

Insights into the Recent Use of Modified Adsorbents in Removing Heavy Metal Ions from Aqueous Solution

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Received: 30.03.2021; Revised: 6.05.2021; Accepted: 10.05.2021; Published: 10.06.2021

Abstract: Natural water gets contaminated with heavy metal ions because of industrial effluents' discharge into the aquatic environment. As these heavy metal ions cause various health hazards, they should be removed from the aqueous solution. Heavy metal ion concentration in the aqueous solution is very less, so conventional metal removal and recovery processes cannot be applied here. The adsorption method is a great alternative to all these processes as it is a cost-effective and easy method. The use of natural, low-cost materials as adsorbents is eco-friendly also. However, metal uptake capacity of low-cost materials is very less. So, modification is required for low-cost materials to increase their efficiency. In the present review, different modification procedures adopted by different researchers have been discussed. Different low-cost materials used are sawdust, fruit and vegetable wastes, soil, minerals, etc. The modifying agents are heat, acids, bases, and other chemicals. Nevertheless, most of the studies are limited to batch tests only. Future research should be carried out on the extension of batch tests to column study for the large-scale treatment of contaminated water, and the cost of modification procedures and their impact on the environment should also be assessed.

Keywords: adsorbent; modification; modifying agents; low-cost materials; batch test; column study.

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1. Introduction

Water plays a major role in the survival of our lives. But this important natural resource is getting contaminated due to rapid industrialization and population growth [1]. When industrial wastewater is released into the environment, natural water gets contaminated with heavy metal ions. The wastewater of various industries such as pulp and paper mills, fertilizers, steelworks, metal plating, organic chemicals, aircraft plating, finishing, petroleum refineries, tanning, power plants, etc., contains heavy metal ions. These heavy metals exist as ions like Cu(II), Zn(II), Hg(II), Cd(II), Ag(I), Pb(II), Co(II), Ni(II), Cr(III)/Cr(VI), Fe(II)/Fe(III) in aqueous solution. These heavy metal ions cannot be degraded biologically and accumulate in various organisms through the food chain. These are toxic to living organisms, including human beings, and cause various health disorders like organs/nervous system damage, cancer, etc. [2,3]. The maximum contamination level (MCL) for different heavy metal ions in an aqueous solution has been fixed by the United States Environmental Protection Agency (USEPA) [4].

So, industrial wastewater should be appropriately treated before its release into the aqueous environment. Various treatment options are coagulation, ion-exchange, complexation, foam floatation, chemical precipitation, solvent extraction, electrochemical deposition, etc. For

the removal of low concentrated metal ions from the aqueous solution, these methods are expensive. So, adsorption technology can be a great alternative to all these methods as it has been proved to be economically favorable, and removal of low concentrated metal ions can also be possible due to its high selectivity and high efficiency [5].

The adsorption process surface of the adsorbent plays a major role in which atoms, ions/molecules known as adsorbate accumulate. The adsorption process is simple, cost-effective, and non-toxic. Researchers are also maintaining its popularity by increasing its environmental sustainability by choosing different natural, low-cost materials as adsorbents. Sawdust, pine bark, waste tea, coconut husk, groundnut hull, sugarcane bagasse, cassava peel or cassava roots, cashew nutshell, orange peel, clay, wool, etc., are some examples of natural, low-cost adsorbents [6-9]. However, the metal removal capability of these materials is low. These uptakes can be maximized by performing the processes at optimum conditions. Many researchers have also reported the remarkable improvement of various materials' uptake capacities after modifying their surfaces [10]. Therefore, the present work's main objective is to discuss the mechanism of different surface modification processes, different modification procedures adopted by different researchers, and the improvement in metal uptake capacity of some modified adsorbents when used for heavy metal ions removal.

2. Mechanism of Modification

The performance of an adsorbent depends on the physical and chemical properties of its surface. A good adsorbent is characterized by large surface area, minimum volume, high chemical and thermal stability, high mechanical strength, high porosity, small pore diameter. These factors lead to the high adsorption capacity of an adsorbent [11]. Surface modification is an act in which a material's physical, chemical, or biological characteristics are modified from its original form, leading to higher uptake capacity [12]. In modification procedures, surface impurities may be removed, producing physical and chemical changes. After modification of surface charge, surface energy, surface area, roughness, hydrophobicity, and functional groups, reactivity is improved [13]. Modification is mainly carried out by mechanical, thermal, or chemical processes. In the thermal process, porosity is developed, whereas surface area is increased in the chemical process. In the chemical modification process, the use of acid, alkali, or salts are involved and the surface functional groups are introduced or improved. Similarly, in the physical modification process, density and solubility increase. Surface modification can also be carried out using different methods, such as thermochemical or mechanochemical methods [14]. Chemical surface modification is better compared to the physical surface modification process. Because it is less time-consuming, and the material's surface chemistry is also influenced directly [15]. Chemical surface modifications also add some new surface properties [16]. After modification, an inexpensive material can be transformed into a valuable product with high adsorption capacity.

2.1. Acid modification.

It is the wet oxidation modification process. Acid modification is carried out using mineral acids and other oxidizing agents like HCl, H₂SO₄, HNO₃, H₃PO₄, H₂O₂, HClO, etc. [17]. After modification, the adsorbent surface becomes more acidic, and the adsorbent's hydrophilic nature also increases due to the reduction of mineral contents [18]. Acidification increases the polar oxygen-containing functional groups on the surface like carboxyl, quinone,

hydroxyl, carbonyl, carboxylic anhydride, nitro, and lactone, etc. [19]. It increases the negative charge properties of the adsorbent surface and increases the adsorption of positively charged pollutants. Acid treatment also introduces H^+ ions on the adsorbent surface. So, there is an increase in the adsorption of negatively charged pollutants [20]. The introduction of H_2SO_4 , HNO_3 , H_3PO_4 also increases the functional groups such as CN, NO, S, and P [21]. Treatment of activated carbon by HCl increases different surface oxygen complexes by which the reduction rate of Cr(VI) is increased [22]. HCl treatment of activated carbon also changes the surface morphology of the material by introducing different activating agents. Surface modification of coking coal by H_2SO_4 increases surface area, pore-volume, hydrophobic, lipophilic, zeta potential values [23]. After modification with acids, more acidic functional groups are introduced. The rising % of oxygen is resulted from increasing O/C and H/C molar ratios after H_2SO_4 treatment. When O/C and H/C ratios increase, there is a decrease in hydrophobicity. After treatment with HNO_3 , the pore walls are broken, and micropores are expanded into meso and macropores [24]. After acid treatment of brown alga, cylindrical pores are developed on its surface due to the release of trapped gases from the biomass, increasing the adsorption capacity [25]. The effect of organic acids is weaker because of their lower strength.

2.2. Alkaline modification.

Alkali treatment means the addition of NaOH, KOH, LiOH, Na_2SiO_3 , Na_2CO_3 , oxides. Alkaline modification is carried out by treating the adsorbent surface by reducing agents also. Due to this alkali treatment non-polar nature on the adsorbent surface is increased [26]. Alkali treatment also introduces a positive charge on the adsorbent surface to increase the adsorption of negatively charged adsorbate [18]. Treatment of NaOH on activated carbon reduces the functional groups containing oxygen. With the increase of alkali concentration, pore volume and the specific surface area also increase [27].

2.3. Modification by impregnation and organic solvents.

Impregnation is another type of adsorbent modification process in which uniform distribution of one type of chemical occurs on the porous adsorbent's internal surface. Metal impregnation is carried out by ferric chloride, zirconium, cerium, carbonates, hydroxides, nitrates, etc. [13]. After impregnation stability and regeneration of the adsorbent increase, the adsorbent's practical utility is also increased. While using Zr impregnated activated carbon, Rehman *et al.* observed that after impregnation, there is an increase of thermal stability, porosity and oxygen functionality [18]. Organic solvents like ethanol can also be used for the modification of adsorbent surfaces. They introduce some species onto the adsorbent surface so that their adsorption capacity increases. However, its practical application is limited because of its high cost, unsafe and unstable nature. Organic solvents introduce a large number of functional groups on the adsorbent surface [28].

2.4. Other modifying agents.

Apart from acidic and basic modifications of adsorbent surfaces, modifications are also carried out by other chemicals such as neutral solutions (NaCl, $ZnCl_2$), oxidants ($KMnO_4$, H_2O_2). According to Wang *et al.*, when wood biochar is treated with $KMnO_4$, its surface is covered by ultrafine particles of MnO_x containing more no of oxygen-bearing surface

functional groups leading to more surface area with much-improved metal uptake capacity towards Pb(II), Cd(II) and Cu(II) [29].

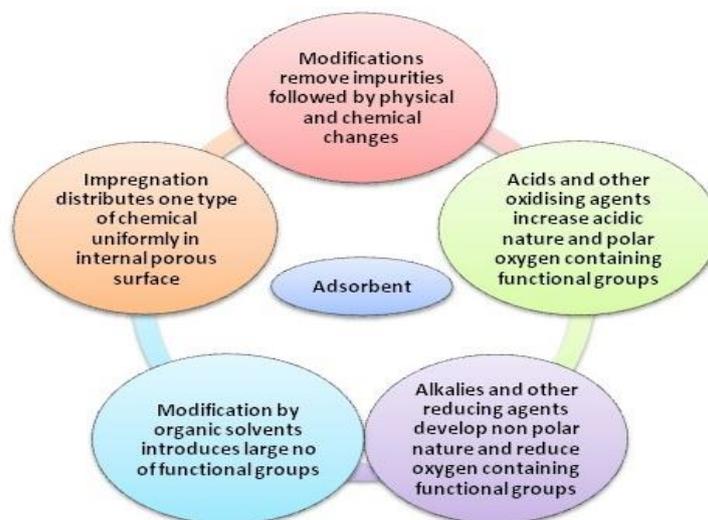


Figure 1. Effect of modifications on the adsorbent.

Different other chemicals have also been used for the modification processes by many researchers, and these are ethanol, acetone, chloroform, H₂O₂, polymerization, tetra ethylene glycol, diethyl ether, glycol, KCl, Fenton's reagent, hexadecyl trimethyl ammonium bromide, cetyl pyridinium chloride, n-heptyl benzyl alcohol, halloysite and sepiolite, carbon disulfide, citric acid, peroxy dehydroxide, maleic anhydride, etc. Some of these cases carried out for the removal of heavy metal ions are discussed below.

3. Use of Modified Adsorbents for Removal of Various Metal Ions

3.1. Cd(II).

Styrofoam waste was treated with sulphuric acid. The sulfonated form of that waste was thus formed for Cd (II) removal from an aqueous solution. The effect of the weight of the waste, sulphuric acid concentration, contact time, and temperature was observed for the sulfonation process, and the maximum sulfonation occurred with 18 M sulphuric acid, 60 °C, 6 h, and 5 g of styrofoam. The surface properties of the modified adsorbent were studied through SEM, XRD, and FTIR. The adsorption experiments were in batch-wise mode. The sulfonated form of styrofoam obeys the Langmuir isotherm model and pseudo-second-order kinetics. In contrast, unmodified styrofoam follows Freundlich isotherm and intraparticle diffusion mechanism. The Cd(II) uptakes on modified and unmodified forms of styrofoams were 51.6 and 7.09 mg/g, respectively [30]. Argun and Dursun [31] studied the modification of pine bark, a natural adsorbent with Fenton's reagent, and determined its Cd(II) removal capacity from an aqueous solution. The effect of Fe²⁺/H₂O₂ ratio, pH, and contact time on adsorption was studied. The reaction follows pseudo-first-order kinetics and Langmuir adsorption isotherm. The Langmuir monolayer adsorption capacity was 30.2 mg/g at 293 K temperature. The reaction was also found to be spontaneous and exothermic in natural conditions. The maximum Cd(II) removal (97 %) was achieved at pH - 7, contact time - 90 minutes, initial Cd(II) concentration-35 mg/L and solid:liquid ratio - 2.5 g/L. *Dendrocalamus strictus* (Bamboo) charcoal was prepared by carbonizing the properly cleaned pieces in a muffle furnace for 2 h at 450 °C. Then it was cooled, ground and 150 µm size was considered

to be unmodified adsorbent. Some part of this unmodified adsorbent was treated with 1 % nitrilotriacetic acid (NTA) to prepare modified adsorbent, i.e., NTA-modified *Dendrocalamus strictus* charcoal powder. The surfaces of both modified and unmodified forms of adsorbents were characterized by SEM, XRD, EDX, BET, and CHNS analyzer. Kinetic/isotherm interpretation of the data showed Langmuir and pseudo-second-order isotherm/kinetic models' suitability. Langmuir monolayer adsorption capacities were 142.85 and 166.66 mg/g for unmodified and modified adsorbents, respectively. Thermodynamic studies showed Cd(II) adsorption on both modified and unmodified forms of adsorbents to be endothermic and spontaneous. The modified and unmodified adsorbents could be regenerated using 0.5 % calcium chloride and 1 M sulphuric acid [32].

3.2. Cu(II).

Salihi and his team used raw sugarcane bagasse and microwave incinerated sugarcane bagasse ash (MISCBA) to remove Cu(II) from aqueous solution and compared the adsorption capacities of both. They found pH 6 and 3 hrs contact time is the optimum conditions for Cu(II) removal. Cu(II) uptake capacity of MISCBA was 38.84 mg/g whereas, that of raw sugarcane bagasse was 9.73 mg/g. Langmuir isotherm obeyed well compared to Freundlich for both the adsorbents [33]. Sabela and his team used activated carbon prepared from vegetable waste for Cu(II) removal from wastewater. The dried vegetable waste after KOH treatment for 24 h was calcined for 10 minutes at 800 °C temperature. The activated carbon thus prepared was washed with 1M HCl to remove excess KOH. The effect of adsorption conditions like pH, adsorbent/adsorbate doses, and contact time were studied in batch adsorption mode. The adsorbent surface was characterized by SEM, TGA, DSC, FTIR, etc. The Langmuir uptake capacity was 75 mg/g and is equivalent to the Cu(II) uptake capacity of other reported materials [34]. Saed and Jaleel [35] studied Cu(II) adsorption by using modified and non-modified can papyrus in both batch and continuous flow of adsorption. Can papyrus was modified by urea and thiourea. Cu(II) removal was 61 % for urea-modified cane, 68 % for thiourea-modified cane compared to 56 % for an unmodified cane. Yeet *al.* [36] studied the adsorption of Cu(II) on modified rice husk. The required amount of rice husk was treated with 3 M NaOH at 60 °C for 2 h to remove all silica. Then it was carbonized in the presence of N₂ for 45 minutes within the temperature range 400 to 650 °C. The activated carbon thus prepared was used for Cu(II) removal. The results showed that Langmuir monolayer adsorption capacity on modified rice husk at pH 7, 25 °C temperature and initial Cu(II) concentration 400 mg/L, was 43.5 mg/g. Both Langmuir and Freundlich isotherms suited well.

3.3. Cr(VI).

Banana peels grafted by acrylonitrile (GBPs) were used for Cr(VI) removal. Banana peels were treated with 10 % HCl and 10 % NaOH, bleached with sodium chlorate in the presence of H₂O₂ and glacial CH₃COOH. Then grafting co-polymerization of this bleached pulp was initiated with acrylonitrile in the presence of Fenton's reagent (Fe⁺²/H₂O₂). The optimum pH and contact time for Cr(VI) adsorption on this modified adsorbent were 3 and 120 minutes, respectively. The surface of the adsorbent GBPs was characterized. The adsorption followed both Freundlich and Langmuir isotherms. Langmuir's maximum adsorption capacity on GBPs was found to be 6.2 mg/g. Pseudo-second-order kinetics was obeyed well, and the adsorption was found to be spontaneous and exothermic. GBPs has been proved to be a low-

cost and efficient adsorbent for removing Cr(VI) [37]. Teff husk-activated carbon was used for Cr(VI) removal. 95.6 % Cr(VI) was removed at 1.92 pH, 87.83 mg/L initial Cr(VI) concentration, 2.07 h contact time and 20.22 g/L adsorbent dose. Langmuir isotherm and pseudo-second-order kinetics were obeyed well with Langmuir's maximum uptake capacity of 7.48 mg/g. The authors have planned to extend this small-scale batch adsorption study to a column study [38]. The newspaper waste was separated into pieces and treated with concentrated sodium bicarbonate solution to remove ink, bleaching material, i.e., chlorine dioxide and grease present in the newspaper. It was then refluxed with 5 % Na₂HPO₄ for 3 h using a condenser so that the phosphate's impregnation takes place into the cellulose matrix. After that, the solution was cooled and filtered through Whatman 40 filter paper. The treated waste newspaper (TWNP) was then used for Cr(VI) removal in batch mode. The optimum contact time was 60 minutes, whereas the optimum pH was 3. Langmuir isotherm fitted well with maximum Langmuir's uptake capacity of 59.88 mg/g. The said adsorption also obeyed pseudo-second-order kinetics and the rate constants were from 0.0019 to 0.0068 g/mg.min at an initial Cr(VI) concentration of 5 - 20 mg/L [39].

3.4. Co(II).

Co(II) from aqueous solution can be removed by chemically modified chitosan, i.e., chitosan vanillin (polymer 1) and chitosan ortho vanillin (polymer 2). At pH 4 and 2 h of contact time, maximum removal of Co(II) (93.2%) was achieved. Highest Co(II) uptakes for polymer 1 and 2 were 5.9 and 7.6 mg/g, respectively. The Co(II) uptakes by both of these polymers were spontaneous as well as endothermic in nature. The nature of the interaction between Co(II) and both of these polymers was found to be chemisorption [40]. Coir pith was modified chemically by esterification with succinic anhydride. Then it was activated by NaHCO₃ to get a suitable adsorbent for Co(II) removal. This chemical modification of the adsorbent improved maximum Co(II) loading, indicating more adsorption sites after modification. The adsorbent can be regenerated using 1N HCl. The adsorption data followed Langmuir and Freundlich's isotherms both. After modification Co(II) uptake increased from 12.82 to 34.13 mg/g [41]. The clearing nut (*Strychnos potatorum*) seed powder is a suitable adsorbent for Co(II) removal. It possesses C-N, C-O, and -OH surface functional groups and porous structure. Langmuir's maximum adsorption capacity was found to be 4.25 mg/g. Adsorption of Co(II) on the said adsorbent was spontaneous and exothermic by nature. From a 20 mg/L Co(II) solution, Co(II) uptake on unmodified and H₂SO₄ modified adsorbents CNSP were 1.825 and 2.838 mg/g, respectively [42]. The increase of adsorption capacity on modified adsorbent is due to the reduction of the adsorbent's organic content after acid treatment and more binding sites because of increased porosity.

3.5. Ni(II).

Coconut coir pith modified by H₂SO₄ can be a low-cost biosorbent to remove Ni(II) from an aqueous solution. Different adsorption parameters' effect on the said adsorption was also investigated. The maximum Ni(II) removal was achieved at pH - 6.0, initial Ni(II) concentration - 50 mg/L, and adsorbent dose - 2.0 g/L. Adsorption is endothermic. Langmuir isotherm fits well with the adsorption data, and Langmuir's monolayer uptake was 24.39 mg/g. Pseudo-first-order/second-order kinetics and thermodynamic parameters were evaluated [43]. Samarghandi and his team first decolorized sawdust with 1% formaldehyde, followed by

activation in a hot air oven for 24 h at 80 °C. Again the material was reactivated by H₂SO₄ for 24 h at 150 °C, followed by neutralization of the excess acid by NaHCO₃. The material thus prepared was dried in an oven for 24 h at 105 °C for the preparation of a modified adsorbent for Ni(II) removal. Maximum Ni(II) uptake (22.47 mg/g) was achieved at 7 pH. The removal efficiency increased with the increase of pH whereas, it decreased with the Ni(II) concentration. Langmuir was the better-suited isotherm whereas, pseudo-second-order kinetics obeyed well for the said adsorption [44]. Shah and his group have reviewed Ni(II) adsorption on chemically modified different agricultural wastes. Those are NaOH modified rice straw, walnut shell, hazelnut shell, peanut hulls, soybean hulls, sawdust, and acid-modified *Pouteria sapota* seeds, pine sawdust, *Ficus religiosa* (peepal) leaves, coconut husk, teak tree bark, and many more. Similarly, other modifying agents are ethanol, H₂O₂, mercaptoethanoic acid, formaldehyde, K₂CO₃, etc. Different other modified agricultural wastes were peat soil, cow dung, digested paddy husk, coir fibers, jute fiber, fluted pumpkin waste, etc. Ni(II) adsorption on all these modified agricultural wastes ranges from 3.37 to 101.01 mg/g. K₂CO₃ modified activated carbon prepared from waste apricot showed this highest Ni(II) uptake [45].

3.6. Zn(II).

A new low-cost adsorbent *Xanthocerasorbifoliabungehull* activated carbon (XSBLAC) was prepared by treating *Xanthocerasorbifoliabungehull* with H₃PO₄ followed by carbonization at 500 °C. The adsorbent was characterized based on N₂ adsorption-desorption isotherms, XRD, FTIR, SEM, and EDX etc. Langmuir's isotherm and pseudo-second-order kinetics suited well. Langmuir's maximum Zn(II) uptake was found to be 103.82 mg/g. Entropy, enthalpy, and free energy changes suggested the process to be spontaneous and endothermic. HNO₃ was found to be the best desorbing agent for this adsorption [46]. The barley straw, which is a waste of Polish agriculture, has been tried for Zn(II) removal. For the improvement of Zn(II) sorption capacity, two modifications have been tried. The first one is the modification by citric acid at a higher temperature, and the other one is the esterification of the straw by methanol. In the citric acid-modified biosorbent, there was an increase in Zn(II) uptake compared to the unmodified adsorbent. However, with the methanol modified one Zn(II) sorption was reduced to half of the sorption of that with unmodified sorbent. It was assumed that methanol-modified biosorbent followed an ion-exchange adsorption mechanism where Ca²⁺ and Mg²⁺ ions from the straw surface are released into the aqueous solution and compete with Zn(II) adsorption [47]. The potential application of a low-cost, plentifully available agricultural waste *Eucalyptus sheathiana* bark as adsorbent was tested for Zn(II) removal. The raw bark, as well as its NaOH modified form, was tried for Zn(II) removal. XRD, FTIR, BET, SEM-EDX of both the adsorbents were studied. From the kinetic studies, it has been observed that the process is rapid, multistep, and diffusion controlled in nature. Pseudo-second-order kinetics obeyed well for both the raw and modified adsorbents. Both Freundlich and Langmuir isotherms were obeyed for the modified and unmodified adsorbents. Langmuir's monolayer adsorption capacity on NaOH-treated *Eucalyptus sheathiana* was 250 mg/g. Different thermodynamic parameters suggested the process to be physical and spontaneous [48]. Microwave incinerated sugarcane bagasse ash (MISCBA) can be used to remove Zn(II) from wastewater. At low pH, competition between H⁺ and metal ion Zn(II) arises for the adsorption sites. The optimum pH for adsorption was 6, and the optimum contact time was 180 minutes.

The maximum Zn(II) uptake was 28.6 mg/g. The Zn(II) adsorption on MISCBA was found to be multilayer and chemisorptions in nature [49].

3.7. *Pb(II)*.

Maize tassel powder was refluxed in a fume cupboard for 4 h in the presence of 97 % H₂SO₄. To neutralize the excess acid, it was treated with 1 % NaHCO₃. Then it was washed several times, dried, and kept for use as an adsorbent. Thus, activated carbon prepared from maize tassel has been used for Pb(II) removal from an aqueous solution by Moyo and his team. The adsorbent surface was characterized, and the effect of different adsorption parameters was studied covering a wide range such as contact time (5 – 300 minutes), pH (2 – 12), Pb(II) concentration (10 – 50 mg/L), adsorbent dose (0.1 – 2.5 g). The optimum contact time and pH of adsorption were found to be 60 minutes and 5.4, respectively. Langmuir isotherm fitted better compared to Freundlich isotherm, and Langmuir adsorption capacity was 37.31 mg/g. The adsorbed Pb(II) can be recovered from the loaded adsorbent by HCl. The authors have expected that the activated carbon prepared from maize tassel can effectively be used for Pb(II) removal in wastewater treatment plants [50]. Natural zeolite modified by cobalt hexacyanoferrate(III) can be used as an adsorbent for Pb(II) removal. Pb(II) uptake was increased 1.8 times after modification. Before modification, it was 60 mg/g, whereas, after modification, it was improved to 100 mg/g at optimum condition. The optimum contact time for adsorption was 2 h, and the optimum pH was within the range of 3 to 6. Pb(II) removal attained a maximum of 90 % at an adsorbent dose of 2 g/L. The double exponential model explained the sorption kinetics, and the Langmuir model was the best-suited isotherm [51]. Algerian bentonite is a low-cost material, and after modification, it is proved to be a very good Pb(II) remover from the aqueous solution. The clay was modified with H₂SO₄, CaCl₂, and NaCl separately to get three modified adsorbents, such as acid-activated clay (HC10), calcium homoionic clay (CHC), and sodium homoionic clay (SHC), respectively. As in other adsorption studies, surface properties were evaluated after characterization (BET, XRD, FTIR, and chemical analysis). The effect of different adsorption parameters was also studied. Pseudo-second-order was the better-suited kinetics, and the Langmuir isotherm model fitted best compared to Freundlich and Temkin's model in all the cases. SHC was proved to be the best-modified clay as the Langmuir maximum uptake capacities were found to be 83.33, 76.9 and 23.8 mg/g for SHC, CHC, and HC10, respectively. All these adsorbents are more selective towards Pb(II) compared to Cu(II) [52].

3.8. *As and Hg*.

Arsenic (As) is considered a human carcinogen (group I) as it is highly toxic and found in soil, rocks, atmosphere, natural water, and organisms. The groundwater of more than 70 countries is contaminated with arsenic. So, As removal from polluted water is a great challenge today, The currently available techniques are costly and require a skilled workforce. So, the adsorption technique using natural, low-cost materials for removal and recovery of As from the aqueous solution has been given more priority. To increase the efficiency, these low-cost materials may be modified chemically. Asere and his coworkers have reviewed the topic "Arsenic removal by chemically modified natural adsorbents". Under these natural materials, rocks, clay, soil, hydroxylapatite and struvite, industrial wastes, biosorbents, and zeolites are included. These are modified either by heat, acid treatment, or by other chemicals. As arsenic

has a high affinity towards iron and aluminum oxides, natural materials treated with iron or/and aluminum oxide can be a very good adsorbent for As removal. Removing using biosorbents can reduce total treatment costs by more than 20 % compared to other conventional methods. Biosorbents also have low As removal capacity. Chemical modification of biosorbents also increases As removal capacity. Biosorbents like chitosan after chemical treatment show enhanced As removal capacity, and its mechanical strength and acid resistance also increase [53]. Mercury (Hg) is considered to be another most toxic heavy metal like As. Since the conventional treatment technologies are not practically feasible, Attari and his team have tested a low-cost material, i.e., a synthesized zeolite Linde Type A (LTA) from coal fly ash (CFA - ZA). Hg(II) removal on this CFA - ZA was 94 % from a 10 mg/L Hg(II) solution, and the result is comparable to that of commercial activated carbon. The equilibrium contact time was 120 minutes, and the adsorption was described well by Freundlich isotherm and pseudo-second-order kinetics [54].

3.9. Adsorption of multi-metal ions.

Two adsorbents, oxidized sugarcane bagasse and oxidized cellulose were prepared by treating sugarcane bagasse and cellulose with $\text{H}_3\text{PO}_4\text{-NaNO}_2$ mixture so that a large number of carboxylic groups are introduced on the adsorbent surface. These adsorbents were used to remove Cu(II) and Co(II) from the aqueous solution. Maximum Co(II) uptake on oxidized cellulose and oxidized sugar cane bagasse were 0.68 and 0.37 m mol/g, respectively, whereas Cu(II) uptake on the same was 1.20 and 0.57 m mol/g, respectively. Oxidized sugarcane bagasse was proved to be an effective biosorbent for large-scale use [55]. Cassava (*Manihotesculenta crantz*) roots and cassava peels processing residues were modified by H_2SO_4 , NaOH, and H_2O_2 to prepare suitable adsorbents for the removal of Cr(III), Cd(II), and Pb(II) from the polluted water. The effect of contact time, pH, adsorbent/adsorbate doses, and temperature were studied. The data were fitted to Freundlich, Langmuir, pseudo-first/second-order kinetics, and different thermodynamic parameters such as enthalpy, entropy, and free energy changes were calculated. The optimum contact time for removing all the 3 ions by the said adsorbents is 40 minutes. Langmuir isotherm obeyed well, indicating monolayer adsorption in all the cases. Maximum Cd(II) and Pb(II) uptake were observed for the NaOH modified adsorbents and were 19.54 and 42.46 mg/g, respectively, whereas maximum Cr(III) uptake was observed with H_2O_2 modified adsorbent and was found to be 43.97 mg/g. It has been proved to be an efficient, cost-effective, plentifully available, and renewable adsorbent to eliminate different metals from industrial wastewater [56]. To eliminate heavy metals from the aqueous solution, a green adsorbent was synthesized by treating glass waste hydrothermally followed by HCl's surface activation. This novel adsorbent was then characterized by BET, SEM, XRF, and XRD. Removal of Cu, Cd, Zn, Pb, and Fe was tested with the said adsorbent on batch experiments. The effect of different adsorption parameters, isotherms, and kinetic equations was tested for all the above-mentioned adsorption studies. Langmuir isotherm and pseudo-second-order kinetics were obeyed well in all the cases. 99 - 100 % removal of all the metals occurs at pH 7 and 2 h of contact time. This adsorption study was applied to healthy water for metal removal [57]. KCl chemically reactivated agricultural waste-activated carbon. It was then utilized to remove As(III) and Pb(II) from aqueous solution in batch methods. Effect of pH, contact time, temperature, and adsorbent/adsorbate doses were determined. The adsorbent surface was characterized based on BET, FTIR, XRD, and SEM-EDX. As(III) and

Pb(II) uptakes were 200 and 250 mg/g, respectively. The adsorption data were fitted best with the Langmuir model. Kinetics and thermodynamic studies conclude the process as pseudo-second-order, spontaneous, physical, and exothermic. As(III) and Pb(II) uptakes on this agricultural waste composite, activated carbon (AWCAC) was found to be comparable to the other reported adsorbents [58].

Figure 2(a) summarizes the preparation methods of modified adsorbents from different low-cost materials such as agricultural and household wastes, plant and animal wastes, soil, clay, ores, etc. Simple heat/acid/base/chemical treatments are used for modifications. In some cases, heat and chemicals are both used for modifications. Heat is applied first, followed by chemical treatment or vice versa. Figure 2(b) shows that after modifying the adsorbent surfaces, there is an improvement in surface area, adsorption capacity, mechanical strength, and acid resistance power. Before adsorption, the modified adsorbents' surface properties are evaluated by characterizing through XRD, BET, SEM, FTIR, EDX, etc. The adsorption processes for the removal of different metal ions by modified adsorbents in most of the cases are found to be spontaneous; it follows Langmuir isotherm and pseudo-second-order kinetics.

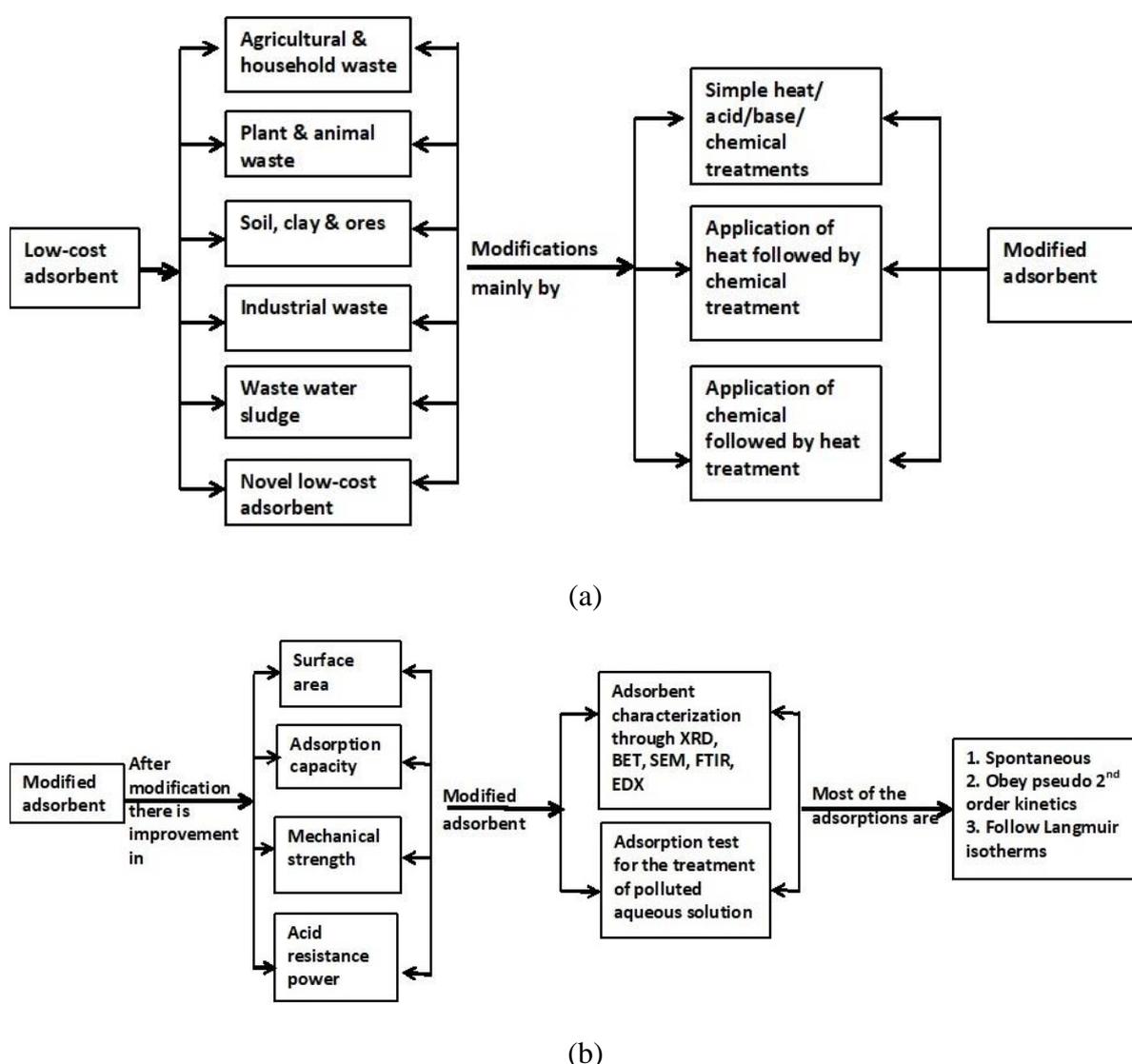


Figure 2. (a) Preparation methods of modified adsorbents out of different low-cost materials ; (b) Use of modified adsorbents in the adsorption studies.

After modifying the adsorbent, surface properties are developed, thereby increasing their metal uptake capacities. Some examples are highlighted below in Table 1.

Table 1. Use of some modified adsorbents for heavy metal removal along with their improvement in metal uptake capacities.

Sl. No	Low-cost natural material	Modifying agent	Metal contaminants	Improvement in metal uptake capacities	References
1	Wheat straw	Lactic acid	Pb(II)	Introduction of COOH and OH groups after modification. 79 % removal by raw wheat straw and 97 % by modified wheat straw.	[59]
2	Agricultural waste (Macademia activated carbon)	(i) H ₂ SO ₄	Cr(VI)	(i) Uptake was decreased from 22.3 to 9.66 mg/g after H ₂ SO ₄ treatment	[21]
		(ii) HNO ₃	Cr(VI)	(ii) Surface area increased from 545 to 824 m ² /g, and uptake capacity increased from 22.3 to 40.99 mg/g	
3	Activated carbon fiber	HNO ₃	As(III)	Uptake by raw and modified adsorbents was 2.06 to 2.98 mg/g, respectively	[60]
4	Onion skin	Thioglycolic acid (organic)	Pb(II)	Uptake by raw and modified adsorbents were 4.9 to 6.17 mg/g respectively	[61]
5	Pisha sandstone	NaCl	(i) Cd(II)	(i) Uptake improved from 8.2 to 65.9 % after modification	[62]
			(ii) Cu(II)	(ii) Na ⁺ is grafted onto PS after modification and uptake improved from 1.3 to 99.8 %	
6	Rice husk	NaOH	Cu(II)	48.841 mg/g Cu(II) uptake on the modified adsorbent. Due to modification, there are an increase in the intensity of OH, CH and C=O groups, which have high ionic exchange capacity	[63]
7	Saudi clay (i) Tabbuk clay	H ₂ O ₂	Co(II)	BET surface area increased from 1.478 to 1.488 m ² /g, and uptake improved from 3.94 to 12.9 mg/g	[64]
	(ii) Bahhah clay	NaCl	Co(II)	BET surface area increased from 0.3799 to 0.7809 m ² /g, and uptake improved from 3.44 to 12.55 mg/g	
8	Doum palm (<i>Hyphaene thebaica</i>) seed coats	(i) Physical activation by carbonization (300 °C, 1h)	Ni(II)	Uptake increases from 3.24 to 4.93 mg/g	[65]
		(ii) Soaking it in 28 % H ₃ PO ₄ for 24 h followed by carbonization in the absence of air (300 °C, 1 h)		Uptake increases from 3.24 to 13.51 mg/g	
9	Dead biomass of brown alga <i>Sargassum</i> sp.	0.1 N HCl	(i) Cd(II)	(i) Uptake increases from 2.31 to 2.89 mg/g	[25]
			(ii) Zn(II)	(ii) Uptake increases from 1.39 to 1.85 mg/g	
10	Sugarcane bagasse	(i) Heat treatment (550 °C, 30 min)	Hg(II)	(i) BET surface area increases from 5.21 to 182.69 m ² /g, pore volume increases from 0.002 to 0.081 cm ³ /g, and removal increases from 21 to 95%,	[66]
		(ii) Sugarcane bagasse treated with ZnCl ₂ followed by heat activation		(ii) BET surface area increases from 5.21 to 182.92 m ² /g, pore volume increases from 0.002 to 0.079 cm ³ /g, and removal increases from 21 to 85 %,	
		(ii) Treated with ZnCl ₂ followed by heat activation		(ii) BET surface area increases from 5.21 to 7.44 m ² /g, pore volume increases from 0.002 to 0.013 cm ³ /g, and removal increases from 21 to 88 %,	

3. Conclusions and Future Scope

The use of low-cost materials as adsorbents to eliminate metal ions from the aqueous environment is a cost-effective and eco-friendly method. After heat or, chemical treatments their surface properties are improved, increasing their sorption capacities. Modification of adsorbents increases their metal uptake capacities and increases their mechanical strength and acid resistance power. In almost all adsorption cases studied here, pseudo-second-order kinetics and Langmuir isotherm models were observed well. Thermodynamic studies also showed all the processes to be spontaneous. Till now, the use of modified adsorbents for heavy metal removal is limited to laboratory scale only. Therefore, further research is essential for understanding real adsorption mechanisms. The batch adsorption studies should be shifted to the column to treat real contaminated water on a large scale. Due to these chemical treatment methods, the treatment cost and environment are also affected. So, it is essential to assess the cost of chemical treatment and its environmental effect.

Funding

This research received no external funding.

Acknowledgments

The author thanks The President, Siksha 'O' Anusandhan (Deemed to be University), Bhubaneswar, for his kind permission to publish this paper.

Conflicts of Interest

The author declares no conflict of interest.

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