Review Article

Waste Material Adsorbents for Zinc Removal from Wastewater: A Comprehensive Review

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This review examines a variety of adsorbents and discusses mechanisms, modification methods, recovery and regeneration, and commercial applications. A summary of available researches has been composed by a wide range of potentially low-cost modified adsorbents including activated carbon, natural source adsorbents (clay, bentonite, zeolite, etc.), biosorbents (black gram husk, sugar-beet pectin gels, citrus peels, banana and orange peels, carrot residues, cassava waste, algae, algal, marine green macroalgae, etc.), and byproduct adsorbents (sawdust, lignin, rice husk, rice husk ash, coal fly ash, etc.). From the literature survey, different adsorbents were compared in terms of Zn^{2+} adsorption capacity; also Zn^{2+} adsorption capacity was compared with other metals adsorption. Thus, some of the highest adsorption capacities reported for Zn^{2+} are 168 mg/g powdered waste sludge, 128.8 mg/g dried marine green macroalgae, 73.2 mg/g lignin, 55.82 mg/g cassava waste, and 52.91 mg/g bentonite. Furthermore, modification of adsorbents can improve adsorption capacity. Regeneration cost is important, but if consumption of virgin adsorbent is reduced, then multiple economic, industrial, and environmental benefits can be gained. Finally, the main drawback of the already published Zn^{2+} adsorption researches is that their use is still in the laboratory stage mostly without scale-up, pilot studies, or commercialization.

1. Introduction

Water is a source of energy and life, although millions of people worldwide are suffering from the shortage of clean drinking and fresh water. Rapid pace of population expansion, industrialization, and unplanned urbanization have largely contributed to the severe water pollution and surrounding soils. Discharge of toxic industrial wastes and untreated sanitary, dumping of industrial effluent, and runoff from agricultural fields can be the main sources of freshwater pollution. It is well known that 70 to 80% of all illnesses in developing countries are related to water contamination, particularly susceptible children and women [1].

Contamination of aqueous environments by heavy metals is a worldwide environmental problem due to their toxic effects and accumulation through the food chain [2].

The major pollutants are heavy metals in ground, marine, industrial, and even treated wastewaters [3]. The presence of heavy metals in drinking water will be hazardous to consumers. Zn, Cd, Hg, Pb, Cr, Cu, and so forth can damage liver and nerves and block functional groups of vital enzymes and bones [4]. Metal ions in water can occur naturally from anthropogenic sources and from leaching of ore deposits, which mainly include solid waste disposal and industrial effluents. The levels of heavy metals in water system have substantially increased over time with rapid development of industrial activities [5].

Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems. However the metal ions are being added to the water stream at a much higher concentration than the prescribed limits by industrial activities, thus leading

to health hazards and environmental degradation (Table 1) [6]. In Malaysia, the discharge of heavy metals to the water bodies should be stipulated to the limits of standard A and B according to the Environmental Quality (Sewage and Industrial Effluents) Regulations, Environmental Quality Act 1974 [7].

However, high zinc can cause eminent health problems, such as stomach cramps, vomiting, skin irritations, anemia, and nausea [8]. Various methods are available to remove and isolate these heavy metals from water and wastewater such as ion-exchange, chemical precipitation, membrane filtration, adsorption, and electrochemical treatment technologies [9]. Adsorption is one of the safest, easiest, and most cost-effective methods because it is widely used in effluent treatment processes [10].

On the other hand, solid waste is offered in giant quantities or bound waste merchandise from agricultural operations. Other than that, industrial activities additionally leave behind an enormous quantity of solid waste within the variety of ash. Within the close future, additional increase within the quantity of those waste materials is anticipated to occur, particularly in Malaysia, where rising economies are expected to provide the biggest increase in energy consumption [11].

Therefore, an attempts are made to utilize waste materials as various adsorbents, particularly waste-derived siliceous materials. As a result of their low price, once these materials have been spent, they will be disposed of while regeneration is not expensive. In addition, cost is an important factor for comparing the sorbent materials. However, cost information is rarely reported, and the expense of each sorbent varies depending on local availability and the degree of processing required.

In general, an adsorbent is assumed as “low-cost” if it needs very little processing, is abundant in nature, or could be a byproduct or waste material from another business. As well, enhanced sorption capacity may reward the cost of additional processing. A summary of some of the literature follows reported adsorption capacities that are remarked when possible to give some idea of sorbent effectiveness.

In fact, this review paper provides an outline of a number of the literatures on utilization of low price adsorbents for zinc removal from contaminated water. The authors suggest that the provided review be taken as an example of adsorbents utilized in Zn^{2+} removal that may be examined beneath a particular set of conditions. Reported adsorption method is noted when there is potential to convey some plan of adsorbent effectiveness. However, the literature usually is not ready to report the full conditions and sufficient area is absent to include conditions here. The readers are requested to seek advice from the original articles for additional data on experimental conditions.

2. Current Wastewater Treatment Technologies

Many conventional methods for removal of metal ions from aqueous solutions include ion exchangers, chemical precipitation, chemical oxidation/reduction, electrodialysis, reverse

osmosis, and ultrafiltration [12]. However these conventional techniques have their own inherent limitations (Table 2) such as sensitive operating conditions, less efficiency, and production of secondary sludge and further the disposal is a costly affair [9, 13]. On the other hand, adsorption technology has gained high attention due to its advantages. Applied adsorption science is concerned since early ancient times. Some of the carbon materials such as charcoals were mostly used by few rare specialists [14].

The term adsorption relates to the accumulation of a substance at the interface between two phases such as liquid and solid or gas and solid. The substance which accumulates at the interface is called “adsorbate” and the solid on which adsorption occurs is adsorbent. As well, the adsorption technology has been widely used for the removal of solutes from solutions and gases from air atmosphere. At the solids surface, there are unbalanced forces of attraction which are responsible for adsorption. In cases where the adsorption is due to weak van der Waals forces, it is called physical adsorption. In addition, there may be a chemical bonding between adsorbent and adsorbate molecule and such type of adsorption is referred to as chemical adsorption [14].

In terms of heavy metals removal, adsorption by activated carbon is a popular technology for treating industrial and domestic wastewater [15]. However, the high cost of activated carbon and its loss during the regeneration restricts its application. Since 1990's the adsorption of heavy metal ions by low-cost renewable organic materials has gained momentum [16]. The utilization of moulds, seaweeds, yeasts, and other dead microbial biomass and agricultural waste materials for removal of heavy metals has been explored by Bai and Abraham [17].

Consequently, there is a growing requirement for efficient, novel, and cost-effective techniques for the remediation of metal bearing wastewaters before their discharge into the environment. Over the last two decades, biosorption is one approach which has shown considerable potential for metal removal from aqueous media; that is, the use of raw or natural materials and wastes from agricultural and industrial activities to adsorb metals from aqueous solutions [18].

In addition to that a number of studies have evaluated the application of adsorption for the removal of Zn^{2+} . These include the use of natural materials such as bagasse [19], moss [20], bentonite [21], and mixed mineral [22]; microbial and algal biomass including seaweed, yeast, fungi, and bacteria [23]; industrial and agricultural wastes such as corncobs, peanut hulls, hazelnut shells, corn-starch, waste tea leaves, sea nodule residue, blast furnace slag, sugar beet pulp, lignite, lignin, and powdered waste sludge [3, 16, 24–29]. Despite the relative simplicity and potential cost-effectiveness of adsorption, metal removal using low-cost adsorbents is relatively unproven and needs more development before it may be applied routinely in practice.

3. Chemically Modified Adsorbents

Adsorption as one of the physicochemical treatment processes was found to be effective in removing heavy metals

TABLE 1: Permissible limits and health effects of various toxic heavy metals.

Metal contaminant	Permissible limits for industrial effluent discharge (in mg/L) (DOE Malaysia, 1979) [7]	Permissible limits for drinking water (in mg/L) (WHO, 2011) [6]	Health hazards
	A	B	WHO
Arsenic	0.05	0.01	0.01
			Carcinogenic, producing liver tumors and skin and gastrointestinal effects
Mercury	0.005	0.05	0.006
			Corrosive to skin, eyes, and muscle membrane, dermatitis, anorexia, kidney damage, and severe muscle pain
Cadmium	0.01	0.02	0.003
			Carcinogenic, cause lung fibrosis, dyspnea, and weight loss
Lead	0.1	0.5	0.01
			Suspected carcinogen, loss of appetite, anemia, muscle and joint pains, diminishing IQ, cause sterility, kidney problem, and high blood pressure
Chromium	0.2	1	0.05
			Suspected human carcinogen, producing lung tumors, and allergic dermatitis
Nickel	0.2	1	0.07
			Causes chronic bronchitis, reduced lung function, cancer of lungs, and nasal sinus
Zinc	1	1	3
			Causes short-term illness called “metal fume fever” and restlessness
Copper	0.2	1	2
			Long term exposure causes irritation of nose, mouth, and eyes, headache, stomachache, dizziness, and diarrhea

TABLE 2: Comparison among wastewater treatment technologies.

Technique	Advantage	Disadvantage
Chemical precipitation	(i) Simplicity (ii) Inexpensive capital cost (iii) Adapted to treat high heavy metal ions concentration	(i) Ineffective when metal ion concentration is low (ii) Not economical (iii) Produce large amount of sludge
Ion-exchange	(i) Widely applied for heavy metal removal (ii) Ion-exchange resins can be regenerated	(i) Secondary pollution can be caused due to regeneration by chemical reagents (ii) Expensive when treating a large amount of wastewater so cannot be used at large scale
Membrane filtration	High heavy metal ions removal efficiency	(i) High cost and complex process. (ii) Membrane fouling has limited heavy metal removal
Coagulation-flocculation	Good sludge settling and dewatering characteristics	(i) It involves chemical consumption (ii) Increased sludge volume generation
Flotation	(i) High metal selectivity (ii) High removal efficiency (iii) High overflow rates (iv) Low detention periods	(i) High initial capital cost (ii) High maintenance and operation costs.
Electrochemical	(i) Regarded as rapid and well controlled which requires fewer chemicals (ii) Provide good reduction yields and produce less sludge	(i) Involving high initial capital investment (ii) Expensive electricity supply
Adsorption	(i) The high cost of AC limits its use in adsorption (ii) Many varieties of low-cost adsorbents have been developed and tested to remove heavy metal ions (iii) Biosorption is a relatively new process that has proven very promising for the removal of heavy metal from wastewater	(i) Removal of heavy metals from low wastewater concentration (ii) Adsorption efficiency depends on the type of adsorbents

from aqueous solutions. It was showed that an adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing, and is a byproduct of waste material from waste industry. Plant wastes are cheap as they have no or very low economic value [16]. Untreated plant wastes have received a wide attention of adsorption studies such as peanut hull pellets [30], papaya stem [31], rice husk ash, and neem bark [32] saltbush (*Atriplex canescens*) leaves [33]. Using plant wastes for wastewater treatment has some of the advantages such as simple technique, requiring little processing, adsorption of heavy metal ions, good adsorption capacity, selective, low-cost, and free availability, and easy regeneration.

The chemical modification of plant wastes as adsorbents can solve several problems such as low adsorption capacity, high chemical oxygen demand (COD), biological chemical demand (BOD), and total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials. The increase of the COD, BOD, and TOC can cause depletion of oxygen content in water and can threaten the aquatic life. Therefore, plant wastes need to be chemically treated or modified before being applied to the decontamination of heavy metals. Also, pretreatment of plant wastes can extract soluble organic compounds and enhance chelating efficiency [34].

Pretreatment methods using different kinds of modifying agents have been used such as base solutions (sodium

hydroxide, calcium hydroxide, and sodium carbonate), mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, and thioglycolic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, and methanol), oxidizing agent (hydrogen peroxide), and dye (Reactive Orange 13). For the purpose of removing soluble organic compounds, eliminating coloration of the aqueous solutions and increasing efficiency of metal adsorption have been performed by many researchers [35–38].

3.1. Activated Carbon. Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment throughout the world. Charcoal, the forerunner of modern activated carbon, has been recognized as the oldest adsorbent known in wastewater treatment. Activated carbon is produced by a process consisting of raw material dehydration and carbonization followed by activation. The product obtained is known as activated carbon and generally has a very porous structure with a large surface area ranging from 600 to 2000 m²/g [14]. Activated carbon has been found to be a versatile adsorbent, which can remove diverse types of pollutants such as metal ions [39].

In spite of better uses of activated carbon, its applications are sometimes restricted due to its higher cost. Therefore, researchers are looking for low-cost adsorbents for water

pollution control, where cost factors play a major role. As such, for quite some time, efforts have been directed towards developing low-cost alternative adsorbents. Low-cost alternative adsorbents can be prepared from a wide variety of raw materials, which are abundant and cheap, having high organic (carbon) content and low inorganic content and these can be easily activated [40].

Several advantages are shown due to preparation of low-cost adsorbents from waste materials, mainly of environmental nature and economic. A wide variety of low-cost adsorbents have been prepared from different waste materials utilizing agricultural wastes as well as industrial and municipal wastes. Although many studies have been shown so far discussing the importance of low-cost adsorbents in water pollution control, many of them are generally either adsorbate specific (metals, dyes, phenols, etc.) or adsorbent specific [41, 42].

3.2. Natural Source Adsorbents. The adsorption ability of clay is caused by a net negative charge on the structure of fine-grain silicate minerals. This negative charge is neutralized by the adsorption of positively charged species, giving clay the ability to attract and hold cations such as heavy metals. The large surface area of clays (up to 800 m²/g) also contributes to the high adsorption capacity [43]. There are three basic classes of clays: kaolinite, micas (such as illite), and smectites (e.g., montmorillonite). Of the three species, montmorillonite clays have the smallest crystals, the largest surface area, and the highest cation exchange capacity. Thus montmorillonite clays would be expected to have the highest adsorption capacity.

Gonzalez Pradas et al. [44] examined two types of modifications with natural bentonite, adsorbing Zn and Cd. Results showed that adsorption capacity decreased by using acid-treatment, while the heat treatment did improve capacity. Whether tailored or in their natural state, due to their abundance, low-cost, and adsorption capabilities, montmorillonite clays are a potential alternative to activated carbon for the adsorption of heavy metals. However, the low permeability of clays could require an artificial support for use in columns.

On the other hand, zeolite can be defined as aluminosilicates with Si/Al ratios between 1 and infinity. There are about 40 types of natural zeolite and over 100 synthetic zeolite, they are also considered as selective adsorbents. Zeolite based materials are extremely versatile and their main use includes ion-exchange resins (i.e., water softeners), detergent manufacture, separation process (i.e., molecular sieves), catalytic applications in the petroleum industry, and being an adsorbent for water, carbon dioxide, and hydrogen sulfide. Various zeolite adsorbents have been used for the removal of pollutants [45].

3.3. Biosorbents. Heavy metals biosorption from aqueous solutions is a relatively new process that has been verified as a very promising process in the removal of heavy metal contaminants. The major advantages of biosorption are the use of inexpensive biosorbents and its high effectiveness in

reducing the heavy metal ions. Biosorption processes are particularly suitable to treat dilute heavy metal wastewater. Typical biosorbents can be derived from three sources as follows [46]: (1) nonliving biomass such as bark, lignin, shrimp, krill, squid, and crab shell; (2) algal biomass; (3) microbial biomass, for example, bacteria, fungi, and yeast.

On the other hand, biosorbents process has been shown as repetitively used in cycles. The regeneration of adsorbent assents its reuse in further cycles and enables recovery of the adsorbed materials. Adsorbents regeneration can be done by specific methods which involve using chemical reagents. The metal-loaded papaya wood was completely desorbed with 0.1 M HCl. During repeated biosorption-desorption for five cycles, no loss in the efficiency of heavy metals removal from their respective solutions and the metal-loaded biomass was noted. The study points to the potential of a novel use of papaya wood itself, a cause of environmental degradation, and otherwise of no utility for the treatment of wastewaters contaminated with heavy metals [31].

The Zn⁺² ions were successively desorbed from *Botrytis cinerea* (*B. cinerea*) biomass using 10 mM HCl solution [23]. Desorption and reusability studies indicated that the biosorbent could be regenerated with up to 98% recovery and reused five times in biosorption-desorption cycles successively.

3.3.1. Agriculture Waste Adsorbents. There are different forms of inexpensive and non-living plant material such as black gram husk [47], eggshell [48], sugar-beet pectin gels [49] and citrus peels [50] are considered as a potential adsorbents. Adsorption of divalent heavy metal ions particularly Cu²⁺, Zn²⁺, Co²⁺, Ni²⁺, and Pb²⁺ onto acid and alkali treated banana and orange peels was performed by Annadurai et al. [51]. The authors reported that residues of banana and orange peels are cellulose-based wastes. Hence, they can be processed and converted to be adsorbents because they have large surface areas, high swelling capacities, and excellent mechanical strengths, are convenient to use, and have great potential to adsorb harmful contaminants such as heavy metals.

In addition, the acid and alkali solutions used for modification of adsorbents were HNO₃ and NaOH. Generally, the adsorption capacity decreases in the order of Pb²⁺ > Ni²⁺ > Zn²⁺ > Cu²⁺ > Co²⁺ for both adsorbents. Banana peel exhibits higher maximum adsorption capacity for heavy metals compared to orange peel. The reported maximum adsorption capacities were 7.97 (Pb²⁺), 6.88 (Ni²⁺), 5.80 (Zn²⁺), 4.75 (Cu²⁺), and 2.55 mg/g (Co²⁺) using banana peel and were 7.75 (Pb²⁺), 6.01 (Ni²⁺), 5.25 (Zn²⁺), 3.65 (Cu²⁺), and 1.82 mg/g (Co²⁺) using orange peel. Acid treated peels showed better adsorption capacities followed by alkali and water treated peels. Based on regeneration studies, it was reported that the peels could be used for two regenerations for removal and recovery of heavy metal ions.

Heavy metals such as Cr³⁺, Cu²⁺, and Zn²⁺ were able to be removed from wastewater using HCl treated carrot residues. Acid treatment was performed in order to remove resins, tannins, colored materials, and reducing sugars. According

to Nasernejad et al. [52], adsorption of metal ions onto carrot residues was possible due to the cation exchange properties of these residues which was attributed to the presence of carboxylic and phenolic functional groups, which exist in either the cellulosic matrix or in the materials associated with cellulose, such as hemicellulose and lignin. Based on kinetic study, more than 70% metal ions were removed in the first 10 min and equilibrium was achieved in 70 min. More metals were adsorbed at higher pH values of the solutions (pH 4 for Cr^{3+} and pH 5 for Cu^{2+} and Zn^{2+}). Maximum adsorption capacities were 45.09, 32.74, and 29.61 mg/g for Cr^{3+} , Cu^{2+} , and Zn^{2+} , respectively.

Chemically modified adsorbent could also be prepared by thiolation (a process of introducing-SH group) method.

Abia et al. [53] carried out an experiment of determining the optimal concentration of thioglycolic acid (HSCH_2COOH) for the removal of Cd^{2+} , Cu^{2+} , and Zn^{2+} ions by cassava waste. Cassava waste consists of ligands such as hydroxyl, sulfur, cyano, and amino which could bind heavy metal ions. It was noticed that adsorptivity of the cassava waste was greatly improved as the concentration of modifying agent (thioglycolic acid) was increased from 0.5 to 1.0 M due to the increase in sulfhydryl groups; $-\text{SH}$. Adsorption was reported to take place on the cell wall of the biomass. Optimum adsorptions of all three heavy metals were achieved in less than 30 min. The order of maximum adsorption capacity among the three heavy metal ions after treating cassava waste with 1.0 M thioglycolic acid is as follows: $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$. The authors however did not conduct a detailed experiment on the kinetic model of adsorption.

Horsfall Jr. and Abia [54] investigate the effect of modifying agent concentration on the adsorption of Zn^{2+} and Cd^{2+} ions onto thioglycolic acid for treating cassava waste. Cassava waste treated with 0.5 M and untreated adsorbent showed lowest removal of Cd^{2+} and Zn^{2+} ions compared to 1.0 M thioglycolic acid but the time to reach equilibrium remained similar for treated and untreated adsorbent. It was discovered that treated cassava waste sustains a much higher adsorption capacity for Zn^{2+} and Cd^{2+} ions compared to untreated sample. The adsorption capacities of treated cassava waste were reported to be 647.48 mg Cd/g and 559.74 mg Zn/g, as compared to only 86.68 mg Cd/g and 55.82 mg Zn/g when using untreated cassava waste.

The increase in adsorption capacity of Zn and Cd after acid treatment could be related to the formation of micro-porosity, which leads to enhanced thiol ($-\text{SH}$) groups on the adsorbent surface. The relative release of exchanging hydrogen atoms of the thiol groups with heavy metal ions results in improved level of adsorption. Desorption studies showed that untreated cassava waste showed better recovery of Zn^{2+} and Cd^{2+} . The authors suggest that the low recovery of heavy metal ions by acid treated cassava waste was due to enhancement in binding sites after acid treatment, which enables the metal ions to bind strongly to the adsorbent surface.

3.3.2. Biomass Adsorbents. Many biomass source adsorbents have been widely investigated as potential biosorbents for

heavy metals. Algae, a renewable natural biomass which proliferates ubiquitously and abundantly in the littoral zones of the world, have attracted the attention of many investigators as organisms to be tested and used as new adsorbents to adsorb metal ions. Several advantages in applying algae as biosorbent include the wide availability, low-cost, high metal sorption capacity, and reasonably regular quality [55].

There are a large number of research works on the metal biosorption using algal biomass. Examples of recent reports include the biosorption of Cu^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} using dried marine green macroalga (*Caulerpa lentillifera*) [56]. The biosorption of Cu^{2+} and Zn^{2+} by dried marine green macroalga (*C. linum*) was investigated by Ajjabi and Chouba [57]. At the optimum particle size (100 to 315 μm), biosorbent dosage (20 g/L), and initial solution pH 5, the dried alga produced maximum Cu^{2+} and Zn^{2+} uptake values of 1.46 and 1.97 mmol/g, respectively. Biosorbents were characteristic of broad sources, low-cost, and rapid adsorption. Unfavorably, these researches were still in the theoretic and experimental phase. Moreover, the separation of biosorbents would be difficult after adsorption.

3.4. Byproduct Adsorbents

3.4.1. Sawdust. Sawdust is obtained from wood industry as an abundant byproduct which is easily valid in the countryside at inexpensive price. It has been found that it contains several organic compounds (cellulose, lignin, and hemicellulose) with polyphenolic groups that could bind heavy metal ions through different mechanisms. Sciban et al. [58] studied the removal of heavy metal using sawdust. During the adsorption, the leaching of colored organic matters can be removed by pretreatments with formaldehyde in acidic medium, with sodium hydroxide solution after formaldehyde treatment, or with sodium hydroxide only.

In another experiment on the use of sawdust in the removal of Cu^{2+} and Zn^{2+} ions was reported by Sciban et al. [59]. Two types of sawdust, fir and poplar woods, were treated with NaOH (fiber swelling agent) and Na_2CO_3 solutions and the adsorption capacities were compared with the untreated sawdust. Both unmodified sawdust types of woods showed higher uptakes of Cu^{2+} ions than Zn^{2+} ions. Both types of sawdust record equivalent amounts of adsorption capacities for Zn^{2+} and Cu^{2+} ions, although it showed that these two adsorbents have different chemical compositions and anatomical structures. Increasing in adsorption capacity was observed after treating with NaOH for both heavy metal ions, especially for Zn^{2+} ions (2.5 times for Cu^{2+} and 15 times for Zn^{2+}). The adsorption capacities showed by Langmuir model were 15.83 mg/g (poplar sawdust) and 13.41 mg/g for Zn^{2+} (fir sawdust) and 6.92 mg/g (poplar sawdust) and 12.70 mg/g (fir sawdust) for Cu^{2+} , respectively.

3.4.2. Lignin. Srivastava et al. [60] studied adsorption of Pb and zinc (Zn) onto lignin. The lignin was extracted from black liquor, a waste product of the paper industry. Waste black liquor can be purchased for \$1.00/ton, and the lignin can be processed for approximately \$60/ton, as compared

to activated carbon at \$100/ton. The adsorption capacity for lignin at 30°C was found to be 1587 mg/g for Pb and 73 mg/g for Zn, which increased to 1865 and 95 mg/g, respectively, at 40°C. The high adsorption capacity of lignin is in part due to polyhydric phenols and other functional groups on the surface. Ion-exchange may also play a role in the adsorption of metals by lignin.

3.4.3. Rice Husk and Rice Husk Ash. Rice husk has good chemical stability, is insoluble in water, possesses a granular structure, and has high mechanical strength, which shows it is a good adsorbent material for removal of heavy metals from wastewater. Rice husk has been extensively reviewed by Chuah et al. [61] for heavy metals removal. Many heavy metal ions studied include Zn, Pb, Cd, Cu, Co, Au, and Ni. Rice husk in the form of either untreated or modified by different modification methods has been widely used to treat heavy metals. Sodium carbonate and hydrochloric acid [36], epichlorohydrin and sodium hydroxide [32], and tartaric acid are common chemical treatment methods of rice husk [62].

Rice husks pretreatment can remove hemicellulose and lignin, reduce cellulose crystallinity, and increase the surface area or porosity. In general, unmodified rice husk showed lower adsorption capacities on heavy metal ions than on treated or chemically modified rice husk. It was reported by Kumar and Bandyopadhyay [36] that rice husk treated with sodium carbonate, sodium hydroxide, and epichlorohydrin enhanced the adsorption capacity of heavy metal. Also it was reported that, for instance, interference with adsorption property might happen due to using the base treatment NaOH to remove base soluble materials on the rice husk surface.

Bhattacharya et al. [32] has studied rice husk ash with pretreatment for Zn^{+2} removals. It was found that 96.8% of Zn^{+2} removals were obtained at a pH value of 5. The Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data. Both of the models were fitted well. The adsorption capacity was obtained at 14.30 mg/g at optimum pH 5.0.

In another study by Montanher et al. [63], rice bran was evaluated for its potential use as an adsorbent for Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} . Rice bran adsorbent is able to successfully adsorb the metal ions from aqueous solutions. Maximum efficiency of 72% for Zn^{2+} removal was observed in chloride medium and NaCl 0.1 mol/L has been used throughout the work. The experimental data were well fitted to the Freundlich equation, with good correlation coefficients.

Two types of adsorbents made from rice husk by two different routes of preparation were examined by Daifullah et al. [64]. The efficiency of both sorbents in the removal of the complex matrix containing six heavy metals (Fe, Mn, Zn, Cu, Cd, and Pb) was $\approx 100\%$. These heavy metals are found in the drain containing the agriculture and sewage wastewater.

3.4.4. Coal Fly Ash. Since the industrial revolution which started in the 1920s a wide scale coal burning for power generation began. Although there were many millions of tons

of related byproducts and ash that have been generated, it was estimated that the current annual production of coal ash worldwide is around 600 million tons, with fly ash forming about 500 million tons at 75–80% of the total ash produced. Thus, the amount of fly ash as a coal waste released by thermal power plants and factories has been increasing throughout the world. Likewise, a serious environmental problem has become evident due to the disposal of the large quantities of fly ash. Nowadays utilization of ash on worldwide basis varied widely from a maximum of 57% to a minimum of 3%, so the world average amounts only to 16% of the total ash present. In fact, consumers companies are facing many utilizing problems due to the significant cost of the mostly amount of ash has disposed of in landfills or/and lagoons [65].

Gangoli et al. [66] reported the utilization of fly ash for the removal of heavy metals from industrial wastewaters. As a low-cost adsorbent, fly ash has been widely utilized for the removal of heavy metal. Among these metal ions Zn, Ni, Cu, Pb, As, Cr, Cd, and Hg are the most often investigated metals. As early as 1975, the use of fly ash for removal of heavy metals was reported. Bayat [67] investigated the removal of Zn^{2+} and Cd^{2+} and Zn^{2+} , Ni^{2+} , and Cu^{2+} [68], using lignite-based fly ash and activated carbon and discovered that fly ash was effective as activated carbon. The percent adsorption of Zn^{2+} and Cd^{2+} increased with an increase in concentration of Zn^{2+} and Cd^{2+} , dosage of fly ash, and temperature; maximum adsorption occurred in the pH range of 7.0–7.5. The effectiveness of fly ash as an adsorbent modified with increased calcium content (CaO).

Fly ash and fly ash/lime mixture were reported for removal of Zn, Ni, Cu, Cd, and Pb [69, 70]. The extent of removal was achieved in the order of $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. Due to formation of calcium silicate hydrates (CSH), metals removal efficiency may increase and desorption rate may decrease. Two fluidized-bed-sourced fly ashes were investigated by Rio et al. [71] with different chemical compositions; sulfocalcic fly ash and silicoaluminous fly ash were reported to remove Zn^{2+} , Cu^{2+} , Cr(III), Ni^{2+} , Pb^{2+} , and Cr(VI) from aqueous solutions. The percentage of ions removal was lower when they were treated with sulfocalcic fly ash than when treated with silicoaluminous fly ash, except in the case of the ion Ni^{2+} . Mercury is bound to the ash surface due to several chemical reactions between mercury and various oxides (silicon, aluminum, and calcium silicate), on the surface of the ash.

A series of investigations was conducted on the adsorption of heavy metals, using bagasse fly ash adsorbent. Bagasse fly ash from sugar industries was used for the removal of zinc and copper from aqueous solutions [72, 73]. Zinc and copper are adsorbed by the developed adsorbent up to 90 to 95% in column and batch experiments. The removal of Zn is 100% at low concentrations, whereas removal is 60 to 65% at higher concentrations. The removal decreases with increased temperature, suggesting that the process is exothermic in nature.

After the adsorption process, fly ash can be regenerated using certain reagents. Batabyal et al. [74] reported that

saturated fly ash can be regenerated using 2% of aqueous H_2O_2 solution. The regenerated fly ash was dried, cooled, and used for further adsorption. The adsorption rate and equilibrium time were the same as the fresh fly ash particles.

4. Adsorbents Application in Industrial Scale

Innovative processes for treating real industrial wastewater containing heavy metals often involve technologies for reduction of toxicity in order to meet effluents and technology-based treatment standards. Recently, there are a large number of adsorption studies on zinc removal, mostly from synthetic wastewater in a lab scale [75]. However, the potential of zinc adsorption remains great in wide range of industrial applications. Subsequently, selection and identification of an appropriate commercial adsorbent is one of the key issues for industrial applications [76]. A number of materials have been extensively investigated as adsorbents in water pollution control. Some of the commercial ones include silica gel, activated alumina, zeolites, and activated carbon [14].

Activated carbon is the most commercially used adsorbent material. The world demand for virgin activated carbon is forecasted to expand 5.2 percent per year through 2012 to 1.15 million metric tons. The consumption of activated carbons for industrial use has now become an indicator of development and environmental management efficiency. The per capita consumption of activated carbons per year is 0.5 kg in Japan, 0.4 kg in the United States, 0.2 kg in Europe, and 0.03 kg in the rest of the world [77]. In addition, natural zeolite was applied in full scale treatment plant for heavy metal removal from industrial effluents. The adsorbent was dosed in two separate tanks, in order to reach maximum removal efficiency [78].

Cost factor of commercial application of adsorption is another key issue and should not be ignored. Low production cost with higher removal efficiency of adsorbents would make the process economical and efficient. However, limited attempts for detailed economic and market analyses of scale-up (from lab to industry) are available [76]. As adsorption is applied in industry, modification of adsorbent is necessary for solid/liquid separation. Packed columns offer a potential configuration for industrial implementation, especially for the removal of Zn. Modified adsorbent beads can then be packed in sorption column, which is perhaps the most effective device for continuous operations [79].

In contrast, reactive filtration columns using natural adsorbent (Pine Bark) materials constitute a promising and suitable process for zinc remediation as a suitable alternative to the conventional sand porous media, due to their additional adsorptive. Ultimately, up to 95% of Zinc was removed during the first month of the operation [80]. At real-scale, heavy metal removal efficiency of 95% was also achieved in reactive filters using iron oxide [81].

Heavy metal removal from pharmaceutical industry and hospitals was conducted in a pilot scale using granular activated carbon. The pilot plant system consisted of two adsorbent columns in series. The GAC system removed 99.8% of the mercury from the wastewater. It was also effective in

removing 90% of copper. The treatment system was also effective for removal of turbidity (99%), color (99%), and phenols (96%) from the wastewater [82]. Ramísio and Vieira [83] have installed a dual-media adsorptive filter using kaolinite and sand adsorbents, and it consisted of two reservoirs and three columns. Adsorption of metals to filter materials has been studied using different heavy metal removals. Outputs data show that Zn is the most mobile metal with retention efficiency values decreasing to less than 50%.

Furthermore, a subsurface permeable reactive barrier (PRB) was used to remediate acid mine drainage in a shallow alluvial groundwater containing elevated concentrations of Zn, Pb, Cd, Cu, SO_4 , and NO_3 . The PRB was filled with 90 tons of reactive Apatite II (US Patent number 6,217,775), a biogenically precipitated apatite material that is derived from fish bones. The emplaced PRB has been operating successfully and has reduced the concentrations of Zn from 64.5 to 0.086 mg/L [84].

As compared to many commercial adsorbents, biosorbents have presented commercial potential and application feasibility in wide range of industrial applications. A considerable amount of research on biosorbent materials has developed a solid basis of knowledge and indicated their enormous potential [85]. The company Resource Management & Recovery offers commercial portable regimes for heavy metal removal from aqueous solutions. It consists of two columns each containing 7 L of the biosorbent. The company declares effluent treatment efficiency of 0.5 L/min and that it is possible to construct larger systems with 100 times higher treatment efficiency by implementing larger columns or adding additional columns to the system [86].

Mayes et al. [87] investigated the biosorption of Zn^{2+} from metal mine water using pelletised and recovered hydrous ferric oxide adsorbent. The treatment system consisted of baffled treatment tank filled with adsorbent media. At a low mean residence time of 49 mins, a mean treatment efficiency of 32% was achieved. United States Bureau of Mines (Golden, Colorado) produced the granular biofix, which has been tested extensively for the treatment of acid mine waste [88]. The results showed that the Zn binding to the biosorbent BIO-FIX is about 4-fold higher than the ion-exchange resins. The metal affinity was as follows: $Al^{3+} > Cd^{2+} > Zn^{2+} > Mn^{2+}$ and a much lower affinity for Mg^{2+} and Ca^{2+} .

The future aspects are clear. The main future target of market is to move the adsorption process to an industrial scale. It is relatively less difficult to demonstrate it in a laboratory; it is a little more challenging to demonstrate it at a pilot scale, but to really scale it up to a large scale would call for a significant financial and technological effort. This mismatch between scientific progress in adsorption research and stagnation in industrial technology innovation needs to be corrected through translational research and technology transfer with a push for commercialization of research.

5. Adsorbents Regenerations and Limitations

The adsorption process shows flexibility in design and operation and in many cases will produce high-quality treated

TABLE 3: Adsorption capacities of different adsorbents for the removal of Zn^{2+} from water.

Adsorbent	Zn^{+2} mg/L	Modifying agent(s)	Q_{max} mg/g	Source
Bagasse	200	Sulfuric acid	31.11	[19]
Moss	100	Distilled water	14.7	[20]
Bentonite	300	—	52.91	[95]
<i>Botrytis cinerea</i>	100	NaOH	12.98	[23]
Sea nodule residue	200	Hydrochloric acid	32.46	[24]
Powdered waste sludge	200	H_2O_2	168	[25]
Waste activated sludge	16	—	36.9	[26]
Sugar beet pulp	160	Deionized water	17.78	[27]
Papaya wood	10	Deionized water	13.64	[31]
Clarified sludge	25	Distilled water	15.53	
Rice husk ash		Distilled water	14.30	
Neem bark		Distilled water	13.29	[32]
Activated alumina		—	13.69	
Saltbush leaves	—	HCl	32.7	[33]
Natural zeolite	120	—	2.21	[45]
Black gram husk	10	Distilled water	33.81	[47]
Carrot residues	500	HCl	29.61	[52]
Cassava waste	—	Untreated	55.82	
		Thioglycollic acid + HNO_3	559.74	[54]
<i>Caulerpa lentillifera</i>	10	Tab water	2.66	[56]
Dried marine green macroalga	260	$CaCl_2$	128.8	[57]
Sawdust-oak	—	Unmodified	7.1	
Sawdust-oak	—	Formaldehyde	6.1	
Sawdust-oak	—	Formaldehyde + NaOH	9.3	
Sawdust-oak	—	NaOH	8.3	
Sawdust-black locust	—	Unmodified	5.2	[58]
Sawdust-black locust	—	Formaldehyde	5.3	
Sawdust-black locust	—	Formaldehyde + NaOH	9	
Sawdust-black locust	—	NaOH	6.7	
Sawdust-poplar	196	Unmodified	1	
Sawdust-fir	196	Unmodified	1	
Sawdust-poplar	130	NaOH	15.8	[59]
Sawdust-fir	40	NaOH	13.4	
Lignin	6.5	HCl + ether + benzene	73.2	[60]
Bagasse fly ash	50	Hydrogen peroxide	2.34	[72]
	850	Activated carbon (10°C)	24.06	
Bagasse	800	Activated carbon (25°C)	31.11	[19]
	775	Activated carbon (40°C)	54	
Coal fly ash		Unmodified (30–60°C)	6.5–13.3	
Fe impregnated fly ash		$Fe(Cl)_3$ (30–60°C)	7.5–15.5	[96]
Al impregnated fly ash		$Al(NO_3)_3$ (30–60°C)	7.0–15.4	
Rice husk ash + coal fly ash + palm oil fuel ash	15	Sol gel method	16.95	[97]

effluent. Choosy adsorption utilizing biological materials, mineral oxides, activated carbon, and polymer resins have generated much excitement among researchers, scientists, and environmental engineers [8]. After the adsorbents are exhausted, they are either to be disposed of or regenerated for use. This depends upon the demand, economics involved, and the kind of pollutant that was adsorbed.

Although adsorption is sometimes correctable, adsorbents can be regenerated by suitable desorption process. Furthermore, very few regeneration studies of adsorbents loaded with zinc are detailed in the literature [89–91]. Once zinc is recovered in the concentrated solution, the issue of how to dispose of this concentrated zinc product must be addressed. The metal ion attached on the adsorbent creates

disposal problem as it is hazardous matter. This problem may be controlled to some scope by using elution methods. The elution of the heavy metals provides recovery of the metal ions in the concentrated form and the regenerated adsorbents. The concentrated metal solution may be convenient for recovery of the metal. The regenerated adsorbent may be recycled for reuse and ultimately the adsorbents must be incinerated [92].

This is a difficult task; the limitation is low-cost and properties of the suggested adsorbents discourage significant investment in regeneration. Adsorbent regeneration may account for a large portion of operating costs. Also, adsorbent regeneration may cause secondary pollution. Under such circumstances, a feasible solution is proposed to dispose the adsorbent and its contaminations into a sanitary landfill. In many cases, spent adsorbents are to be treated as hazardous waste and need to be incinerated (which in many countries causes a set of environmental and societal problems) [93].

6. Comparison of Zn^{2+} Adsorption Capacity by Different Adsorbents

Adsorption capacity is the key-point of each adsorbent material. The adsorption capacity (mg/g) is the amount of the molecule adsorbed (the adsorbate) per unit mass of the adsorbent at a given gas-phase concentration under equilibrium conditions. It corresponds to one point on the adsorption isotherm [94]. The maximum adsorption capacities of different adsorbents for the removal of Zn^{2+} have been compared with extensive reports in the literature and the values of adsorption capacities have been shown in Table 3. Nevertheless, the maximum adsorption capacity ($Q_{\max}$ mg/g) is usually calculated from an adsorption isotherm equation, based on equilibrium data. Also, it was noticed that modification of the adsorbents can also improve Zn^{2+} adsorption capacity. The experimental data of the present enquiries are comparable with the reported values.

7. Conclusion

During this review article, an assay has been made to specialize in the recent developments associated with Zn^{2+} removal by low-cost adsorbents utilizing agriculture and agroindustrial wastes. It absolutely was demonstrated from the literature that utilization of waste materials as low-cost adsorbents for removing Zn^{2+} presents many enticing features particularly their contribution within the reduction of costs for waste disposal, hence promoting environmental protection. Also, adsorbents may be regenerated and recycled for reuse but may account a large portion of operating costs. Due to their low-cost, after these materials have been expended, they can be disposed of without expensive regeneration. The literature indicated that only limited references are available on industrial applications and only a few studies were reported. Furthermore, more studies should be carried out for Zn^{2+} removal in large scale.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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