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A Review on Manganese Sources, Occurrences, Negative Impacts, and Potential Treatment Using Adsorption Process

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ABSTRACT

Manganese is one of the most abundant heavy metals that has been detected in surface water lately. This has become an environmental concern as manganese pose negative impacts on the ecosystem and water supply. The current water treatment process faces challenges in the efficient treatment of manganese at a low cost. This paper reviews the sources, occurrences and negative impacts of manganese towards living organisms as well as the treatment using the adsorption process. The potential synthesizes of low cost and environmentally friendly agricultural waste adsorbent to remove manganese is elucidate in this paper. The outcomes have the potential to reduce manganese concentration in the surface water and minimize the cost of water treatment.

Key words: Adsorption, Agricultural Waste, Manganese, Negative Impacts, Occurrences, Sources.

1. INTRODUCTION

Water is a source of life, an essential component to maintain life and all the organisms to survive, as well as a critical element in all social and economic development [1]. In Malaysia, 98% of the total water use is mainly derived from the river [2], [3]. Unfortunately, due to the rapid industrial revolution without appropriate management often results in environmental issues that increased the number of polluted rivers. High amount of wastes from the domestic, industrial, and commercial will end up being disposed into water bodies [3], [4]. This includes the discharge of heavy metals directly or indirectly into the river [5], [6].

Heavy metal appears as a natural element in the environment. It is a major environmental problem due to its toxicity, accumulation, non-biodegradable and persistent in water [7], [8]. Heavy metals are categorizing as the element having a density above 5g/cm^3, and those elements in this category are usually extremely water-soluble, known for its toxicity and cancer-prone contaminant. Heavy metal could pose a hazard to the human as well as the flora and fauna of the receiving water bodies. Among essential elements that are considered as heavy metals are zinc, selenium, manganese, iron, and aluminium, while the non-essential elements as heavy metals are copper, chromium, nickel, arsenic, cadmium, mercury, lead, etc. [9]–[11]. The heavy metals that contain in surface water and groundwater is a serious global concern, especially in surface water because it can transport the heavy metals over a long distance and contaminate vast area [12].

The industrial effluents that produced heavy metals and discharge it to the river had alarmed the public and waterworks industry [13]. About 300–400 million tonnes (MT) of heavy metals, toxic sludge, solvents, and other harmful materials from an industrial activity are being disposed into the water bodies annually [14]. The waste generated in Malaysia particularly that contain heavy metals is generated from the industries that manufacture electroplating, metal treatment and steel fabrication [15]. Apart from that, the contamination of heavy metals that are detected in the water bodies also came from the operations of mine, metal smelters, microelectronics, radiator, batteries, plastics, textiles manufacturers, wood preservatives, and agricultural activity [16].

Manganese (Mn) is an essential element that can be found in the environment and naturally occur in certain geographical condition. It is commonly high concentration in soil and water due to natural occurrences. It can be detected in surface and groundwater through anthropic activities [17]–[19]. According to a study by [20], manganese can be found in surface and groundwater with inconsistent concentration levels. This element is the 12th most abundant in the earth's crust, usually found in water, rocks, soil and food [21]. Manganese is a pinkish-grey, chemically active, strong metal with a density of 7.43 g/cm^3. It has the boiling melting point of 1962^{o}C and 1244^{o}C, respectively. It can react with water and iron that form rust and dissolve in dilute acids [20], [22]–[24]. Table 1 shows the chemical and physical characteristics of manganese.

Manganese exists in water as a bi-valent ion (Mn^{2+}) and soluble in water, but due to its organoleptic properties, it is considered a pollutant. Manganese (+2) is the most stable oxidation state, which appears as a pale pink colour. When exposed to air, manganese that dissolved in water becomes insoluble and turn brown-red colour [20], [25]. Manganese is also known as trace minerals because it is needed in the human body at a certain amount that functions in many enzymes and cellular reactions. But excessive intake of this mineral may cause manganese toxicity that disturbs the central nervous system [26]. Furthermore, manganese also causes turbidity and a black-brown colour to drinking water [27],[28].

Table 1: Properties of manganese

Properties	Manganese	References
		[29]
Element name/ Symbol	Manganese, Mg	[30]
Atomic number	25	[31]
Atomic weight (g/mol)	54.9380	[24]
Electronegativity (Pauling Scale)	1.55	[32]
Colour	Pinkish-gray	[20]
Melting point (^{o}C)	1244	[23]
Boiling point (^{o}C)	1962	
Density (g/cm^3)	7.21-7.44 at 20 ^{o}C	
Water solubility (g/L)	Decomposes	

1.1 Sources of manganese contamination

The number of water sources that are polluted in Malaysia is increasing over time due to the uncontrollable waste disposal and effluent discharge from the industry [20]. The high concentration of manganese in the water source will pose a threat to human health especially when the contaminant enters the food chain [33], [34]. Water sources that are contaminated by manganese are due to anthropogenic activities such as discharge of industrial wastewater effluent, mining, pesticides, organic chemicals, rubber, plastics, wood products, processing of metal, tanneries, and pharmaceuticals. This contaminant will become surface runoff and contaminate water bodies downstream from the industrial area [20], [35].

The point source of manganese contamination is from the wastewater treatment plant, quarry operation of mine, and discharge of industrial effluent such as steel alloy production, battery manufacturing, food processing, etc. This because manganese is widely utilized by the industry that produced steel alloys, batteries, glass, fireworks, fertilizer, stock food additive and organic synthesis catalyst [24]. Table 2 shows the major sources of manganese and other heavy metals from various industries. In the iron and steel alloys production, manganese is usually used as an oxidant for cleaning, bleaching, and disinfection [20]. Reference [36] reveals that manganese is mainly used in the steel manufacturing process that approximately accounts for 90% of the total manganese demand. Figure 1 shows the projection of global manganese production from the year 2012 to 2022. Manganese production had been significantly increased from the year 2016 to 2018. It is projected to be slightly decreasing in the future years.

Table 2: Major sources of manganese and other heavy metals from various industry [37]

Industrial effluents	Pb	Cu	Mn
Pulp and paper mills	√	√	-
Fertilizers	√	√	√
Inorganic chemicals, alkali, chlorine	√	-	-
Petroleum refining	√	√	-
Organic chemicals, petrochemicals	√	-	-
Basic Steelworks foundries, iron-steel refining	√	√	√
Basic non-ferrous metal works foundries	√	√	√
Motor vehicle, aircraft, and metal plating	-	√	-

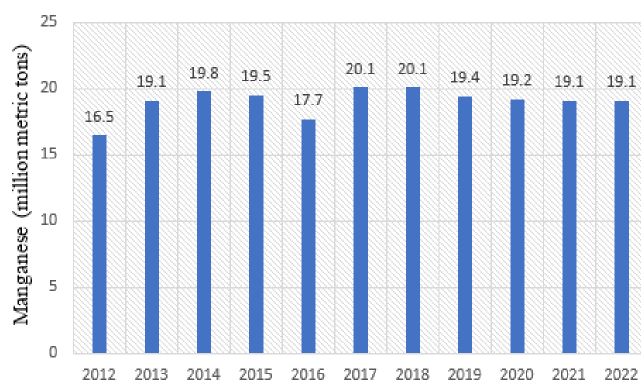


Figure 1: Projection of global manganese production (in million tonnes) from 2012-2022 [38]

The [38] reported that the global demand for steel in 2019 had increased by 1.3% (1,735 million tonnes) from 2018. By 2020, it is predicted that the demand will grow by 1.0%, reaching 1,752 million tonnes. In 2018, Malaysia ranked 38th with 3,500 million tonnes of crude steel production among 50 other countries around the world [39]. With growing numbers of steel production reported worldwide, the manganese contamination will affect the public health and environment.

The non-point source contamination results from tin mine runoff, landfills, weathering, volcanic activities and natural occurrences below the ground. This manganese will end up in the river or groundwater that eventually enters the water treatment plant. However, during the water treatment process, some of the manganese especially insoluble form may not be removed in the treatment plant. Thus, this will contaminate the drinking water source of the consumer. Figure 2 shows the possible routes of manganese contamination in the environment. Apart from that, manganese can also be found in milk or soy-based infant formula, foods such as nuts, oats, tea, spinach, as well as pesticides and petrol additives [20], [40]. Soy-based formulas contain high manganese than cow-based formulas and human breast milk [41]. Figure 3 shows the sources of manganese.

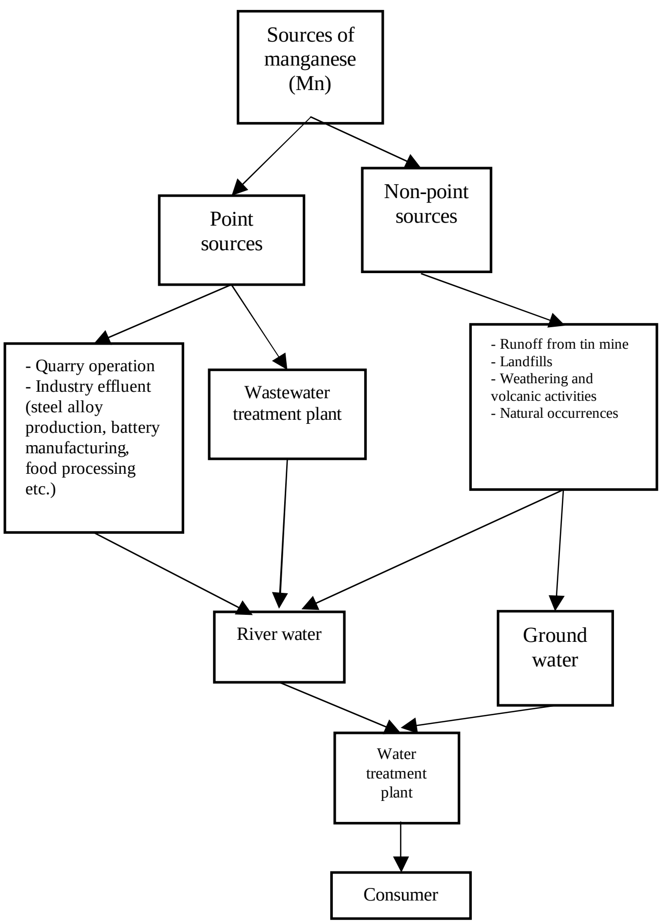


Figure 2: Routes of manganese contamination

Figure 3: Sources of manganese [26], [40]

1.2 Occurrences of manganese contamination

Manganese able to accumulate for long period and exist in the water, sediments and living things. It is transferred into sediments by physical, chemical or biological processes that can affect living organisms as the waterbody is exposed to the toxic contaminant [42]. Metals tend to accumulate or reacts with particulates and finally settles in bottom sediments of streams. Eventually, only small amounts of free metal ions that are detected dissolved in water [43], [44].

Table 3 shows the range of manganese concentrations detected in waterbody worldwide. The highest concentration of 17 mg/L has been detected in Xiangjiang River, Chine at site 6 (submerged area) due to the severe metal pollution from industrial effluents of which manganese and ferum are presence in both sediment pore water and overlying water. [24] stated that manganese was found in mine water effluent. In Malaysia, the manganese concentration was detected in Kepayang River, Perak about 4.7 mg/L that is caused by tin mine effluents. This has exceeded the standard for raw and drinking water quality of 0.2 mg/L and 0.1 mg/L, respectively as set by the Ministry of Health, Malaysia [45].

Other studies that conducted water sampling at Tar Creek, Lytle Creek also detect manganese ions in mine waste pile runoff, mine drainage discharge and Tar Creek upstream [46]. Contamination water sources of manganese could also cause by metal corrosion, atmospheric deposition, soil erosion, leaching, re-suspension of sediment and metal evaporation from water sources to soil and groundwater [47].

Quarry operations also one of the contributors to manganese pollution in water. According to the study by [48], the presence of manganese with inconsistent concentration due to quarry activities is reported in Iyuku. Quarry operations had caused serious environmental degradation, possible contamination in groundwater and soil, in which the contamination will be streamed to the nearby water bodies.

The presence of dissolved manganese in some deep lakes and reservoirs might be due to stratification results from the occurrence of anaerobic conditions at the bottom sediments. Water that contained manganese would cause stained, bad taste and appearance to the water. Also, manganese in water that exposed to air will become chalky and turn brown-red colour due to the oxidation of manganese to Mn^{4+} states which are not suitable for consumption [49].

A high level of manganese was also detected due to the discharge from the dam impoundment. The release of dam water may cause an ecological problem on the downstream. The suspended matter may adsorb pollutants flowing in river water, then accumulate in the sedimentation and deposited into the reservoir. Consequently, the flushing of dam water might release these pollutants from the sediment into the river [50].

Table 3: The occurrences of manganese in the waterbody worldwide

Location	Concentration (mg/L)	References
Kepayang River, Perak, Malaysia	4.673	[52]
Tar Creek Mining (Oklahoma, USA)	0.919 –2.43	[47]
Jiulong River Estuary, China	17	[53]
New South Wales, Australia	0.14	[54]
Xiangjiang River, China	0.022- 2.737	[55]
Mvudi River, South Africa	0.081–0.521	[56]
Eleias Prefecture, Greece	0-3.7	[57]

1.3 Negative impacts

Heavy metal pollution is the main environmental concern lately where manganese is one of the contaminants that has been detected in the river due to the discharge of industrial effluent. The United States Environmental Protection Agency and the EU Directive have established 0.05 mg/L as the maximum manganese concentration level in domestic water supplies [31]. In addition, the World Health Organizations (2011) also have set a standard for manganese should not exceed 0.05 mg/L of the permitted limits.

Manganese in drinking water usually will affect aesthetic water quality and operational problems in the distribution systems like corrosion of iron pipe [27], [51]. The formation coatings of oxide layers in corrosion of pipes in drinking water system due to the presence of toxic metals such as manganese, lead, copper and iron will affect the water flow, deteriorating water quality and increase distribution cost [52]. Excessive presence of manganese in water may cause reddish colour, stains to the laundry, bad odour and taste to the drinking water. The presence of manganese could form deposits in distribution pipes, pressure tanks or heater, which lead to excessive cost of maintenance either for domestic or industrial operation [53].

Furthermore, the growth of several types of micro-organisms that is chlorine-tolerant due to the presence of manganese also arises the problem in water distribution system. As a result, the biota will form sites for harmful organisms that will affect human health [54].

High concentration of manganese in drinking water is considered unacceptable. This is because Mn^{2+} will be oxidized to Mn^{4+} and precipitated when the water is exposed to air. The precipitate will stain the laundry and utensils of household. Discoloration of products from the usage of water that contains manganese in the industry of finished paper, textile, food, and beverage products had caused serious losses to an industrial economy and also reduce the carrying capacity of the pipeline. Manganese precipitate also causes bad odour with metallic, bitter and medicinal taste to the water [54].

Overexposure and ingestion to high doses of manganese from drinking water can cause neurological disorders [19]. It is reported that excessive accumulation of manganese in specific brain areas produce neurotoxicity that leads to a degenerative brain disorder [55], [56]. Neurotoxicity by inhalation has been commonly known, especially among workers and miners with relatively high levels of exposure. Although manganese is an essential mineral, there have been concerns by many studies that over consume of manganese in drinking water could lead to neurological adverse effects in terms of intellectual and cognitive development [57].

Table 4: Adverse effects of manganese exposure

Adverse effects	References
Affect aesthetic water quality such as reddish colour, bad odour and taste to the drinking water.	[27], [58], [60]
Operational problem in the distribution systems e.g. corrosion of the iron pipe.	[27], [58]
The growth of several types of micro-organisms that is chlorine-tolerant in water distribution system.	[61]
Neurological adverse effects in terms of intellectual and cognitive development.	[64]
Lower IQ level.	[18]

Impotence in men than have been prolonged exposure.	[65]
Manganism condition that is similar to Parkinson's disease.	[17], [41]
Neurological disorder characterized by parkinsonism, dystonia, cognitive and behavioural dysfunction.	[66]
Impaired manual dexterity, speed, short-term memory and visual recognition in children.	[24]
Memory disability, repetitive stammered speech, poor balance, coordination, and motor skills in children.	[24]
Accumulate in the food chain and environment.	[24]
Occurrence of tremors and coordination failure when uptake through the skin.	[20]

Research finds that long-term exposure to manganese in drinking water acts differently with cognition levels in boys and girls. The girls with high levels exposure to manganese in drinking water most probably have lower IQ Performance than the boys [18]. While for adults specifically men, prolonged exposure towards high manganese could lead to impotence [58].

Manganese contains naturally in several foods such as nuts, oats, tea, spinach that is needed in a small amount for optimal biological functioning of living organisms [17], [26], [40]. However, high dosage exposure to manganese can produce toxic effects and lead to manganism condition, which results in psychological, emotional disturbances and motor symptoms that are similar to Parkinson's disease [17], [40]. According to studies by [59], the initial toxic symptoms associated with manganese is psychiatric nature disorder known as locura manganica that resembling schizophrenia, followed by a permanently crippling neurological (extrapyramidal) disorder clinically similar to Parkinson's disease where this chronic manganese poisoning occurs in miners working with manganese ores.

The industrial sector such as mining, welding and battery manufacture are generally affected by manganese toxicity because the workers are more vulnerable during work through fumes inhalation [40]. A study by [60] indicated that occupation that has chronic and high exposure to manganese has been historically connected to a serious, atypical neurological disorder characterized by parkinsonism, dystonia, cognitive and behavioural dysfunction. When manganese uptake through the skin, tremors and coordination failure could occur [20].

Apart from that, adverse neurological conditions such as declines in cognitive and motor function not only occur in occupation, but it is also associated with adults and children that are susceptible to the expose environment [61]. According to studies by [24], children exposed to 240-350 µg/L of manganese in water demonstrate impaired manual dexterity, speed, short-term memory, visual recognition when compared to the children with controlled manganese exposure. Children that drink water containing manganese above 1.0 µg/L had memory disability, repetitive stammered speech, poor balance, coordination, and motor skills.

Moreover, unethical discard of dry-cell batteries or other toxic wastes from industry may contribute greater levels of manganese in water and cause health problems to the public [24]. As opposed to organic wastes, manganese cannot be degraded biologically into other safe forms. Consequently, manganese tends to accumulate in the food chain and environment, thus increasing its threat to the ecosystem [15], [16]. The toxicity from manganese contamination has endangered marine organisms. The contaminant will accumulate in tissues and organs of aquatic organism which then being consumed by humans and eventually caused long-term health risks to humans [42]. Table 4 shows the adverse effects of manganese exposure. While figure 4 displays the pathways of manganese contamination in humans

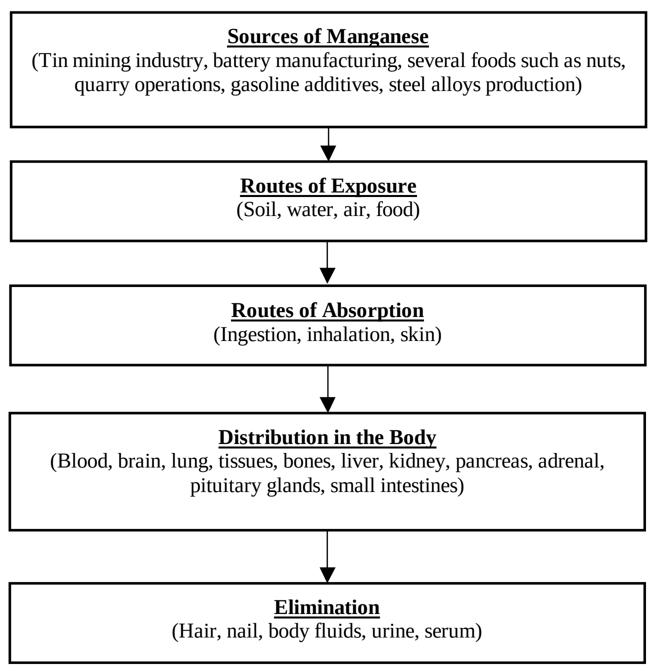


Figure 4: Pathways of manganese contamination in human [41], [62], [63]

2. WATER TREATMENT TECHNOLOGY FOR MANGANESE REMOVAL

In recent years, there has been growing attention towards the adverse impacts of heavy metals on humans and the environment. Nevertheless, the discharge of heavy metal has been improved in many countries due to strict legislation, advanced treatment plant technology, and altered industrial activities. Many conventional methods are available to remove toxic heavy metal [64]. The common treatment technologies that have been developed to treat surface water containing manganese include chemical precipitation, ion exchange, oxidation, electrochemical treatment, ultraviolet irradiation, ozone, and membrane filtration, as shown in figure 5 [7], [52], [65]–[68]. Table 5 shows the performance of water treatment technology in manganese removal.

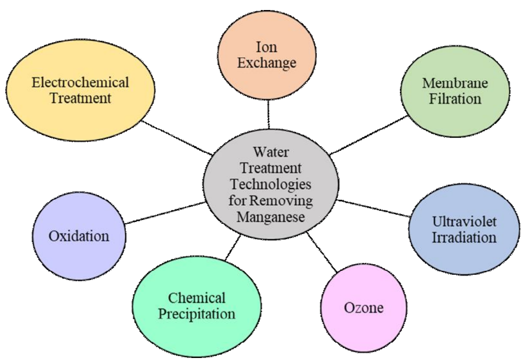


Figure 5: Water treatment technologies for removing manganese

Chemical precipitation is another effective and cheap conventional water treatment to eliminate manganese by adding chemicals to form metal precipitation. But this method is inappropriate to use in water containing low metal ion concentration. Furthermore, the disadvantages of this method are known to be producing a large amount of sludge, hazardous water containing precipitates of insoluble metals which is hard to treat and dispose of, and also involves a great number of chemicals in precipitate the metals [7], [9]. It also requires a large tank to obtain effective precipitation and the cost is high [13].

Apart from that, electrochemical technology is a process involving electron transfer between anode and cathode through the process of an oxidation-reduction reaction. Electrochemical is widely used in treating heavy metal because of the effective redox reaction occurring at anode (oxidation of pollutants) and cathode (reduction of heavy metals). Among the electrochemical technology, electrocoagulation (EC) and electrochemical oxidation (EO) are the most common method used [5], [69], [70]. Nevertheless, the development of this method is restricted because of the high initial capital investment and expensive operating costs of high electricity consumption [31], [70].

Besides, membrane filtration technologies are a great method to be used due to efficient removal, ease of operation, and no pollution loads [6]. Membrane filtration is a selective layer with a porous or non-porous matrix used to create contact between two homogeneous phases to remove pollutants of variable sizes. Four types of membrane filtration process which are reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF), and nanofiltration (NF). However, several drawbacks of this method are poor hydrophilicity, severe membrane fouling, high power demand and maintenance cost for chemical cleaning [71], [72].

The ion exchange process is also a suitable method to remove manganese. It is a physical treatment based on a reversible interchange of ions between the solid and liquid phases. The heavy metal ions will be physically absorbed and associated with functional groups that are attached to the solid medium. Typically, ions in dilute concentrations replace ions of similar charge (lower valence state), but ions in high concentration replace all other ions of similar charge [8], [31], [51]. The disadvantages of the ion exchange process are that the matrix is easily fouled by organic and other solids because it cannot withstand concentrated metal. Therefore, pH is the crucial factor to be considered in this treatment [6]. The advantages and disadvantages of the treatment technologies are summarized in Table 6. The main goal of water treatment is to reduce the risks from biological, chemical and physical contaminants to ensure the water is high in aesthetic quality, taste, odour, and colour that is safe for consumers. Apart from that, water treatment also should be that the process does not cause any operational problems to the system.

Therefore, cost-effective and environmentally friendly technology of water treatment is needed including the requirement to eliminate heavy metal and other organic elements that presence in water sources [20]. All of the water treatment technology applied can remove manganese at certain removal rate. However, most of the methods have drawbacks in terms of treatment capacity, space requirements, complex process, generate a large amount of metallic sludge, increase maintenance, operational costs and required disposal of sludge. Therefore, the treatment methods are not widely applied by the waterworks industry [20], [64], [73]–[75].

3. ADSORPTION PROCESS

The search for economic and environmentally friendly materials for water and wastewater treatment without the generation of hazardous by-products has been in focus recently [76]. The adsorption process is a well-known treatment technology for water that is considered as simple, effective, economical, environmentally friendly, and ease of operation for removal of heavy metal compared to other methods [77], [78]. The process offers flexible design and operation that able to produce treated effluent free of odor, color, and sludge. Adsorption is an attractive and economical process because the adsorbent can be regenerate. This process also able to prevent the production of secondary waste [16], [24], [66]. Adsorption has many advantages over other methods because it produces no sludge during operation and complete removal of metal ions, even from the diluted solutions. According to [79], the adsorption method has the ability to remove pollutants even at a very low concentration with low energy consumption and a variety of raw materials to form the adsorbent [35]. The process of adsorption occurs when a gas or liquid molecules attached to the surface of a solid or a liquid (adsorbent), creates a molecular or atomic film (adsorbate).

Table 5: Water treatment technologies performance in removing manganese

Method used	The optimal condition for maximum manganese removal	Manganese removal efficiency (%)	References
Complexation−ultrafiltration using a copolymer of maleic acid and acrylic acid	i. pH 6.0	99.6	[81]
Solvent extraction, electrodeposition and precipitation methods	i. Completely precipitated at pH 9.0	73	[82]
Peroxymonosulfate-assisted electrooxidation/coagulation coupled with ceramic ultrafiltration membrane	i. Current (I) of 0.2 A ii. Electrolysis time of 60 s iii. pH 7.5	75	[68]
Ultra-thin nanocomposite membranes via dip-coating method composed of chitosan incorporated graphene oxide	i. Low pressure of 3 bars	85	[67]
Advanced oxidation	i. Ozone concentration of 6.2 ppm	97.2	[65]
Ferric Oxyhydroxides Composites	i. pH = 7.5 ii. Contact time of 25 minutes iii. Sodium hypochlorite was 0 to 2.0 iv. The catalyst 0.5 g	98.8	[83]

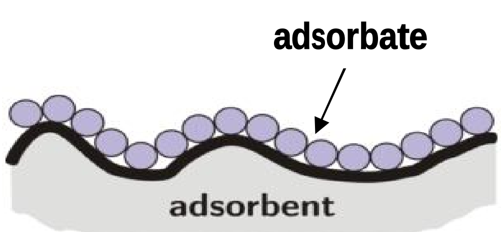
Table 6: Advantages and disadvantages of water treatment technologies for manganese removal [10], [84], [85]

Method	Advantages	Disadvantages
Electrochemical method	i. Metal selective ii. No consumption of chemicals iii. High removal efficiency	i. High capital cost ii. Required high energy iii. Need to control initial solution pH and current density
Membrane filtration	i. High separation of metals ii. Small space requirement iii. No pollution loads	i. High operational cost ii. Membrane fouling iii. Required high energy
Chemical precipitation	i. Simple operation ii. Low capital cost iii. Most metals can be removed	i. Sludge generation ii. Extra operational cost for sludge disposal iii. Ineffective for treatment of water with a low concentration of heavy metals
Ion exchange	i. High treatment capacity ii. High removal efficiency iii. Fast kinetics process	i. High cost due to synthetic resins ii. Regeneration of the resins cause serious secondary pollution

According to [80], adsorption is an interaction process of binding liquid phase component to the surface of solid adsorbent through the interaction of either physical or chemical depending on the intermolecular forces. It is a segregation process that is used to separate the selected metal ion from the reaction mixture and can be carried out either by batch, semi-batch or continues. The process of adsorption occurs due to the existence of unbalanced or residual forces on the surface of liquid or solid phase. The residual unbalanced forces tend to attract and retain the molecular species when it meets the surface. Adsorption process will involve two elements which are adsorbent and adsorbate. The adsorbent is the component base on the surface of which occurrence of adsorption, while adsorbate is the element that is being adsorbed on the adsorbent surface. Figure 6 illustrated the adsorbent and adsorbate in the adsorption process. The adsorbate gets absorbed by adsorbent where the attraction between adsorbate and adsorbent occurs due to the bonding forces. The possible forces of attraction to occur are by Vander der Waal forces (weak forces) or covalent bonds (strong forces).

Adsorption can be categorized into two which are based on physical and chemical [73]. Physical adsorption occurs when the absorbent and adsorbate are attracted by the weak van der Waals forces, hydrogen bonding, and dipole-dipole interaction [86]. It electrostatically attracts the metal ions through the surface of materials. Moreover, it occurs at lower or almost the same temperature of the adsorbed components. Meanwhile, chemical adsorption is the process between solid and surface of the adsorbent through the chemical bonding. It is a permanent reaction and also called activated adsorption which requires large activation energy. The process is irreversible unlike the physical adsorption [33], [79], [87]. Figure 7 shows the mechanism of physical and chemical adsorption between adsorbent and adsorbate.

Adsorbate (manganese ions) is bind on the external surface of the adsorbent and then diffused on the available adsorbent pores. During adsorption process, all the available exposed active sites are occupied either by physical adsorption or



chemical adsorption [88]. Adsorption appears to be more attractive method than the other treatment in view of its efficiency and capacity to remove heavy metals [24].

Figure 6: Adsorbent and adsorbate in the adsorption process

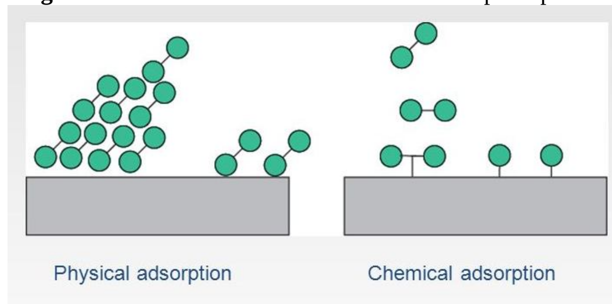


Figure 7: The mechanism of physical and chemical adsorption [89]

3.1 Factors affecting the adsorption process

Adsorption is a surface phenomenon in which the heavy metal ions are adsorbed on the surface of an adsorbent either through physical or chemical bonding. There are many factors that affect the adsorption process which includes temperature, pH, the concentration of heavy metals, contact time, size of the particle, adsorbent dosage, etc. This is shown in figure 8 [12].

The pH of a solution is an important factor that influences the performance of adsorbent towards adsorption of heavy metal ions. The degree of ionization of a material is affected by the pH because of the presence of weak acid or weak base [86]. According to a study by [55], manganese efficiency removal by using biochar will be increased by increasing the pH solution. High removal efficiency of more than 80% is recorded at less acidic pH because of low hydrogen ion concentration, which indicated less competition with manganese ion for adsorption onto negatively charged biochar surfaces. Excess of hydrogen ions in acidic solution will surround the binding sites of biochar which make the adsorption less favourable.

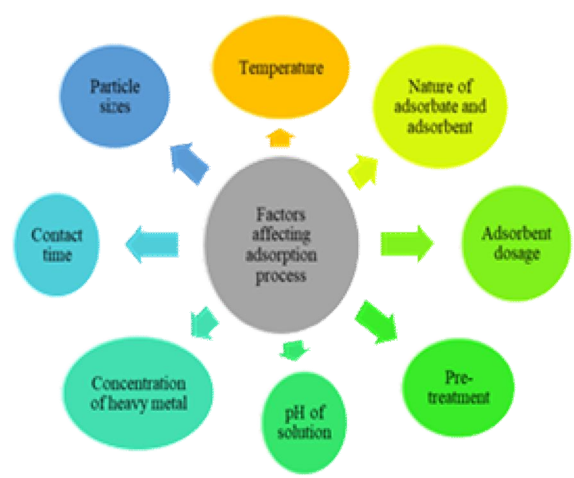


Figure 8: Factor affecting the adsorption process [12], [86]

Other than that, the adsorbent dosage is also important parameter affecting the uptake of manganese during adsorption process. High adsorbent concentration will increase actively exchangeable adsorption sites. However, excessive adsorbent dosage also could decrease the adsorption due to interference caused by the interaction of active sites of an adsorbent [90]. A study by [91] reveals that the increase in biosorbent dose of polyvinyl alcohol/chitosan (PVA/CS) from 0.1 g /100 ml to 1.0 g /100 ml had increased the removal efficiency of manganese ion from 30.5% to 84.5 %.

The increase in adsorption capacity is due to the greater surface area of PVA/CS and the greater amount of adsorption surface sites. Other studies that utilized untreated and chemically treated banana peels as adsorbent also confirmed that increased adsorbent dosage will increase the percentage adsorption of manganese ion removal from 37% at a lower adsorbent dose (1 g/L) to 94% at a higher adsorbent dose (4 g/L) [92].

The particle sizes of an adsorbent have a great impact on adsorption capacity. Greater internal surface area will result in higher adsorption capacity. Smaller particle sizes of adsorbent have the capability to achieve full adsorption because it is able to reduce internal diffusional and mass transfer limitations to the attachment of the adsorbate. But, the limitation of adsorbent with small surface area is that larger molecules may be too large to enter the small pores which require longer contact time to obtain similar results, as diffusion must occur through the aggregates [86].
Contact time also plays a vital role in the adsorption process. According to [86], a shorter interaction time in achieving equilibrium adsorption indicates that the materials chosen as adsorbent is very efficient. In the water treatment industry, short contact time is favourable as this will enhance the process efficiency and decrease the operational cost. A study utilizing Moringa oleifera seeds adsorbent reveals that manganese removal increased with the increased contact time until it reaches equilibrium. The optimum contact time was 5 minutes with 95% removal of manganese ion [93].

Temperature is another parameter in the adsorption process which provides estimation of thermodynamic parameters (Gibbs energy change: ΔG^0, enthalpy change: ΔH^0, and entropy change: ΔS^0). The thermodynamic parameter will predict the adsorption mechanism (physical or chemical) and examine the temperature range in which the adsorption is promising or not. The value of ΔH^0 helps to identify the type of adsorption either physical adsorption (2.1 –20.9 kJ/mol) or chemical adsorption (80 –200 kJ/mol). Positive value of ΔH^0 indicates the endothermic nature associated with a higher temperature which increases the adsorption process. On the contrary, the negative value of ΔH^0 reveals exothermic nature which the adsorption capacity will decrease at higher temperatures [11]. Generally, van't Hoff equation is used in adsorption studies. The ΔG^0 can be computed from Equation (1) and (2).

$$\Delta G^0 = -RT \ln K \quad (1)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (2)$$

Definition 1: Where the constant R is the universal gas constant (8.314 J/mol K), T is the absolute temperature in Kelvin and K is the thermodynamic equilibrium constant.

Study by [55] reveal that higher temperature had low manganese removal. The process is identified as an exothermic reaction. This is because higher temperature leads to the higher kinetic energy of manganese ions, which weaken the electrostatic forces between manganese and the adsorbent (biochar).

4. AGRICULTURAL WASTE AS A LOW-COST ADSORBENT

Adsorption process has been broadly utilized owing to its low cost, ease of operation, versatility and efficient removal. Many have studied various materials that can be used as potential adsorbents. The adsorbents can be classified into two, which are conventional and non-conventional. The conventional adsorbent is a commercial adsorbent such as activated carbons, ion-exchange resins (polymeric organic resins) and inorganic materials such as activated aluminas, silica gel, zeolites, etc. While non-conventional is adsorbent from waste materials include industrial (e.g.; blast furnace sludge, slag, flue dust, sawdust, fly ash, black liquor lignin, red mud), agricultural wastes (e.g.; rice husk, peanut husk, sunflower seed shell, potato peel, walnut shell, sugarcane bagasse), biomass, etc. which usually proposed as low-cost, efficient and green adsorbents [94]. Most of the materials have high surface area to volume ratio and contain many active binding sites (e.g. -COOH, $-NH_2$, -OH, -SH groups) on the adsorbent surface. Thus, enable to bind and remove heavy metals effectively [11], [85], [95].

Among non-conventional adsorbents, agricultural waste is widely used compared to the other type of waste materials [86]. Economic adsorbents can be synthesized from agricultural waste for the removal of heavy metals in water treatment [74]. Adsorbents made from agricultural waste are a natural, environmentally friendly material that can be obtained locally with abundant sources availability. Agricultural waste has been known as an efficient adsorbent for the removal of heavy metal ions owing to the presence of functional groups such as carbonyl, phenolic, acetamido, alcoholic, amido, amino and sulfhydryl group, etc. [96]. The selection of adsorbent should be based on potential of efficient removal and the ability to be regenerate [80].

Moreover, the utilization of agricultural wastes as adsorbent is the practice of waste-to-wealth concept. Instead of disposing the agricultural waste to the landfills, it can be used to produce low cost and green adsorbent [77]. The performance of various agricultural wastes that is used as adsorbent for manganese removal is shown in Figure 9.

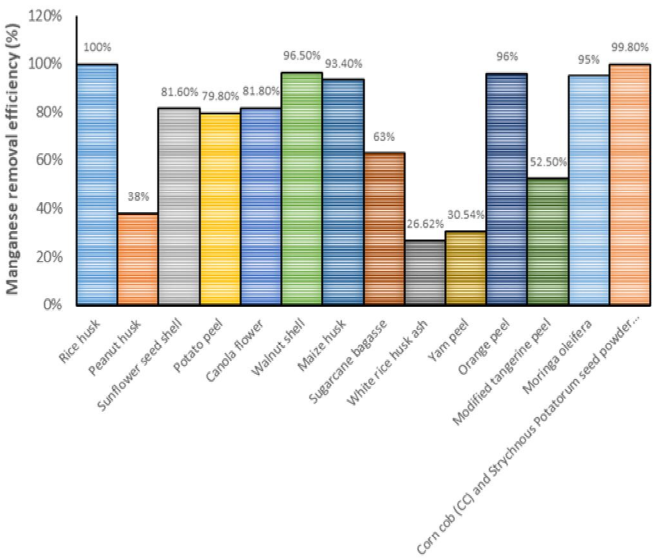


Figure 9: The performance of various agricultural waste as adsorbent for manganese [58], [93], [105], [106], [97]–[104]

5. CONCLUSIONS

Water is an essential component for living organisms to survive and for nation development where river is the main source of water supply in Malaysia. The quality of surface water has been severely degraded due to the rapid growth of industrialization, urbanization, and population. Heavy metals that are disposed into the surface water without proper treatment had posed a threat to human health and environment. Although manganese is a trace element, prolonged exposure could cause neurotoxicity effect to the brain which leads to manganism and Parkinson. Ingestion of manganese by children demonstrates short term memory, low IQ performances, repetitive stuttered speech, etc. The demand for clean water is increasing over the years. Among the various treatment technology available for treating water containing manganese, adsorption is the best method owing to its effectiveness, low cost, and simple process. Adsorbent made of agricultural waste has great potential to remove manganese in surface water.

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