxy silane and (iii) silylated nanotubes were treated with 1:1 (v/v) sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$): ethylenediaminetetraacetic acid (EDTA, >99) followed by addition of sodium diethyldithiocarbamate at pH 9, maintained by adding 1M NaOH. It is important to note that without molybdenum support only 27.07 mg g^{-1} of Pb^{+2} ions was adsorbed. On the other hand, the molybdenum based nano-composite efficiently adsorbed 90.0 mg g^{-1} of Pb^{+2} ions. Adsorption mechanism followed ion-exchange and electrostatic interactions of Pb ions with the surface of nano-composite and resulted in the formation of $PbMoO_{4-x}S_x$ complex. The formation of this complex was further ascertained by X-ray diffraction and scanning electron microscopy-energy dispersive spectrometry.

Queen *et al*. reported metal-organic frameworks based polymer composite as adsorbent in the removal of both Pb^{+2} and Hg^{+2} ions [77]. The metal Fe was utilized and framed with 1,3,5-benzenetricaboxylate employing Yoon's procedure [78], resulted in mesoporous and microporous sites of framework with 29 Å and 8.6 Å, respectively. Then this metal framework was subjected to the oxidation using dopamine to give redox active sites of Fe^{3+} (Figure 2) [79].

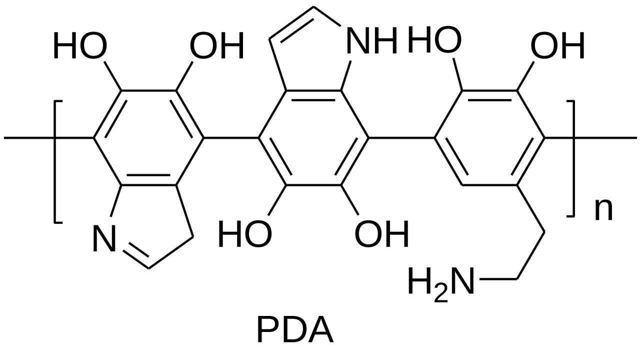
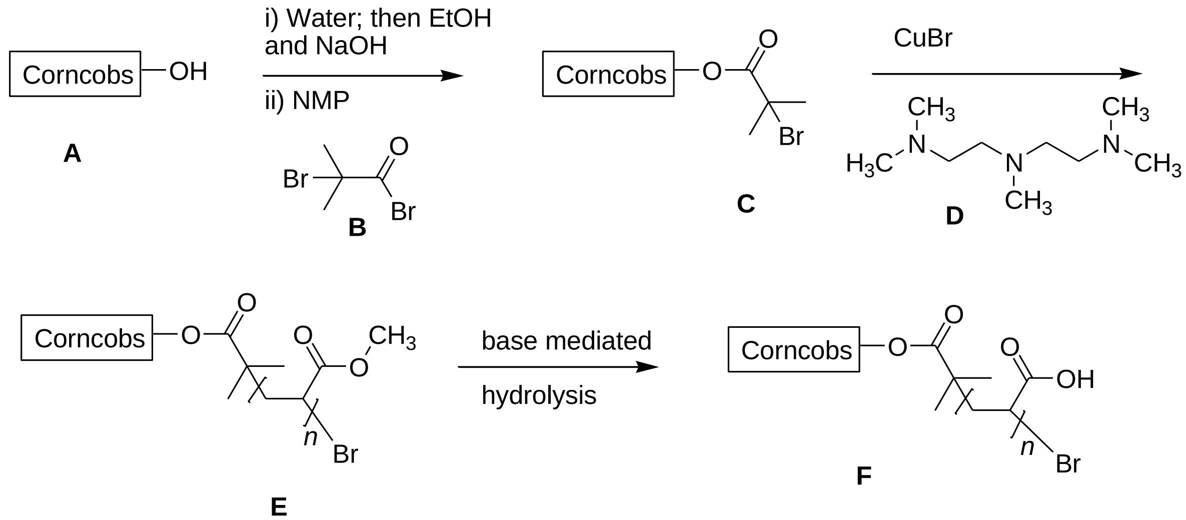


Figure 2. Metal–organic frameworks (MOFs).

Interestingly, the oxidation of metal followed by the formation of active sites of Fe^{3+} was noticed by changing color from orange to dark purple. Then, readily prepared polymer nano composite was tested for water sample contaminated with 1-ppm Pb^{+2} ions, which efficiently adsorbed 99.8% (394 mg/gram) under the optimized conditions. Encouraged by these results they extended the scope of this material to the water samples collected from river and sea, both were highly contaminated with Pb^{+2} ions in 850 and 1050 ppb, respectively. Notably, the nano composite was efficiently adsorbed 2.2 ppb of lead ions. Furthermore, it could be concluded that this polymer-based nano composite is highly selective in adsorbing Pb and Hg ions. This was proven by the investigation of a sample containing a high concentration of Na^+ (14000 times more than Pb^{+2}) ions, which was not adsorbed under these conditions.

2.1.4. Polymers.

Zhao and coworkers reported polymer based functionalized corncobs as adsorbent [80]. The preparation of polymer was achieved by atom transfer radical polymerization of Chinese based corncobs. Firstly, the corncob treated with water, then NaOH followed by addition of N-methyl-2-pyrrolidone.



Scheme 2. Functionalization of Corncob-supported acid and ester.

The resulting nucleophile was then treated with α-bromoisobutyryl bromide (**B**) to provide the corresponding bromo derivative (**C**). The obtained bromo derivative (**C**) was then subjected to the CuBr catalyzed grafting with N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) and methyl acrylate. In order to hydrolyse of ester moiety, the various base has been tested such as NaOH, DBU, LDA, DIPEA and *t*-BuOK, the best results were obtained with *t*-BuOK. Thus, the hydrolysis of ester (**E**) was carried out using *t*-BuOK at pH 7 resulted in the formation of carboxylic acid (**F**). The maximum adsorption of Pb^{+2} ions was observed 20gm/75 mL of wastewater. Success of grafting for ester (**E**) and acid (**F**) was calculated using equation 5 and 6, respectively.

$$\mathrm{GY}(\%) = \frac{\mathrm{m}_2 - \mathrm{m}_1}{\mathrm{m}_1} \text{ X } 100 \quad \text{eq. 5}$$

Where, GY(%) = yield of grafted polymer; m_1(g) = weight of dried bromo-substituted corncobs; m_2 (g) = weight of dried products after grafting

$$\mathrm{HY}(\%) = \frac{m_4}{m_3} \text{ X } 100 \quad \text{eq. 6}$$

Where, HY(%) = yield of hydrolysis product; m_3 (g) = weight of dry corncob acid (**F**); m_4 (g) = weight of dry corncob after hydrolysis, ester (**E**)

2.1.5. Chitosan.

Hu and coworkers described a novel method to remove Pb^{2+} ions from the aqueous solution [81]. Their protocol involved carboxymethyl chitosan-based adsorbent with magnetic properties (Figure 3). Adsorbent was prepared by mixing nano-sized ferroferric oxide and carboxymethyl chitosan, then subjected to cross coupling with glutaraldehyde at 60 ^{o}C (Figure 3).

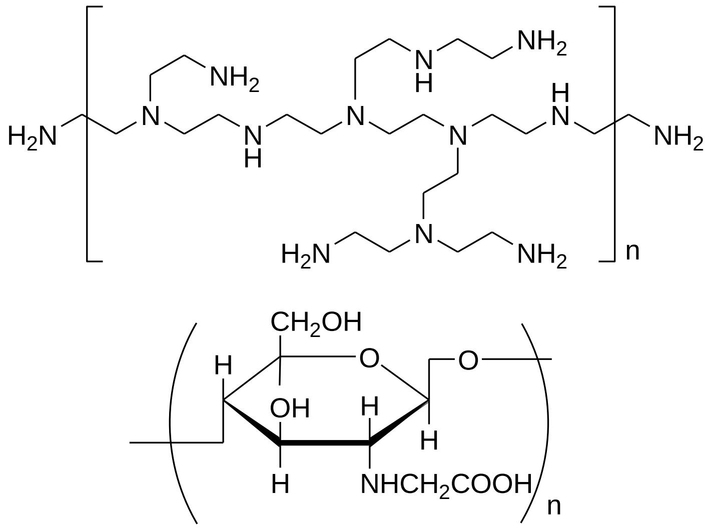


Figure 3. Chitosan based adsorbent.

The obtained material was then treated with 1-ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride, subsequently exposed to N-hydroxyl succinimide and polyethylenimine at pH 7-8 to provide the corresponding carboxymethyl chitosan. Characterization of these chitosan showed nanoparticles of 400 nm sizes. In order to investigate the adsorption study, the authors took a water sample contaminated with Pb^{+2} ions, it was found that 124.0 mg/g of Pb^{+2} ions has been adsorbed. Furthermore, the thermodynamic parameters, such as Langmuir, Freundlich and Elovich model revealed that the adsorption of Pb^{+2} was a spontaneous and exothermic process.

In an attempt, the efficiency of adsorbent was further confirmed by testing a water sample contaminated with Pb^{+2} ions in addition to K^+, Na^+, Ca^{2+} and Mg^{2+}. Notably, it was observed that the chitosan nanoparticles showed great affinity and selectively adsorbed only Pb^{+2} ions. The authors also investigated the regeneration of adsorbent by employing desorption mechanism using a mixture of EDTA:HCl:NaOH (0.1 mol/L). Regenerated adsorbent resulted in consistency for consecutive 5 cycles and removed up to 85% of Pb^{+2} ions at pH 4.5.

$$qt = (C_0 - C_1)\,X\,\frac{V}{m} \quad eq.7$$

Where, q_t = adsorption amount (mg/g); C_o and C_t = initial concentration of adsorbate (mg/L); V = volume of adsorbate solution (L); m = mass of adsorbents (g)

Elovich kinetic model

$$qt = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t \quad eq.8$$

Where, qt (mg/g) and qe (mg/g) are the adsorption capacities at time t (min) and equilibrium, respectively. k_1 (min^{-1}) and k_2 (g/(mg min) are the pseudo-first-order and pseudo-second-order rate constant, α (mg/(g min) and β (g/mg) represent the initial adsorption rate and desorption constant in Elovich model.

2.1.6. Cellulose.

Shiralipour *et al*. developed a dithizone-modified cellulose acetate nano-sponges as adsorbent to remove Pb^{+2} ions using batch process [82]. In this context the nano-sponges were prepared from cellulose acetate, which was processed from photographic film tapes. Firstly cellulose acetate was tested for adsorption study, which holds only 2.0% of Pb^{2+} ions from aqueous solution. Therefore, the cellulose acetate was then treated with alkyldimethyl benzylammonium chloride followed by diphenylthiocarbazone under basic medium. The resulted nano-sponges found 100 nm in size. Utilizing these nano-sponges, the adsorption study was conducted and it was found that 99.5% of Pb^{+2} ions were adsorbed within 6 seconds.

Later, they developed another strategy to remove Pb from wastewater, utilizing alkyl dimethyl benzylammonium-modified bagasse as adsorbent [83]. Bagasse is a waste-material in sugar industries and also readily available. Thus, bagasse was thoroughly washed with water and powdered to 70-mesh, then treated with 10% KOH solution to attain pH 7. The alkaline bagasse was subjected to alkylation using alkyl dimethylbenzyl ammoniumchloride and mixed with diphenylthiocarbazone to provide modified bagasse. Amongst the various screened parameters the best results were obtained within 10 minutes at pH 6-7, efficiently adsorbed >99.5% of Pb^{+2} ions at 25 °C. Since the adsorption was carried out in alkaline conditions, the Pb^{+2} ions converted to the corresponding hydroxide salt ($Pb(OH)_2$). Their study also includes reusability of bagasse-modified absorbent, which revealed that >95% of Pb^{+2} ions adsorbed consecutively for four cycles without any loss of activity.

2.1.7. Lignin.

Decades before, Srivastava [84], Demirbas and [85] Carrot [86], has been exploited lignin as adsorbent. Later, Zhang *et al*. utilized a lignin isolated from the paper industry as adsorbent to remove Pb^{+2} and other transition metal ions [87]. Such lignin showed the presence of functional groups, such as –OH, Ar-OH, -COOH, Ph-CH_2-O-, -OCH_3. In order to prepare adsorbent, a byproduct of wood pulp was isolated from the paper industry, then subjected to acidification at pH 2-3 using SO_2. This material efficiently removed 2–9.0 mg/g of Pb^{+2} ions from wastewater.

2.1.8. Clay.

Koyuncu and coworkers developed bentonite clay and the corresponding activated bentonite as adsorbent [88]. This clay material was obtained from Turkey. In order to activate bentonite, firstly it was refluxed with 5N HCl subsequently dried and powdered to 235-mesh. Both the screened clays and activated bentonite showed greater efficiency than the natural bentonite. In order to find the cation exchange capacity of these materials, a methylene blue test (ASTM C837-76) was performed, which showed 65 and 97 mequiv./100 g of efficiency, respectively. It was also found that the rate of adsorption was increased at higher temperature. Various kinetic models were considered, for example Lagergren, Weber, Morris and Ho's model, indicated adsorption follows pseudo-first order, pseudo-second-order and intra-particle diffusion model, respectively [89-90].

The kaolin is natural material with the presence of various metals, such as Al (21.58%), Fe (2.50%), Ca (3.05%), Na (1.35%), Mg (0.47%) and K (0.11%) and named as hard kaolin. Earlier, the research group of Ikhsan [91], Katsumata [92], Adebowale [93], and Sari [94], has been utilized as adsorbent to remove various heavy metals. Now, Li and coworkers drew inspiration from their work and developed Chinese kaolin-based adsorbent to remove Pb^{+2} ions [95]. The maximum adsorption of Pb^{+2} ions was found by exposing contaminated water and kaolin adsorbent for 16 h, efficiently adsorbed 165.11 mg g^{-1} at pH≥ 7.2 and 25 ◦C. On the other hand, the desorption process of Pb^{+2} ions resulted 85% of Pb ion separation by lowering the pH 2-3 with aq. NaOH.

Elouear *et al*. utilized naturally occurring phosphate rock as adsorbent to remove Pb^{+2} and other metal ions [96]. The phosphate rock and water samples are selected from Tunisia. In order to activate the phosphate rock, a phosphate ore sized between 200-500 μm was treated with 1M solutions of NaOH and HNO_3. Since the rate of adsorption depends on conditions, therefore authors screened various parameters. Amongst them, the maximum adsorption of Pb^{+2} ions was observed at pH 2-3 and higher temperature 283 to 313 K, respectively.

2.1.9. Calcite.

Aragonite and calcite are naturally occurring material in the form of razor clam shells and oyster shells, respectively has been exploited by Zhu and coworkers as adsorbent to remove Pb^{2+} and Cd, Zn ions [97]. These shells were collected from China. The adsorbent was processed by water treatment; drying and then pulverization to 20, 35, 60, 100, 200 and 400 mesh respectively. Both the materials calcite (oyster shell) and aragonite (razor clam shells) subjected to adsorption, amongst them the former act as better adsorbent due to crystal lattice. However, aragonite contains organic matter ultimately slows the adsorption rate. Adsorption medium showed 100% capacity to remove Pb^{+2} ions at pH 6.

The Sri Lankan soil is naturally acidic, quite similar to clay with 0.5 to 50 μm micropores and excellent cation-exchange capacity. Paranavithana and coworkers reported Sri Lankan soil and coconut shell biochar as adsorbent to remove Pb^{+2} ions [98]. The adsorbent material was prepared by mixing coconut shell (75 μm) with soil. Their study included coconut shell biochar, Sri Lankan soil and biochar-soil combination, which efficiently adsorbed Pb^{+2} ions in 63.6-92.5% (44.8–46.7 mmol/g), respectively at pH 3.

2.1.10 Membrane.

Earlier Jha [99] has been reported that cationic resin PS-EDTA and Amberlite IR120, respectively, to remove Pb from water. Kor and coworkers developed another protocol utilizing cationic resin Purolite S-930 to remove Pb^{+2} from domestic water [100]. This cationic resin was supported by co-polymer styrene-di-vinyl benzene containing imino-diacetic acid functional groups; these groups are responsible to trap alkaline earth and transition metals *via* chelation. In order to facilitate their study, adsorption of Pb^{+2} ions was performed on pilot plant. For this purpose a column 1.6-meter height filled with bed of resin 40 mesh size, efficiently 95.42% of Pb^{+2} ions have been removed at pH 6.5. Although, the study was monitored for 21 days in the form of continuous process; however, it was found that the level of sodium utilized during resin wash, detected above the permissible level 10 μg/L.

Ma and Sun together developed membrane-based adsorption of lead ions [101]. Such membrane was prepared from cellulose acetate and poly-(methacrylic acid) using electro-spinning technique. The developed electro-spun membrane showed excellent hydrogel layer with sufficient thickness, endowed excellent super-hydrophilic as compared with other conventional hydrogel adsorbents. Utilizing these properties maximum adsorption capacity of Pb^{+2} was 146.21 mg g^{-1}. Regeneration of the membrane was performed with higher pH and successfully employed for 5 consecutive cycles; the adsorption capacity was decreased to 58 mg g^{-1} due to saturation.

2.1.11. Chemical.

Karimi reported $Ca(OH)_2$ as adsorbent to remove Pb^{+2} from wastewater [102]. This study was carried out using a batch process and jar test equipment. The interaction of leaded wastewater and $Ca(OH)_2$ resulted in precipitation of solid, which was separated by simple filtration. The formation of precipitate was observed when different pH levels such as 3, 5, 7, 9 and 11 were mixed with 100, 200, 300, 400, 500 and 600 mg/L concentration of lead ions, higher the pH directly affect the efficiency of adsorption. The lead ions were detected on atomic absorption spectrophotometer. It was concluded that 95% of Pb^{+2} ions adsorbed at pH 11. However, they did not state about the water pH after the removal of lead ions.

3. Conclusions

Water is a global problem, since most of drinkable water is contaminated with fungi, heavy metals. Amongst the heavy metals, Pb is considered as highly toxic and very close to Hg. In order to remove Pb^{+2} from wastewater several effective methods have been employed. In this article we discussed recent developments for the removal of Pb^{+2} ions. Naturally occurring and synthetically modified materials have been presented in separate sections. Although such work is limited to small scale or pilot plant, however, their implementation for domestic purposes is limited. There is a great scope in developing new technology which will be low cost, ecofriendly and efficient in removing heavy metals.

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Conflicts of Interest

The authors declare no conflict of interest.

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