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# Removal of Heavy Metals from Wastewater by Adsorption

*Athar Hussain, Sangeeta Madan and Richa Madan*

## Abstract

Adsorption processes are extensively used in wastewater treatment for heavy metal removal. The most widely used adsorbent is activated carbon giving the best of results but its high cost limits its use. It has a high cost of production and regeneration. As the world today faces a shortage of freshwater resources, it is inevitable to look for alternatives that lessen the burden on existing resources. Also, heavy metals are toxic even in trace concentrations, so an environmentally safe method of their removal necessitated the requirement of low cost adsorbents. Adsorption is a cost-effective technique and gained recognition due to its minimum waste disposal advantage. This chapter focuses on the process of adsorption and the types of adsorbent available today. It also encompasses the low-cost adsorbents ranging from agricultural waste to industrial waste explaining the adsorption reaction condition. The cost-effectiveness, technical applicability and easy availability of raw material with low negative impact on the system are the precursors in selecting the adsorbents. The novelty of the chapter lies in covering a wide range of adsorbents with their efficiency in removal of heavy metals from wastewater.

**Keywords:** adsorption, low-cost adsorbent, isotherm, wastewater, heavy metals

## 1. Introduction

Heavy metals are toxic elements having specific gravity greater than  $5\text{g/cm}^3$  e.g. Zn, Fe, Cu, Cr, Hg, Pb, Ni, Co, etc. [1]. The main natural sources of heavy metals include volcanic processes, weathering of rocks and soil erosion. While the anthropogenic sources include mineral processing, fuel combustion and industrial activities like mining, metal processing, chemical fertilizers and dye manufacturing etc. Heavy metals are non-biodegradable, recalcitrant and have high mobility in aqueous media, so they tend to accumulate in soils and living organisms leading to environmental repercussions. Heavy metals are taken up by plants which biomagnify through food chains in animals and humans causing serious negative health effects due to their carcinogenicity [2–5]. **Table 1** gives the maximum contaminant level (MCL) in drinking water given by USEPA [7] along with their harmful effects.

Heavy metals have a high tendency to form complexes, are highly reactive and have increased biochemical activity which makes them very persistent in the environment. They are transported through aqueous medium and can concentrate in soil and water resources. This makes them extremely dangerous to all kinds of life forms and the environment. Hence, it is necessary to remove these toxic metals

S.No.	Heavy Metal	MCL (mg/L)	Harmful effects
1.	Zn	0.80	Skin irritation, nausea, depression, anemia, neurological symptoms
2.	Hg	$3.0 \times 10^{-5}$	Neurotoxin, Kidney dysfunction, Circulatory & Neurological Disorder
3.	Pb	$6.0 \times 10^{-3}$	Central Nervous System Damage, Cerebral Disorders, Kidney, Liver Reproductive System Dysfunction
4.	Ni	0.20	Carcinogen, Dermatitis, Gastrointestinal Disorder, Lung, Kidney Damage
5.	Cu	0.25	Liver Damage, Convulsions, Insomnia
6.	Cr	0.05	Carcinogen, Nausea, Diarrhea
7.	Cd	0.01	Carcinogen, Kidney Dysfunction
8.	As	0.05	Skin Problems, Visceral Cancer

**Table 1.**  
*Harmful Effects of Heavy Metals [6]*

from wastewater before discharge to prevent further detrimental consequences. Conventional methods like membrane filtration [8–12], chemical precipitation [13–17], ion exchange [17–22], etc. have been used to remove of heavy metals from wastewater. However, these methods suffer from some disadvantages like low efficiency, high energy requirement, precipitation of toxic substances, cost ineffectiveness, etc. [3, 23]. To get past these demerits, processes like adsorption are investigated, since it greatly impacts the bioavailability and transport of toxic metals. It is low-cost and efficient technique for remediation of heavy metals from wastewater. Adsorption process is often reversible in many cases, so the adsorbent can be regenerated back adding another advantage to this process [24, 25]. Many factors such as temperature, pH, initial concentration, contact time and rotation speed affect the efficacy of adsorbents [23, 25].

### 1.1 Overview of adsorption process

Adsorption is a surface phenomenon in which a solution containing the adsorbate gets adsorbed on the surface of an adsorbent. Adsorption phenomenon can be of two types; one is physisorption, in which the adsorbate binds to adsorbent due to van der Waals forces, and other is chemisorption, which occurs due to chemical reactions between adsorbate and adsorbent. Physisorption is reversible, weak and is usually endothermic, while chemisorption is irreversible, selective and exothermic [26–28].

### 1.2 Adsorption isotherm and models

Adsorption isotherms are representations that estimate the amount the solute that is adsorbed on the surface of the adsorbent per unit weight as a function of equilibrium concentration at a constant temperature. The most commonly used are Langmuir and Freundlich isotherms that describe the adsorption process [29]. Some other models are also used such as Redlich and Peterson [30], Radke and Prausnitz [31], Sips [32], Toth [33] and Koble and Corrigan [34].

### **1.3 Types of adsorbents**

Adsorbents are typically classified on the basis of their origin i.e. natural and synthetic. Natural adsorbents include clays, minerals, charcoal, ores and zeolites. While the synthetic adsorbents are prepared from industrial wastes, agricultural wastes, waste sludge etc.

## **2. Removal of heavy metals from wastewater by adsorption**

Adsorption is presumed to be an efficient and cost-effective method as compared to other wastewater treatment technologies for heavy metal removal. The main advantage this method provides is the production of a high-quality effluent. The process of adsorption has an edge over other processes since it is an economic method for heavy metal remediation. In most cases, the adsorbent can be regenerated back and can be used further [35]. Adsorption is easy to use and does not generate any toxic pollutants, hence it is an environment friendly technique [36]. The prominent criteria of selection of adsorbents include their cost effectiveness, high surface area and porosity, distribution of functional groups and their polarity [37, 38]. Conventional and commercial adsorbents comprise of activated carbon [39–42], zeolites [43–46], graphenes and fullerenes [47–51] and carbon nanotubes [52–56]. Carbons and their derivatives are the most prominently used adsorbents due their great adsorption efficiency. Their exceptional ability comes from their structural characteristics giving them a large surface area with easy chemical modifications which makes them universally acceptable to a wide spectrum of pollutants [57]. The activated carbons suffer from a few flaws which makes their use quite limited. They are expensive to manufacture; the spent activated carbon is difficult to dispose and their regeneration is cumbersome and not economical. Thus, there was extensive research in the area of low-cost adsorbents. The non-conventional adsorbents are cheap, abundantly available and have great complexing capacity due to their varied structure which binds the pollutant ions. They range from agricultural waste to industrial waste sludge and spent slurry [58, 59].

### **2.1 Activated carbon adsorbents**

Activated carbon (AC) is one of the most widely used adsorbents due to its high efficiency, porosity and high surface area. It is commercially manufactured from the carbonization of like coal and wood, so it is expensive and its use is limited [24, 60–62]. They are mainly produced by pyrolysis of carbonaceous material at temperatures lower than 1000°C. The preparation of activated carbon involves two steps, one is the carbonization of raw material at temperature less than 800°C in inert atmosphere, second is activation of the produced product at temperature between 950°C and 1000°C [63]. Hence, most of the carbonaceous material can be used as raw material for activated carbon production, though the characteristics of the final product will rely on the raw material used and activated conditions [63]. Carbon is the main component of activated carbon adsorbent, other elements such as hydrogen, oxygen sulfur and nitrogen are also present. They are produced in both powdered and granular forms. The powdered one has large pores and smaller internal surface area; while the granular one has large internal area and small pores. The adsorptive capacity of an activated carbon is determined by its high porosity and surface area along with its chemical structure. Hence, other low cost raw materials

such as agricultural wastes are looked upon for increasing the cost effectiveness of activated carbon.

Kobyas studied adsorptive removal of  $\text{Cr}^{4+}$  from aqueous solutions by AC prepared from hazelnut shell and reached a maximum removal of 170mg/g at pH 1.0 [64]. This was found to be higher than other adsorbents like coconut shell and wood AC [65] which had a removal of 58.5 and 87.6mg/g respectively. Karthikeyan et al. studied removal of  $\text{Cr}^{6+}$  from wastewater using activated carbon prepared from wood saw dust. The adsorption capacity of  $\text{Cr}^{6+}$  reached a maximum at 44mg/g at an optimum pH 2.0 [66]. This was significantly higher than other adsorbents for instance coconut shell carbon [67], treated saw dust derived from Indian rose wood [68], coconut tree saw dust [69] and sugarcane bagasse [70]. In these studies, the maximum adsorption was found to be 10.88, 10, 3.60 and 13.40 mg/g respectively. Kongsuwan et al. used eucalyptus bark for preparation of AC in the adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  from low strength wastewater. The adsorption capacity for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  was maximum at was 0.45 and 0.53 mmol/g, respectively [71]. El-Ashtouky et al. studied  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  removal from aqueous solutions by AC prepared from pomegranate peel. Batch adsorption experiments were conducted as a function of adsorbent dosage, contact time and pH. The removal of both the metals reached a saturation at 120 min with optimum pH 5.8, 5.6 for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  [72]. Kavand et al. studied adsorptive removal of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  from aqueous solution using granulated activated carbon. The removal was in the order  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$  at an optimum pH of 2, adsorbent dose of 2g/L and contact time of 80 minutes [73]. Kim et al. conducted a study on the removal of  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cr}^{2+}$  from electroplating wastewater using powdered AC and modified powdered AC. A removal efficiency of around 90% was achieved for both the adsorbents at neutral pH [74].

## 2.2 Zeolites

They are aluminosilicates with a crystalline structure that occur naturally or are manufactured industrially. They are one of the best adsorbents for heavy metal removal as they consist of hydrated aluminosilicate minerals comprising of interlinked alumina and silica. Zeolites possess appreciable ion exchange capacities, hydrophilic properties and high specific surface area which makes them exceedingly good adsorbents for heavy metal remediation [75]. Zeolites can also be modified which attain a better adsorption capacity as compared to unmodified ones. NaX zeolite is one of the most widely used nanosized zeolite for removal of heavy metals from wastewater [76–79]. Rad et al. prepared NaX nanozeolite followed by polyvinylacetate polymer/NaX nanocomposite nanofibers to study removal of  $\text{Cd}^{2+}$ . The maximum adsorption capacity was reported to 838.7mg/g at pH 5.0 [79]. Javadian et al. used fly ash for preparation of amorphous zeolite and obtained a maximum adsorption capacity of 26.246mg/g for  $\text{Cd}^{2+}$  at 5 optimum pH [80]. Similar studies were conducted by Visa who reported that zeolites have a high surface area and porosity which aid in adsorption of heavy metals [81]. Kobayashi et al. studied removal of  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  from aqueous solutions using zeolites prepared from fly ash. The maximum amount of  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  adsorbed were 22.4 mg/g and 30.7mg/g respectively at optimum pH of 5 [82].

## 2.3 Clay minerals

Bentonite, a clay mineral holds the highest cation exchange capacity, is regenerable and around 20 times cheaper than activated carbon [83, 84]. Clay minerals have less removal capacity of heavy metals when compared to zeolites. But they are still used owing to their advantages such as brilliant physical, chemical and

surface properties [84–87]. Jiang et al. studied removal of  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  from wastewater using kaolinite clay and it was found that concentration of  $\text{Pb}^{2+}$  decreased from 160.00 to 8.00 mg/L [88]. Bertagnolli et al. conducted a study on bentonite clay for removal of  $\text{Cu}^{2+}$  and achieved a maximum adsorption capacity of 11.89mg/g [89]. Chai et al. conducted a study using raw kaolinite and acid activated kaolinite for the removal of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  from aqueous solutions and cemetery wastewater. The raw kaolinite adsorbed 69.23%  $\text{Cu}^{2+}$  and 63.37%  $\text{Ni}^{2+}$  whereas acid activated kaolinite adsorbed 77.47% and 68.32% at optimum pH of 7, contact time 60 min and temperature 25°C [90].

## 2.4 Nanostructured materials

In the last decade, carbon nanotubes [91], fullerenes [92] and graphene [93] have occupied an important place in the area of adsorption of heavy metals from effluents. They possess exceptional mechanical and chemical properties, strength, exchange capacity, electrical conductivity and thermal stability. A high surface area along with numerous intermolecular interactions gives them an edge over other adsorbents in remediation of heavy metals.

### 2.4.1 Carbon nanotubes, fullerenes and graphene

Iijima discovered carbon nanotubes (CNTs) in 1991 [94]. They exist as long carbon cylindrical in shape with a continuous hexagonal graphite sheets. They are of two types: single walled CNT, which have a single graphite sheet and multi walled CNTs which have multiple sheets. They have portrayed excellent potential for heavy metal from wastewater for copper [95, 96] lead, [97, 98], chromium [99, 100], nickel [100, 101] and cadmium [100, 102]. CNTs prove to be excellent adsorbents owing to the advantages such as mechanical and surface properties electrical and semiconductor properties [102, 103]. They also provide a high specific surface area (150-1500m<sup>2</sup>/g) and the presence of mesopores increases their adsorption efficiency [104–107]. The presence of different functional groups containing elements such as oxygen, nitrogen and sulfur directly and indirectly affect the adsorption mechanisms that enhance the adsorption of heavy metals [108–111].

Oxidized CNTs also portray exceedingly high adsorption capacity for the removal of  $\text{Cr}^{6+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  from wastewater [112–115]. Wang et al. (2007a) carried out a study using MWCNTs activated with conc.  $\text{HNO}_3$  which escalated the adsorption capacity due to creation of more oxygen functional groups. The equilibrium time for  $\text{Pb}^{2+}$  adsorption was found to be 120 min at an optimum pH 2.0 [116]. Nanocomposites are also prepared using CNTs with ferrous, zirconium, aluminium oxides by coprecipitation method for removal of Pb, As, Cu, Ni and Cr ions [117–122]. Luo et al. synthesized  $\text{Fe}_2\text{O}_3/\text{MnO}_2$ /acid oxidized MWCNT nanocomposites for removal of  $\text{Cr}^{6+}$ . At an optimum pH of 2.0 a maximum removal capacity of 85% was achieved by the nanocomposite [123]. Ge et al. prepared magnetic Fe@MgO nanocomposites for the removal of  $\text{Pb}^{2+}$  from water. A maximum adsorption efficiency of 14746.4 mg/g was achieved for  $\text{Pb}^{2+}$  at 120 min contact time [124]. Stafiej and Pырzyska stated some facts related to adsorption capacity of CNTs and reached a conclusion that pH and concentration of heavy metals significantly affect the CNTs efficiency [125]. CNTs portray excellent adsorption efficiency due to their surface morphology, electrochemical potential and ion exchange capacity [126, 127]. The ability of CNTs to be easily modified makes them selective adsorbents with the merit of enhanced adsorption efficiency [113, 127–130]. They are instituted as great adsorbents in the field of wastewater treatment due to their appreciable mechanical and surface characteristics,

mechanical and magnetic properties and high stability [131]. But the use is restricted due to the accumulation of the active sites by the adsorbate. Hence, activation of CNTs offers the advantage of increasing the sites with functional groups which in turn increases their adsorption efficiency for heavy metal removal from water and wastewater [132–138].

The discovery of fullerenes in 1985 led to another breakthrough in adsorption science [139, 140]. They have a closed-cage structure containing pentagonal and hexagonal carbon rings with the formula  $C_{20+m}$ ,  $m$  being an integer. Their adsorption efficiency can also be attributed to their surface morphology and presence of mesopores which gives them higher ion affinity and higher specific surface area for remediation of heavy metal ions from water and wastewater [141, 142]. Alekseeva et al. conducted a study using fullerenes for the removal of  $Cu^{2+}$  and explained the mechanism through Langmuir model [143]. The maximum adsorption efficiency was found to be 14.6 mmol/g. Spherical fullerene containing 60 carbon atoms is the most explored one. Its striking features comprise of hydroxyl and epoxy functional groups on surface, large surface to volume ratio, hydrophobicity, high electron affinity and low aggregation capacity which make it beneficial for heavy metal removal [144–146]. But their use is often restricted due to their high price. So, research on incorporation of other conventional adsorbents with fullerenes has come up. It was revealed that fullerenes enhance the porous structure of adsorbent leading to increase in the removal efficiency of heavy metals. It was found that adsorption capacity of ACs escalated by 1.5–2.5 times after introduction of fullerenes into their structure [147, 148].

Graphene came into the scene in 2004 and is a 2-D hexagonal lattice of carbon atoms. It also possesses structural, chemical and mechanical properties which aid its use in wastewater treatment. It has a high surface area, active functional groups and sites on its surface which enhance its adsorption capacity [149–151]. Graphene can also be activated by oxidation to increase functional groups which surge the adsorption capacity for removal of heavy metals [114, 152–155]. Deng et al. 2010 conducted a study using functionalized graphene for removal of  $Pb^{2+}$  from aqueous solution. At an optimum pH of 5.0 the maximum adsorption capacity reached was 406.6 mg/g within 40 min [156]. Several studies were conducted to study the properties of graphene oxides for adsorption [157–161]. It was revealed that graphene oxides can also be magnetically modified which increases their adsorption capacity [162, 163]. A study by Zhao et al. used layered graphene oxide for removal of  $Pb^{2+}$  from aqueous solution. The adsorbent layers had oxygen functional groups which greatly enhanced the adsorption capacity reaching a maximum of 1850 mg/g [164]. Jian et al. synthesized a bio-adsorbent polyacrylamide/graphene oxide hydrogel grafted with sodium alginate and studied the removal of  $Cu^{2+}$  and  $Pb^{2+}$  from aqueous solution. The maximum adsorption capacity of  $Cu^{2+}$  was 68.76 mg/g at pH 5 and 240.69 mg/g for  $Pb^{2+}$  at 5.5 pH [165].

## **2.5 Low cost adsorbents**

Although, ACs are the most widely used adsorbents, their use is limited due to their high cost and low regeneration. Same is with other developed adsorbents such as carbon nanotubes, fullerenes and nanocomposites. To make the process of wastewater treatment speed up and effective, it is vital to look for adsorbents that are cost effective as well administer a high adsorption efficiency. Thus, the need for low cost adsorbents came to be realized. Low cost adsorbents comprise of those non-conventional materials that are easily available and cost effective mainly agricultural and industrial waste.

S. No.	Type of wastewater	Type of Adsorbent	Adsorbent Dosage (g/L)	Metal Ion	Amount Adsorbed (mg/g)	Contact Time (min)	Temperature (°C)	pH	References
1.	Hospital Wastewater	Cassava peels	10.0	Pb <sup>2+</sup> Cu <sup>2+</sup>	5.80 8.00	20-120	39.85	8.0	[168]
2.	Aqueous Solution	Ash Gourd Peel Powder	6.0	Cr <sup>6+</sup>	18.70	40-60	28.0	1.0	[169]
3.	Aqueous Solution	Barley Straw	1.0	Cu <sup>2+</sup>	4.64	120	25.0	6.0-7.0	[170]
4.	Aqueous Solution	Cashew Nut	3.0	Ni <sup>2+</sup>	18.86	30	30.0	5.0	[171]
5.	Electroplating Wastewater	Chemically Modified Orange peel	2.0	Cu <sup>2+</sup>	289.0	180	30.0	5.0	[172]
6.	Aqueous Solution	Modified Lawny Grass	0.5	Pb <sup>2+</sup>	137.12	400	29.85	6.0	[173]
7.	Aqueous Solution	Grapefruit Peel	2.0	U <sup>6+</sup>	140.79	60-80	24.85	4.0-6.0	[174]
8.	Aqueous Solution	Peanut Shell	1.0	Cr <sup>6+</sup>	4.32	360	30.0	2.0	[175]
9.	Aqueous Solution	Sugar cane and orange peel biochar	1.0	Pb <sup>2+</sup>	86.96 and 27.86	30	25.0	5.0	[176]
10.	Electroplating Wastewater	Mango Peel	5.0 5.0 5.0	Ni <sup>2+</sup> Cu <sup>2+</sup> Zn <sup>2+</sup>	39.75 46.09 28.21	120	25.0	6.0	[177]
11.	Aqueous Solution	Wheat Shell	10.0	Cu <sup>2+</sup>	17.42	60	25.0	7.0	[178]
12.	Aqueous Solution	Sulfonated Biochar	2.0	Pb <sup>2+</sup> Cd <sup>2+</sup>	191.07 85.76	5	180.0	4.5	[179]

**Table 2.**  
*Agricultural wastes for heavy metal removal.*



S. No.	Type of wastewater	Type of Adsorbent	Adsorbent Dosage (g/L)	Metal Ion	Amount Adsorbed (mg/g)	Contact Time (min)	Temperature (°C)	pH	References
1.	Dye and heavy metals Wastewater	Fly Ash	2.0	Cd <sup>2+</sup> Cu <sup>2+</sup> Ni <sup>2+</sup>	6.36 12.78 1.66	60	25.0	4.8-5.3	[191]
2.	Aqueous Solution	Coal Fly Ash	2.5	Cu <sup>2+</sup> Ni <sup>2+</sup>	158.0 99.0	120 60	20.0	8.0	[192]
3.	Aqueous Solution	Fly Ash Geopolymer	2.0	Cu <sup>2+</sup>	152.0	120	45.0	6.0	[193]
4.	Aqueous Solution	Fly Ash Bottom Ash	2.0	Cd <sup>2+</sup>	142.9 23.3	240	25.0	5.0-6.0	[196]
5.	Aqueous Solution	Red Mud	1.0	Cu <sup>2+</sup>	5.3	60	30.0	5.5	[197]
6.	Aqueous Solution	Activated Red Mud	4.0	Zn <sup>2+</sup>	14.9	480	25.0	6.0	[198]
7.	Aqueous Solution	Red Mud	1.0	Co <sup>2+</sup>	18.0	15	30.0	5.0	[200]
8.	Aqueous Solution	Activated Red Mud	4.0	Pb <sup>2+</sup>	6.0	30	30.0	4.0	[202]
9.	Aqueous Solution	Basic Oxygen Furnace Slag	0.5	Cu <sup>2+</sup>	245.2	60	20.0	3.5	[204]
10.	Synthetic Wastewater	LD Slag Geopolymer Raw LD Slag	2.0	Ni <sup>2+</sup>	84.8 14.3	1440	45	10.0 10.0	[205]

**Table 3.**  
*Industrial wastes for heavy metal removal.*

### 2.5.1 Agriculture waste

Agricultural wastes have the constitution of lignin, cellulose, hydrocarbons, sugars, water and starch along with other functional groups which enhances the adsorption capacity of these agricultural wastes. These wastes can range from rice husk to wheat shells, egg shells, coconut husk, palm fruit, bagasse, groundnut shell, fruit peels, biochar etc. These wastes can be used directly in which they are washed and grounded first. Then they are sieved to get the desirable particle size which are used for adsorption tests. They can also be modified into chars and further activated to increase the adsorption sites [166, 167]. **Table 2** shows the different agricultural wastes used for heavy metal ions removal.

### 2.5.2 Biochar

Biochar is the charred solid material obtained from the carbonization of biomass. The most common method of production of biomass is by pyrolysis which is the thermal decomposition of biomass in absence or limited oxygen. Biochars are less carbonized than AC so more carbon, hydrogen and oxygen remain in their structure. Biochar has shown remarkable potential for remediation of heavy metals from wastewater than other conventional and low-cost adsorbents. They have a mesoporous structure leading to a high surface area and presence of different functional groups and a low ash content makes them excellent and effective adsorbents. Feedstock such as rice husk [180–185], corn husk [180], tea waste [181, 184, 186, 187] and digested sludge have [185, 188] been employed for removal of heavy metals from aqueous solutions as well as wastewater.

## 2.6 Industrial waste

Industrial activities generate huge quantities of waste that are usually sent to landfill sites for disposal. These wastes possess a good adsorption capacity and are solve the problem of waste treatment. Waste products like fly ash [189–196], red mud [197–203] and slag [204, 205] have been effectively used owing to their appreciable capacity for removal of heavy metals from wastewater. Many industrial waste adsorbents have been employed for the remediation of  $Zn^{2+}$  from effluents. The maximum adsorption capacity for lignin was 73.2mg/g, 168mg/g for waste sludge and 55.82mg/g for cassava waste [206, 207]. **Table 3** gives various industrial wastes used for removal of heavy metals from wastewater and aqueous solutions.

## 3. Comparison of conventional and non-conventional adsorbents

For the adsorption process to be efficient, selection of the most appropriate adsorbent is a crucial step. The main basis of selection of an adsorbent include low cost, high adsorption capacity, effective for a broad spectrum of pollutants and having a low footprint [208, 209]. There has been extensive research in the field of conventional and non-conventional adsorption performances and mechanisms. Different adsorbents follow varied mechanisms because of difference in raw material and adsorbent production conditions. Mainly four mechanisms have been identified for efficient adsorption of pollutants; chemisorption, physisorption, ion-exchange and precipitation [210, 211]. Davis et al. stated that ion-exchange does not necessarily describe the mechanism of adsorption but a lot of other factors and mechanisms co-aid to make the process successful [210]. Some other researchers also explained the adsorption mechanisms [212–215]. Literature evidently points

out that activated carbons have proven themselves as brilliant adsorbents due to their high specific surface area, mechanical and structural surface morphology and presence of functional groups which can also be modified. However, non-conventional adsorbents are increasingly employed as low-cost and effectual adsorbents. Their commercialization remains a task but there as upcoming as their available in abundant. More focused research into their engineering and modification can bring them at par some commercial solid adsorbents.

#### **4. Conclusion**

Heavy metal pollution is one the most dangerous situations being faced today. They harmful even in trace concentrations. Many of them are carcinogenic, cause birth defects and are extremely fatal. Hence, it is necessary to remove these toxic metals from wastewater before it is discharged into open waters. Adsorption is one such technique that caters not only to the remediation of heavy metal from wastewater, it is also eco-friendly with a low footprint. Adsorbents like activated are widely used, but it is restricted due to its high cost. So, it is necessary to look for options that are sustainable and aim at remediating the larger prospect of the problem. Low-cost adsorbents like agricultural wastes, industrial wastes and biochar aid not only in removal of heavy metals but are also cheap methods. Their raw material is easily available and these adsorbents can be easily manufactured. So, it is a green technology that greatly enhances the process of wastewater treatment. Further research into developing more low-cost adsorbents can help in further remedial of heavy metals.

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## References

- [1] Srivastava NK, Majumder CB. Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. *Journal of hazardous materials*. 2008 Feb 28;151(1):1-8.
- [2] Baldwin DR, Marshall WJ. Heavy metal poisoning and its laboratory investigation. *Annals of clinical biochemistry*. 1999 May;36(3):267-300.
- [3] Barakat MA. New trends in removing heavy metals from industrial wastewater. *Arabian journal of chemistry*. 2011 Oct 1;4(4):361-77.
- [4] Akpor OB, Ohiobor GO, Olaolu DT. Heavy metal pollutants in wastewater effluents: sources, effects and remediation. *Advances in Bioscience and Bioengineering*. 2014 Nov 10;2(4):37-43.
- [5] Harvey PJ, Handley HK, Taylor MP. Identification of the sources of metal (lead) contamination in drinking waters in north-eastern Tasmania using lead isotopic compositions. *Environmental Science and Pollution Research*. 2015 Aug 1;22(16):12276-88.
- [6] Molinari R, Poerio T, Argurio P. Selective separation of copper (II) and nickel (II) from aqueous media using the complexation-ultrafiltration process. *Chemosphere*. 2008 Jan 1;70(3):341-8.
- [7] US Environmental Protection Agency. Framework for metals risk assessment. US Environmental Protection Agency, Office of the Science Advisor: Washington, DC. EPA 120/R-07/001. 2007.
- [8] Landaburu-Aguirre J, García V, Pongrácz E, Keiski RL. The removal of zinc from synthetic wastewaters by micellar-enhanced ultrafiltration: statistical design of experiments. *Desalination*. 2009 May 15;240(1-3):262-9.
- [9] Zhao M, Xu Y, Zhang C, Rong H, Zeng G. New trends in removing heavy metals from wastewater. *Applied microbiology and biotechnology*. 2016 Aug 1;100(15):6509-18.
- [10] Abdullah N, Yusof N, Lau WJ, Jaafar J, Ismail AF. Recent trends of heavy metal removal from water/wastewater by membrane technologies. *Journal of Industrial and Engineering Chemistry*. 2019 Aug 25;76:17-38.
- [11] Crini G, Lichtfouse E. Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters*. 2019 Mar 1;17(1):145-55.
- [12] Kongsricharoern N, Polprasert C. Electrochemical precipitation of chromium (Cr<sup>6+</sup>) from an electroplating wastewater. *Water Science and Technology*. 1995 May 1;31(9):109.
- [13] Chareerntanyarak L. Heavy metals removal by chemical coagulation and precipitation. *Water Science and Technology*. 1999 Jan 1;39(10-11):135-8.
- [14] Mirbagheri SA, Hosseini SN. Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse. *Desalination*. 2005 Jan 1;171(1):85-93.
- [15] Tanong K, Tran LH, Mercier G, Blais JF. Recovery of Zn (II), Mn (II) Cd (II) and Ni (II) from the unsorted spent batteries using solvent extraction, electrodeposition and precipitation methods. *J. Clean. Prod.* 148 (2017) 233-244.
- [16] Peng H, Guo J. Removal of chromium from wastewater by membrane filtration, chemical precipitation, ion exchange, adsorption electrocoagulation, electrochemical

reduction, electro dialysis, electrodeionization, photocatalysis and nanotechnology: a review. *Environmental Chemistry Letters*. 2020 Jul 23:1-4.

[17] Abo-Farha, SA, Abdel-Aal, AY, Ashour, IA, Garamon, SE. Removal of some heavy metal cations by synthetic resin purolite C100, *J. Hazard. Mater.* 169 (2009)190-194.

[18] Alyuz, B, Veli, S. Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, *J. Hazard. Mater.* 167 (2009) 482-488.

[19] Zanin E, Scapinello J, de Oliveira M, Rambo CL, Franscescon F, Freitas L, de Mello JM, Fiori MA, Oliveira JV, Dal Magro J. Adsorption of heavy metals from wastewater graphic industry using clinoptilolite zeolite as adsorbent. *Process Safety and Environmental Protection*. 2017 Jan 1;105:194-200.

[20] Huang Y, Zeng X, Guo L, Lan J, Zhang L, Cao D. Heavy metal ion removal of wastewater by zeolite-imidazolate frameworks. *Separation and Purification Technology*. 2018 Apr 3;194:462-9.

[21] Hong M, Yu L, Wang Y, Zhang J, Chen Z, Dong L, Zan Q, Li R. Heavy metal adsorption with zeolites: The role of hierarchical pore architecture. *Chemical Engineering Journal*. 2019 Mar 1;359:363-72.

[22] Eccles H. Treatment of metal-contaminated wastes: why select a biological process? *Trends in biotechnology*. 1999 Dec 1;17(12):462-5.

[23] Fu F, Wang Q. Removal of heavy metal ions from wastewaters: a review. *Journal of environmental management*. 2011 Mar 1;92(3):407-18.

[24] Agarwal M, Singh K. Heavy metal removal from wastewater using

various adsorbents: a review. *Journal of Water Reuse and Desalination*. 2017 Dec;7(4):387-419.

[25] Tyagi I, Gupta VK, Sadegh H, Ghoshekandi RS, Makhlof AS. Nanoparticles as adsorbent; a positive approach for removal of noxious metal ions: a review. *Science Technology and Development*. 2017;34(3):195-214.

[26] Tripathi A, Ranjan MR. Heavy metal removal from wastewater using low cost adsorbents. *J BioremedBiodeg*. 2015 Jan;6(6):315.

[27] Singh N, Gupta SK. Adsorption of heavy metals: A review. *Int. J. Innov. Res. Sci. Eng. Technol*. 2016 Feb;5(2):2267-81.

[28] Freundlich HM. Over the adsorption in solution. *J. Phys. Chem*. 1906 Mar;57(385471):1100-7.

[29] Langmuir I. The constitution and fundamental properties of solids and liquids. Part I. Solids. *Journal of the American chemical society*. 1916 Nov;38(11):2221-95.

[30] Redlich OJ, Peterson DL. A useful adsorption isotherm. *Journal of physical chemistry*. 1959 Jun 1;63(6):1024-28.

[31] Radke CJ, Prausnitz JM. Adsorption of organic solutes from dilute aqueous solution of activated carbon. *Industrial & Engineering Chemistry Fundamentals*. 1972 Nov;11(4):445-51.

[32] Sips R. Combined form of Langmuir and Freundlich equations. *J. Chem. Phys*. 1948;16(429):490-5.

[33] Toth J. State equation of the solid-gas interface layers. *Acta chim. hung*. 1971;69:311-28.

[34] Koble RA, Corrigan TE. Adsorption isotherms for pure hydrocarbons. *Industrial & Engineering Chemistry*. 1952 Feb;44(2):383-7.

- [35] Ojedokun AT, Bello OS. Sequestering heavy metals from wastewater using cow dung. *Water Resources and Industry*. 2016 Mar 1;13:7-13.
- [36] Demirbas A. Heavy metal adsorption onto agro-based waste materials: a review. *Journal of hazardous materials*. 2008 Sep 15;157(2-3):220-9.
- [37] Vunain E, Mishra AK, Mamba BB. Dendrimers, mesoporous silicas and chitosan-based nanosorbents for the removal of heavy-metal ions: a review. *International journal of biological macromolecules*. 2016 May 1;86:570-86.
- [38] Ewecharoen A, Thiravetyan P, Wendel E, Bertagnolli H. Nickel adsorption by sodium polyacrylate-grafted activated carbon. *Journal of hazardous materials*. 2009 Nov 15;171(1-3):335-9.
- [39] Rivera-Utrilla J, Sánchez-Polo M, Gómez-Serrano V, Alvarez PM, Alvim-Ferraz MC, Dias JM. Activated carbon modifications to enhance its water treatment applications. An overview. *Journal of hazardous materials*. 2011 Mar 15;187(1-3):1-23.
- [40] Abbaszadeh S, Alwi SR, Webb C, Ghasemi N, Muhamad II. Treatment of lead-contaminated water using activated carbon adsorbent from locally available papaya peel biowaste. *Journal of Cleaner Production*. 2016 Apr 1;118:210-22.
- [41] Wong S, Ngadi N, Inuwa IM, Hassan O. Recent advances in applications of activated carbon from biowaste for wastewater treatment: a short review. *Journal of Cleaner Production*. 2018 Feb 20;175:361-75.
- [42] Duan C, Ma T, Wang J, Zhou Y. Removal of heavy metals from aqueous solution using carbon-based adsorbents: A review. *Journal of Water Process Engineering*. 2020 Oct 1;37:101339.
- [43] Meng Q, Chen H, Lin J, Lin Z, Sun J. Zeolite A synthesized from alkaline assisted pre-activated halloysite for efficient heavy metal removal in polluted river water and industrial wastewater. *Journal of environmental sciences*. 2017 Jun 1;56:254-62.
- [44] Taamneh Y, Sharadqah S. The removal of heavy metals from aqueous solution using natural Jordanian zeolite. *Applied Water Science*. 2017 Jul 1;7(4):2021-8.
- [45] Huang Y, Zeng X, Guo L, Lan J, Zhang L, Cao D. Heavy metal ion removal of wastewater by zeolite-imidazolate frameworks. *Separation and Purification Technology*. 2018 Apr 3;194:462-9.
- [46] Hong M, Yu L, Wang Y, Zhang J, Chen Z, Dong L, Zan Q, Li R. Heavy metal adsorption with zeolites: The role of hierarchical pore architecture. *Chemical Engineering Journal*. 2019 Mar 1;359:363-72.
- [47] Carpio IE, Mangadlao JD, Nguyen HN, Advincula RC, Rodrigues DF. Graphene oxide functionalized with ethylenediamine triacetic acid for heavy metal adsorption and anti-microbial applications. *Carbon*. 2014 Oct 1;77:289-301.
- [48] Yu JG, Yu LY, Yang H, Liu Q, Chen XH, Jiang XY, Chen XQ, Jiao FP. Graphene nanosheets as novel adsorbents in adsorption, preconcentration and removal of gases, organic compounds and metal ions. *Science of the total environment*. 2015 Jan 1;502:70-9.
- [49] Sadegh H, Ali GA, Gupta VK, Makhlof AS, Shahryari-ghoshekandi R, Nadagouda MN, Sillanpää M, Megiel E. The role of nanomaterials as effective adsorbents and their applications in wastewater treatment. *Journal of Nanostructure in Chemistry*. 2017 Mar 1;7(1):1-4.

- [50] Nimibofa A, Newton EA, Cyprain AY, Donbebe W. Fullerenes: synthesis and applications. *J. Mater. Sci.* 2018 Jun 30;7:22-33.
- [51] Baby R, Saifullah B, Hussein MZ. Carbon nanomaterials for the treatment of heavy metal-contaminated water and environmental remediation. *Nanoscale Research Letters.* 2019 Dec 1;14(1):341.
- [52] Mubarak NM, Sahu JN, Abdullah EC, Jayakumar NS. Removal of heavy metals from wastewater using carbon nanotubes. *Separation & Purification Reviews.* 2014 Oct 2;43(4):311-38.
- [53] Yadav DK, Srivastava S. Carbon nanotubes as adsorbent to remove heavy metal ion ( $Mn^{+7}$ ) in wastewater treatment. *Materials Today: Proceedings.* 2017 Jan 1;4(2):4089-94.
- [54] Yu G, Lu Y, Guo J, Patel M, Bafana A, Wang X, Qiu B, Jeffryes C, Wei S, Guo Z, Wujcik EK. Carbon nanotubes, graphene, and their derivatives for heavy metal removal. *Advanced Composites and Hybrid Materials.* 2018 Mar 1;1(1):56-78.
- [55] Ouni L, Ramazani A, Fardood ST. An overview of carbon nanotubes role in heavy metals removal from wastewater. *Frontiers of Chemical Science and Engineering.* 2019 May 22:1-22.
- [56] Fiyadh SS, AlSaadi MA, Jaafar WZ, AlOmar MK, Fayaed SS, Mohd NS, Hin LS, El-Shafie A. Review on heavy metal adsorption processes by carbon nanotubes. *Journal of Cleaner Production.* 2019 Sep 1;230:783-93.
- [57] Crini G, Lichtfouse E, Wilson LD, Morin-Crini N. Conventional and non-conventional adsorbents for wastewater treatment. *Environmental Chemistry Letters.* 2019 Mar 1;17(1):195-213.
- [58] Crini G (2010) Wastewater treatment by sorption. In: Crini G, Badot PM (eds) *Sorption processes and pollution*, chap 2. PUFC, Besançon, pp 39-78.
- [59] Crini G, Lichtfouse É, Wilson LD, Morin-Crini N (2018) Adsorption-oriented using conventional and non-conventional adsorbents for wastewater treatment. In: Crini G, Lichtfouse É (eds) *Environmental chemistry for a sustainable world, green adsorbents for pollutant removal—fundamentals and design*, chapter 2, vol 1. Springer, Berlin, pp 23-71. ISBN 978-3-319-92111-2.
- [60] Jusoh A, Shiung LS, Noor MJ. A simulation study of the removal efficiency of granular activated carbon on cadmium and lead. *Desalination.* 2007 Feb 5;206(1-3):9-16.
- [61] Kang KC, Kim SS, Choi JW, Kwon SH. Sorption of  $Cu^{2+}$  and  $Cd^{2+}$  onto acid-and base-pretreated granular activated carbon and activated carbon fiber samples. *Journal of Industrial and Engineering Chemistry.* 2008 Jan 1;14(1):131-5.
- [62] Deliyanni EA, Kyzas GZ, Triantafyllidis KS, Matis KA. Activated carbons for the removal of heavy metal ions: A systematic review of recent literature focused on lead and arsenic ions. *Open Chemistry.* 2015 Jan 13;1(open-issue).
- [63] Bansal RC, Goyal M. *Activated carbon adsorption.* CRC press; 2005 May 24.
- [64] Kobya M. Removal of Cr (VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies. *Bioresource technology.* 2004 Feb 1;91(3):317-21.
- [65] Selomulya C, Meeyoo V, Amal R. Mechanisms of Cr (VI) removal from water by various types of activated carbons. *Journal of Chemical Technology & Biotechnology: International Research in Process,*

Environmental & Clean Technology.  
1999 Feb;74(2):111-22.

[66] Karthikeyan T, Rajgopal S, Miranda LR. Chromium (VI) adsorption from aqueous solution by Hevea Brasiliensis sawdust activated carbon. Journal of hazardous materials. 2005 Sep 30;124(1-3):192-9.

[67] Babel S, Kurniawan TA. Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. Chemosphere. 2004 Feb 1;54(7):951-67.

[68] Garg VK, Gupta R, Kumar R, Gupta RK. Adsorption of chromium from aqueous solution on treated sawdust. Bioresource technology. 2004 Mar 1;92(1):79-81.

[69] Sharma DC, Forster CF. A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents. Bioresource Technology. 1994 Jan 1;47(3):257-64.

[70] Selvi K, Pattabhi S, Kadirvelu K. Removal of Cr (VI) from aqueous solution by adsorption onto activated carbon. Bioresource technology. 2001 Oct 1;80(1):87-9.

[71] Kongsuwan A, Patnukao P, Pavasant P. Binary component sorption of Cu (II) and Pb (II) with activated carbon from Eucalyptus camaldulensis Dehn bark. Journal of Industrial and Engineering Chemistry. 2009 Jul 25;15(4):465-70.

[72] El-Ashtoukhy ES, Amin NK, Abdelwahab O. Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. Desalination. 2008 Mar 1;223(1-3):162-73.

[73] Kavand M, Kaghazchi T, Soleimani M. Optimization of parameters for competitive adsorption

of heavy metal ions (Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>) onto activated carbon. Korean journal of chemical engineering. 2014 Apr 1;31(4):692-700.

[74] Kim TK, Kim T, Choe WS, Kim MK, Jung YJ, Zoh KD. Removal of heavy metals in electroplating wastewater by powdered activated carbon (PAC) and sodium diethyldithiocarbamate-modified PAC. Environmental Engineering Research. 2018;23(3):301-8.

[75] Choi HJ, Yu SW, Kim KH. Efficient use of Mg-modified zeolite in the treatment of aqueous solution contaminated with heavy metal toxic ions. Journal of the Taiwan Institute of Chemical Engineers. 2016 Jun 1;63:482-9.

[76] Erdem E, Karapinar N, Donat R. The removal of heavy metal cations by natural zeolites. Journal of colloid and interface science. 2004 Dec 15;280(2):309-14.

[77] Ibrahim HS, Jamil TS, Hegazy EZ. Application of zeolite prepared from Egyptian kaolin for the removal of heavy metals: II. Isotherm models. Journal of Hazardous materials. 2010 Oct 15;182(1-3):842-847.

[78] Aliabadi M, Irani M, Ismaeili J, Piri H, Parnian MJ. Electrospun nanofiber membrane of PEO/Chitosan for the adsorption of nickel, cadmium, lead and copper ions from aqueous solution. Chemical engineering journal. 2013 Mar 15;220:237-43.

[79] Rad LR, Momeni A, Ghazani BF, Irani M, Mahmoudi M, Noghreh B. Removal of Ni<sup>2+</sup> and Cd<sup>2+</sup> ions from aqueous solutions using electrospun PVA/zeolite nanofibrous adsorbent. Chemical Engineering Journal. 2014 Nov 15;256:119-27.

[80] Javadian H, Sorkhrodi FZ, Koutenaie BB. Experimental investigation on enhancing aqueous cadmium



- removal via nanostructure composite of modified hexagonal type mesoporous silica with polyaniline/polypyrrole nanoparticles. *Journal of Industrial and Engineering Chemistry*. 2014 Sep 25;20(5):3678-88.
- [81] Visa M. Synthesis and characterization of new zeolite materials obtained from fly ash for heavy metals removal in advanced wastewater treatment. *Powder Technology*. 2016 Jun 1;294:338-47.
- [82] Kobayashi Y, Ogata F, Nakamura T, Kawasaki N. Synthesis of novel zeolites produced from fly ash by hydrothermal treatment in alkaline solution and its evaluation as an adsorbent for heavy metal removal. *Journal of Environmental Chemical Engineering*. 2020 Apr 1;8(2):103687.
- [83] Tripathi A, Ranjan MR. Heavy metal removal from wastewater using low cost adsorbents. *J Bioremed Biodeg*. 2015 Jan;6(6):315.
- [84] Agarwal M, Singh K. Heavy metal removal from wastewater using various adsorbents: a review. *Journal of Water Reuse and Desalination*. 2017 Dec;7(4):387-419.
- [85] Singh SP, Ma LQ, Harris WG. Heavy metal interactions with phosphatic clay: sorption and desorption behavior. *Journal of Environmental Quality*. 2001 Nov;30(6):1961-8.
- [86] Krikorian N, Martin DF. Extraction of selected heavy metals using modified clays. *Journal of Environmental Science and Health*. 2005 Jan 1;40(3):601-8.
- [87] Aşçı Y, Nurbaş M, Açikel YS. Sorption of Cd (II) onto kaolin as a soil component and desorption of Cd (II) from kaolin using rhamnolipid biosurfactant. *Journal of Hazardous Materials*. 2007 Jan 2;139(1):50-6.
- [88] Jiang MQ, Jin XY, Lu XQ, Chen ZL. Adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) onto natural kaolinite clay. *Desalination*. 2010 Mar 1;252(1-3):33-9.
- [89] Bertagnolli C, Kleinübing SJ, Da Silva MG. Preparation and characterization of a Brazilian bentonite clay for removal of copper in porous beds. *Applied Clay Science*. 2011 Jul 1;53(1):73-9.
- [90] Chai JB, Au PI, Mubarak NM, Khalid M, Ng WP, Jagadish P, Walvekar R, Abdullah EC. Adsorption of heavy metal from industrial wastewater onto low-cost Malaysian kaolin clay-based adsorbent. *Environmental Science and Pollution Research*. 2020 Feb 8:1-4.
- [91] Burakov A, Romantsova I, Kucherova A, Tkachev A. Removal of heavy-metal ions from aqueous solutions using activated carbons: effect of adsorbent surface modification with carbon nanotubes. *Adsorption Science & Technology*. 2014 Sep;32(9):737-47.
- [92] Darwish AD. Fullerenes. *Annual Reports Section "A" (Inorganic Chemistry)*. 2013;109:436-52.
- [93] Melezhyk AV, Kotov VA, Tkachev AG. Optical properties and aggregation of graphene nanoplatelets. *Journal of Nanoscience and Nanotechnology*. 2016 Jan 1;16(1):1067-75.
- [94] Iijima S, Helical microtubes of graphitic carbon. *Nature*. 1991; 354:56-58.
- [95] Li Y, Liu F, Xia B, Du Q, Zhang P, Wang D, Wang Z, Xia Y. Removal of copper from aqueous solution by carbon nanotube/calcium alginate composites. *Journal of Hazardous Materials*. 2010 May 15;177(1-3):876-80.
- [96] Rodríguez C, Leiva E. Enhanced heavy metal removal from acid mine drainage wastewater using double-oxidized multiwalled carbon nanotubes. *Molecules*. 2020 Jan;25(1):111.

- [97] Wang H, Zhou A, Peng F, Yu H, Yang J. Mechanism study on adsorption of acidified multiwalled carbon nanotubes to Pb (II). *Journal of Colloid and Interface Science*. 2007 Dec 15;316(2):277-83.
- [98] Kabbashi NA, Atieh MA, Al-Mamun A, Mirghami ME, Alam MD, Yahya N. Kinetic adsorption of application of carbon nanotubes for Pb (II) removal from aqueous solution. *Journal of Environmental Sciences*. 2009 Apr 1;21(4):539-44.
- [99] Pillay K, Cukrowska EM, Coville NJ. Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution. *Journal of hazardous materials*. 2009 Jul 30;166(2-3):1067-75.
- [100] Temitope BM, Saka AA, Alhassan MI, Ochigbo SS, Oladejo TJ, Kamaldeen AO, Roos WD. Selected Heavy Metals Removal from Electroplating Wastewater by Purified and Polyhydroxylbutyrate Functionalized Carbon Nanotubes Adsorbents. *Scientific Reports (Nature Publisher Group)*. 2019 Dec 1;9(1).
- [101] Kandah MI, Meunier JL. Removal of nickel ions from water by multi-walled carbon nanotubes. *Journal of hazardous materials*. 2007 Jul 19;146(1-2):283-8.
- [102] Kuo CY, Lin HY. Adsorption of aqueous cadmium (II) onto modified multi-walled carbon nanotubes following microwave/chemical treatment. *Desalination*. 2009 Dec 15;249(2):792-6.
- [103] Haddon RC, Carbon nanotubes. *Acc. Chem. Res*. 2002; 35: 977-1113.
- [104] Fiyadh SS, AlSaadi MA, Jaafar WZ, AlOmar MK, Fayaed SS, Mohd NS, Hin LS, El-Shafie A. Review on heavy metal adsorption processes by carbon nanotubes. *Journal of Cleaner Production*. 2019 Sep 1;230:783-93.
- [105] Duan C, Ma T, Wang J, Zhou Y. Removal of heavy metals from aqueous solution using carbon-based adsorbents: A review. *Journal of Water Process Engineering*. 2020 Oct 1;37:101339.
- [106] Gupta VK, Agarwal S, Saleh TA. Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes. *Water research*. 2011 Mar 1;45(6):2207-12.
- [107] Wang X, Guo Y, Yang L, Han M, Zhao J, Cheng X. Nanomaterials as sorbents to remove heavy metal ions in wastewater treatment. *J. Environ. Anal. Toxicol*. 2012 Nov;2(7):154-8.
- [108] Sharma M, Singh J, Hazra S, Basu S. Adsorption of heavy metal ions by mesoporous ZnO and TiO<sub>2</sub>@ZnO monoliths: adsorption and kinetic studies. *Microchemical journal*. 2019 Mar 1;145:105-12.
- [109] Yang X, Wan Y, Zheng Y, He F, Yu Z, Huang J, Wang H, Ok YS, Jiang Y, Gao B. Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: a critical review. *Chemical Engineering Journal*. 2019 Jun 15;366:608-21.
- [110] Verma B, Balomajumder C. Surface modification of one-dimensional Carbon Nanotubes: A review for the management of heavy metals in wastewater. *Environmental Technology & Innovation*. 2020 Feb 1;17:100596.
- [111] Li YH, Wang S, Wei J, Zhang X, Xu C, Luan Z, Wu D, Wei B. Lead adsorption on carbon nanotubes. *Chemical Physics Letters*. 2002 May 10;357(3-4):263-6.
- [112] Li YH, Wang S, Luan Z, Ding J, Xu C, Wu D. Adsorption of cadmium

- (II) from aqueous solution by surface oxidized carbon nanotubes. *Carbon*. 2003 Jan 1;41(5):1057-62.
- [113] Robati D. Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multi-walled carbon nanotube. *Journal of nanostructure in Chemistry*. 2013 Dec 1;3(1):55.
- [114] Xu J, Cao Z, Zhang Y, Yuan Z, Lou Z, Xu X, Wang X. A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: Preparation, application, and mechanism. *Chemosphere*. 2018 Mar 1;195:351-64.
- [115] Rodríguez C, Leiva E. Enhanced heavy metal removal from acid mine drainage wastewater using double-oxidized multiwalled carbon nanotubes. *Molecules*. 2020 Jan;25(1):111.
- [116] Wang HJ, Zhou AL, Peng F, Yu H, Chen LF. Adsorption characteristic of acidified carbon nanotubes for heavy metal Pb (II) in aqueous solution. *Materials Science and Engineering: A*. 2007 Sep 25;466(1-2):201-6.
- [117] Yang S, Li J, Shao D, Hu J, Wang X. Adsorption of Ni (II) on oxidized multi-walled carbon nanotubes: effect of contact time, pH, foreign ions and PAA. *Journal of hazardous materials*. 2009 Jul 15;166(1):109-16.
- [118] Gupta VK, Agarwal S, Saleh TA. Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. *Journal of hazardous materials*. 2011 Jan 15;185(1):17-23.
- [119] Ntim SA, Mitra S. Adsorption of arsenic on multiwall carbon nanotube-zirconia nanohybrid for potential drinking water purification. *Journal of colloid and interface science*. 2012 Jun 1;375(1):154-9.
- [120] Tang WW, Zeng GM, Gong JL, Liu Y, Wang XY, Liu YY, Liu ZF, Chen L, Xhang XR, Tu DZ. Simultaneous adsorption of atrazine and Cu(II) from wastewater by magnetic multi-walled carbon nanotubes. *Chem. Eng. J*. 2012; 21-212: 470-478.
- [121] Wang B, Wu T, Angaiah S, Murugadoss V, Ryu JE, Wujcik EK, Lu N, Young DP, Gao Q, Guo Z. Development of nanocomposite adsorbents for heavy metal removal from wastewater. *ES Materials & Manufacturing*. 2018 Dec 4;2(2):35-44.
- [122] Sarma GK, Gupta SS, Bhattacharyya KG. Nanomaterials as versatile adsorbents for heavy metal ions in water: a review. *Environmental Science and Pollution Research*. 2019 Mar 8;26(7):6245-78.
- [123] Luo C, Tian Z, Yang B, Zhang L, Yan S. Manganese dioxide/iron oxide/acid oxidized multi-walled carbon nanotube magnetic nanocomposite for enhanced hexavalent chromium removal. *Chemical Engineering Journal*. 2013 Dec 1;234:256-65.
- [124] Ge L, Wang W, Peng Z, Tan F, Wang X, Chen J, Qiao X. Facile fabrication of Fe@MgO magnetic nanocomposites for efficient removal of heavy metal ion and dye from water. *Powder Technology*. 2018 Feb 15;326:393-401.
- [125] Stafiej A, Pyrzyńska K. Adsorption of heavy metal ions with carbon nanotubes. *Separation and purification technology*. 2007 Dec 1;58(1):49-52.
- [126] Gao Z, Bandosz TJ, Zhao Z, Han M, Qiu J. Investigation of factors affecting adsorption of transition metals on oxidized carbon nanotubes. *Journal of Hazardous Materials*. 2009 Aug 15;167(1-3):357-65.
- [127] Musielak M, Gagor A, Zawisza B, Talik E, Sitko R. Graphene oxide/carbon

nanotube membranes for highly efficient removal of metal ions from water. *ACS applied materials & interfaces*. 2019 Jul 18;11(31):28582-90.

[128] Rao GP, Lu C, Su F. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review. *Separation and purification technology*. 2007 Dec 1;58(1):224-31.

[129] Chen GC, Shan XQ, Zhou YQ, Shen XE, Huang HL, Khan SU. Adsorption kinetics, isotherms and thermodynamics of atrazine on surface oxidized multiwalled carbon nanotubes. *Journal of Hazardous Materials*. 2009 Sep 30;169(1-3):912-8.

[130] Verma B, Sewani H, Balomajumder C. Synthesis of carbon nanotubes via chemical vapor deposition: an advanced application in the Management of Electroplating Effluent. *Environmental Science and Pollution Research*. 2020 Feb 8:1-2.

[131] Egbosiuba TC, Abdulkareem AS, Kovo AS, Afolabi EA, Tijani JO, Roos WD. Enhanced adsorption of As (V) and Mn (VII) from industrial wastewater using multi-walled carbon nanotubes and carboxylated multi-walled carbon nanotubes. *Chemosphere*. 2020 Apr 21:126780.

[132] Ihsanullah, Al-Khaldi FA, Abu-Sharkh B, Abulkibash AM, Qureshi MI, Laoui T, Atieh MA. Effect of acid modification on adsorption of hexavalent chromium (Cr (VI)) from aqueous solution by activated carbon and carbon nanotubes. *Desalination and Water Treatment*. 2016 Apr 2;57(16):7232-44.

[133] Tawabini BS, Al-Khaldi SF, Khaled MM, Atieh MA. Removal of arsenic from water by iron oxide nanoparticles impregnated on carbon nanotubes. *Journal of Environmental Science and Health, Part A*. 2011 Jan 31;46(3):215-23.

[134] Chen H, Li J, Shao D, Ren X, Wang X. Poly (acrylic acid) grafted multiwall carbon nanotubes by plasma techniques for Co (II) removal from aqueous solution. *Chemical engineering journal*. 2012 Nov 1;210:475-81.

[135] Hayati B, Maleki A, Najafi F, Daraei H, Gharibi F, McKay G. Synthesis and characterization of PAMAM/CNT nanocomposite as a super-capacity adsorbent for heavy metal (Ni<sup>2+</sup>, Zn<sup>2+</sup>, As<sup>3+</sup>, Co<sup>2+</sup>) removal from wastewater. *Journal of Molecular Liquids*. 2016 Dec 1;224:1032-40.

[136] Baby R, Saifullah B, Hussein MZ. Carbon nanomaterials for the treatment of heavy metal-contaminated water and environmental remediation. *Nanoscale Research Letters*. 2019 Dec 1;14(1):341.

[137] Ouni L, Ramazani A, Fardood ST. An overview of carbon nanotubes role in heavy metals removal from wastewater. *Frontiers of Chemical Science and Engineering*. 2019 May 22:1-22.

[138] Verma B, Balomajumder C. Surface modification of one-dimensional Carbon Nanotubes: A review for the management of heavy metals in wastewater. *Environmental Technology & Innovation*. 2020 Feb 1;17:100596.

[139] Zhang BT, Zheng X, Li HF, Lin JM. Application of carbon-based nanomaterials in sample preparation: A review. *Analytica chimica acta*. 2013 Jun 19;784:1-7.

[140] Malik S. Structural and electronic properties of nano-carbon materials such as graphene, nanotubes and fullerenes. *Nature*. 1985;318:162-3.

[141] Valcárcel M, Cárdenas S, Simonet BM, Moliner-Martínez Y, Lucena R. Carbon nanostructures as sorbent materials in analytical processes. *TrAC Trends in Analytical Chemistry*. 2008 Jan 1;27(1):34-43.

- [142] Zhang M, Gao B, Cao X, Yang L. Synthesis of a multifunctional graphene-carbon nanotube aerogel and its strong adsorption of lead from aqueous solution. *Rsc Advances*. 2013;3(43):21099-105.
- [143] Alekseeva OV, Bagrovskaya NA, Noskov AV. Sorption of heavy metal ions by fullerene and polystyrene/fullerene film compositions. *Protection of Metals and Physical Chemistry of Surfaces*. 2016 May 1;52(3):443-7.
- [144] Lalia, B.S.; Kochkodan, V.; Hashaikh, R.; Hilal, N. A review on membrane fabrication: Structure, properties and performance relationship. *Desalination* 2013, 326, 77-95.
- [145] Djordjevic, A.; Srdjenovic, B.; Seke, M.; Petrovic, D.; Injac, R.; Mrdjanovic, J. Review of Synthesis and Antioxidant Potential of Fullerenol Nanoparticles. *J. Nanomater.* 2015, 2015, 1-15.
- [146] Jani M, Arcos-Pareja JA, Ni M. Engineered Zero-Dimensional Fullerene/Carbon Dots-Polymer Based Nanocomposite Membranes for Wastewater Treatment. *Molecules*. 2020 Jan;25(21):4934.
- [147] Samonin VV, Nikonova VY, Podvyaznikov ML. Sorption properties of fullerene-modified activated carbon with respect to metal ions. *Protection of Metals*. 2008 Mar 1;44(2):190-2.
- [148] Samonin VV, Nikonova VY, Podvyaznikov ML. Carbon adsorbents on the basis of the hydrolytic lignin modified with fullerenes in producing. *Russian Journal of Applied Chemistry*. 2014 Feb 1;87(2):190-3.
- [149] Geim AK. Graphene: status and prospects. *science*. 2009 Jun 19;324(5934):1530-4.
- [150] Novoselov KS, Fal VI, Colombo L, Gellert PR, Schwab MG, Kim K. A roadmap for graphene. *nature*. 2012 Oct;490(7419):192-200.
- [151] Gopalakrishnan A, Krishnan R, Thangavel S, Venugopal G, Kim SJ. Removal of heavy metal ions from pharma-effluents using graphene-oxide nanosorbents and study of their adsorption kinetics. *Journal of Industrial and Engineering Chemistry*. 2015 Oct 25;30:14-9.
- [152] Huang ZH, Zheng X, Lv W, Wang M, Yang QH, Kang F. Adsorption of lead (II) ions from aqueous solution on low-temperature exfoliated graphene nanosheets. *Langmuir*. 2011 Jun 21;27(12):7558-62.
- [153] Zhao G, Li J, Ren X, Chen C, Wang X. Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. *Environmental science & technology*. 2011 Dec 15;45(24):10454-62.
- [154] Cong HP, Ren XC, Wang P, Yu SH. Macroscopic multifunctional graphene-based hydrogels and aerogels by a metal ion induced self-assembly process. *ACS nano*. 2012 Mar 27;6(3):2693-703.
- [155] Yu G, Lu Y, Guo J, Patel M, Bafana A, Wang X, Qiu B, Jeffryes C, Wei S, Guo Z, Wujcik EK. Carbon nanotubes, graphene, and their derivatives for heavy metal removal. *Advanced Composites and Hybrid Materials*. 2018 Mar 1;1(1):56-78.
- [156] Deng X, Lü L, Li H, Luo F. The adsorption properties of Pb (II) and Cd (II) on functionalized graphene prepared by electrolysis method. *Journal of Hazardous Materials*. 2010 Nov 15;183(1-3):923-30.
- [157] Ren X, Li J, Tan X, Wang X. Comparative study of graphene oxide, activated carbon and carbon nanotubes as adsorbents for copper decontamination. *Dalton Transactions*. 2013;42(15):5266-74.

- [158] Zhang M, Gao B, Cao X, Yang L. Synthesis of a multifunctional graphene–carbon nanotube aerogel and its strong adsorption of lead from aqueous solution. *Rsc Advances*. 2013;3(43):21099-105.
- [159] Arshad F, Selvaraj M, Zain J, Banat F, Haija MA. Polyethylenimine modified graphene oxide hydrogel composite as an efficient adsorbent for heavy metal ions. *Separation and Purification Technology*. 2019 Jan 31;209:870-80.
- [160] Wu Z, Deng W, Zhou W, Luo J. Novel magnetic polysaccharide/graphene oxide@ Fe<sub>3</sub>O<sub>4</sub> gel beads for adsorbing heavy metal ions. *Carbohydrate polymers*. 2019 Jul 15;216:119-28.
- [161] Liu X, Ma R, Wang X, Ma Y, Yang Y, Zhuang L, Zhang S, Jehan R, Chen J, Wang X. Graphene oxide-based materials for efficient removal of heavy metal ions from aqueous solution: A review. *Environmental pollution*. 2019 Sep 1;252:62-73.
- [162] Farooq MU, Jalees MI. Application of Magnetic Graphene Oxide for Water Purification: Heavy Metals Removal and Disinfection. *Journal of Water Process Engineering*. 2020 Feb 1;33:101044.
- [163] Li L, Zhao L, Ma J, Tian Y. Preparation of graphene oxide/chitosan complex and its adsorption properties for heavy metal ions. *Green Processing and Synthesis*. 2020 Jun 6;9(1):294-303.
- [164] Zhao G, Ren X, Gao X, Tan X, Li J, Chen C, Huang Y, Wang X. Removal of Pb (II) ions from aqueous solutions on few-layered graphene oxide nanosheets. *Dalton transactions*. 2011;40(41):10945-52.
- [165] Jiang H, Yang Y, Lin Z, Zhao B, Wang J, Xie J, Zhang A. Preparation of a novel bio-adsorbent of sodium alginate grafted polyacrylamide/graphene oxide hydrogel for the adsorption of heavy metal ion. *Science of The Total Environment*. 2020 Nov 20;744:140653.
- [166] Bhatnagar A, Sillanpää M. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review. *Chemical engineering journal*. 2010 Mar 1;157(2-3):277-96
- [167] Bhatnagar A, Sillanpää M, Witek-Krowiak A. Agricultural waste peels as versatile biomass for water purification—A review. *Chemical Engineering Journal*. 2015 Jun 15;270:244-71.
- [168] Owamah HI. Biosorptive removal of Pb (II) and Cu (II) from wastewater using activated carbon from cassava peels. *Journal of Material Cycles and Waste Management*. 2014 Apr 1;16(2):347-58.
- [169] Sreenivas KM, Inarkar MB, Gokhale SV, Lele SS. Re-utilization of ash gourd (*Benincasahispida*) peel waste for chromium (VI) biosorption: Equilibrium and column studies. *Journal of Environmental Chemical Engineering*. 2014 Mar 1;2(1):455-62.
- [170] Pehlivan E, Altun T, Parlayici Ş. Modified barley straw as a potential biosorbent for removal of copper ions from aqueous solution. *Food chemistry*. 2012 Dec 15;135(4):2229-34.
- [171] Kumar PS, Ramalingam S, Kirupha SD, Murugesan A, Vidhyadevi T, Sivanesan S. Adsorption behavior of nickel (II) onto cashew nut shell: Equilibrium, thermodynamics, kinetics, mechanism and process design. *Chemical Engineering Journal*. 2011 Feb 15;167(1):122-31.
- [172] Feng N, Guo X, Liang S. Adsorption study of copper (II) by chemically modified orange peel. *Journal of Hazardous Materials*. 2009 May 30;164(2-3):1286-92.

- [173] Lu D, Cao Q, Cao X, Luo F. Removal of Pb (II) using the modified lawny grass: Mechanism, kinetics, equilibrium and thermodynamic studies. *Journal of Hazardous Materials*. 2009 Jul 15;166(1):239-47.
- [174] Zou W, Zhao L, Zhu L. Efficient uranium (VI) biosorption on grapefruit peel: kinetic study and thermodynamic parameters. *Journal of Radioanalytical and Nuclear Chemistry*. 2012 Jun 1;292(3):1303-15.
- [175] Al-Othman ZA, Ali R, Naushad M. Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: adsorption kinetics, equilibrium and thermodynamic studies. *Chemical Engineering Journal*. 2012 Mar 1;184:238-47.
- [176] Abdelhafez AA, Li J. Removal of Pb (II) from aqueous solution by using biochars derived from sugar cane bagasse and orange peel. *Journal of the Taiwan Institute of Chemical Engineers*. 2016 Apr 1;61:367-75.
- [177] Iqbal M, Saeed A, Kalim I. Characterization of adsorptive capacity and investigation of mechanism of Cu<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> adsorption on mango peel waste from constituted metal solution and genuine electroplating effluent. *Separation Science and Technology*. 2009 Oct 30;44(15):3770-91.
- [178] Basci N, Kocadagistan E, Kocadagistan B. Biosorption of copper (II) from aqueous solutions by wheat shell. *Desalination*. 2004 Apr 1;164(2):135-40.
- [179] Yu W, Hu J, Yu Y, Ma D, Gong W, Qiu H, Hu Z, Gao HW. Facile preparation of sulfonated biochar for highly efficient removal of toxic Pb (II) and Cd (II) from wastewater. *Science of The Total Environment*. 2020 Aug 6;750:141545.
- [180] Sanka PM, Rwiza MJ, Mtei KM. Removal of Selected Heavy Metal Ions from Industrial Wastewater Using Rice and Corn Husk Biochar. *Water, Air, & Soil Pollution*. 2020 May;231:1-3.
- [181] Khalil U, Shakoor MB, Ali S, Rizwan M, Alyemeni MN, Wijaya L. Adsorption-reduction performance of tea waste and rice husk biochars for Cr (VI) elimination from wastewater. *Journal of Saudi Chemical Society*. 2020 Nov 1;24(11):799-810.
- [182] Shen Z, Zhang Y, McMillan O, Jin F, Al-Tabbaa A. Characteristics and mechanisms of nickel adsorption on biochars produced from wheat straw pellets and rice husk. *Environmental Science and Pollution Research*. 2017 May 1;24(14):12809-19.
- [183] Shi J, Fan X, Tsang DC, Wang F, Shen Z, Hou D, Alessi DS. Removal of lead by rice husk biochars produced at different temperatures and implications for their environmental utilizations. *Chemosphere*. 2019 Nov 1;235:825-31.
- [184] Khalil U, Shakoor MB, Ali S, Rizwan M, Alyemeni MN, Wijaya L. Adsorption-reduction performance of tea waste and rice husk biochars for Cr (VI) elimination from wastewater. *Journal of Saudi Chemical Society*. 2020 Nov 1;24(11):799-810.
- [185] Gao LY, Deng JH, Huang GF, Li K, Cai KZ, Liu Y, Huang F. Relative distribution of Cd<sup>2+</sup> adsorption mechanisms on biochars derived from rice straw and sewage sludge. *Bioresource Technology*. 2019 Jan 1;272:114-22.
- [186] Fan S, Zhang L. Production and characterization of tea waste-based biochar and its application in treatment of Cd-containing wastewater. *Biomass Conversion and Biorefinery*. 2019 Nov 26:1-4.
- [187] Akgül G, Maden TB, Diaz E, Jiménez EM. Modification of tea biochar

with Mg, Fe, Mn and Al salts for efficient sorption of  $\text{PO}_4^{3-}$  and  $\text{Cd}^{2+}$  from aqueous solutions. *Journal of Water Reuse and Desalination*. 2019 Mar 1;9(1):57-66.

[188] Ho SH, Yang ZK, Nagarajan D, Chang JS, Ren NQ. High-efficiency removal of lead from wastewater by biochar derived from anaerobic digestion sludge. *Bioresource Technology*. 2017 Dec 1;246:142-9.

[189] Bayat B. Combined removal of zinc (II) and cadmium (II) from aqueous solutions by adsorption onto high-calcium Turkish fly ash. *Water, Air, and Soil Pollution*. 2002 May 1;136(1-4):69-92.

[190] Wang S, Li L, Zhu ZH. Solid-state conversion of fly ash to effective adsorbents for Cu removal from wastewater. *Journal of Hazardous Materials*. 2007 Jan 10;139(2):254-9.

[191] Visa M, Bogatu C, Duta A. Simultaneous adsorption of dyes and heavy metals from multicomponent solutions using fly ash. *Applied Surface Science*. 2010 Jun 15;256(17):5486-91.

[192] Sočo E, Kalemekiewicz J. Adsorption of nickel (II) and copper (II) ions from aqueous solution by coal fly ash. *Journal of Environmental Chemical Engineering*. 2013 Sep 1;1(3):581-8.

[193] Al-Harashsheh MS, Al Zboon K, Al-Makhadmeh L, Hararah M, Mahasneh M. Fly ash based geopolymer for heavy metal removal: A case study on copper removal. *Journal of Environmental Chemical Engineering*. 2015 Sep 1;3(3):1669-77.

[194] Ma J, Qin G, Zhang Y, Sun J, Wang S, Jiang L. Heavy metal removal from aqueous solutions by calcium silicate powder from waste coal fly-ash. *Journal of Cleaner Production*. 2018 May 1;182:776-82.

[195] Nguyen TC, Loganathan P, Nguyen TV, Kandasamy J, Naidu R, Vigneswaran S. Adsorptive removal of five heavy metals from water using blast furnace slag and fly ash. *Environmental Science and Pollution Research*. 2018 Jul 1;25(21):20430-8.

[196] Park JH, Eom JH, Lee SL, Hwang SW, Kim SH, Kang SW, Yun JJ, Cho JS, Lee YH, Seo DC. Exploration of the potential capacity of fly ash and bottom ash derived from wood pellet-based thermal power plant for heavy metal removal. *Science of The Total Environment*. 2020 Oct 20;740:140205.

[197] Nadaroglu H, Kalkan E, Demir N. Removal of copper from aqueous solution using red mud. *Desalination*. 2010 Feb 1;251(1-3):90-5.

[198] Sahu RC, Patel R, Ray BC. Adsorption of Zn (II) on activated red mud: Neutralized by  $\text{CO}_2$ . *Desalination*. 2011 Jan 31;266(1-3):93-7

[199] Bhatnagar A, Vilar VJ, Botelho CM, Boaventura RA. A review of the use of red mud as adsorbent for the removal of toxic pollutants from water and wastewater. *Environmental Technology*. 2011 Feb 1;32(3):231-49.

[200] Nadaroglu H, Kalkan E. Removal of cobalt (II) ions from aqueous solution by using alternative adsorbent industrial red mud waste material. *International Journal of Physical Sciences*. 2012 Feb 23;7(9):1386-94.

[201] Pulford ID, Hargreaves JS, Ďurišová J, Kramulova B, Girard C, Balakrishnan M, Batra VS, Rico JL. Carbonised red mud—a new water treatment product made from a waste material. *Journal of Environmental Management*. 2012 Jun 15;100:59-64.

[202] Sahu MK, Mandal S, Dash SS, Badhai P, Patel RK. Removal of Pb (II) from aqueous solution by acid activated red mud. *Journal of Environmental*



Chemical Engineering. 2013 Dec 1;1(4):1315-24.

[203] Chen X, Guo Y, Ding S, Zhang H, Xia F, Wang J, Zhou M. Utilization of red mud in geopolymer-based pervious concrete with function of adsorption of heavy metal ions. *Journal of Cleaner Production*. 2019 Jan 10;207:789-800.

[204] Xue Y, Wu S, Zhou M. Adsorption characterization of Cu (II) from aqueous solution onto basic oxygen furnace slag. *Chemical Engineering Journal*. 2013 Sep 1;231:355-64.

[205] Sarkar C, Basu JK, Samanta AN. Removal of Ni<sup>2+</sup> ion from waste water by Geopolymeric Adsorbent derived from LD Slag. *Journal of Water Process Engineering*. 2017 Jun 1;17:237-44.

[206] Srivastava SK, Singh AK, Sharma A. Studies on the uptake of lead and zinc by lignin obtained from black liquor—a paper industry waste material. *Environmental Technology*. 1994 Apr 1;15(4):353-61.

[207] Zwain HM, Vakili M, Dahlan I. Waste material adsorbents for zinc removal from wastewater: a comprehensive review. *International Journal of Chemical Engineering*. 2014 Jan 1;2014.

[208] Crini G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in polymer science*. 2005 Jan 1;30(1):38-70.

[209] Crini G (2010) Wastewater treatment by sorption. In: Crini G, Badot PM (eds) *Sorption processes and pollution*, chap 2. PUFC, Besançon, pp 39-78.

[210] Davis TA, Volesky B, Mucci A. A review of the biochemistry of heavy metal biosorption by brown algae. *Water research*. 2003 Nov 1;37(18):4311-30.

[211] Veglio F, Beolchini F. Removal of metals by biosorption: a review. *Hydrometallurgy*. 1997 Mar 1;44(3):301-16.

[212] Srivastava S, Goyal P. Novel biomaterials: decontamination of toxic metals from wastewater. *Springer Science & Business Media*; 2010 Apr 26.

[213] Naja G, Volesky B. The mechanism of metal cation and anion biosorption. In: *Microbial biosorption of metals 2011* (pp. 19-58). Springer, Dordrecht.

[214] Michalak I, Chojnacka K, Witek-Krowiak A. State of the art for the biosorption process—a review. *Applied biochemistry and biotechnology*. 2013 Jul 1;170(6):1389-416.

[215] Robalds A, Naja GM, Klavins M. Highlighting inconsistencies regarding metal biosorption. *Journal of hazardous materials*. 2016 Mar 5;304:553-6.