

Review

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Review

From Tradition to Innovation: An In-Depth Review of Manganese Removal Techniques in Water Treatment

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Abstract: Contamination of water is currently one of the alarming issues all around the planet. Water that is contaminated with manganese (Mn) could potentially give rise to functional and aesthetic complications. Removal of manganese is critical and often has substantial implications for the layout of treatment trains. Precipitation, ion exchange, depth filtration, oxidation, adsorption, biosorption, and biological methods are the traditional chemical, physical, and biological processes for removing Mn (II) from contaminated water. All these treatment processes have some advantages and disadvantages and are based on which the implementation of any process varies. In recent years, the use of biofiltration to eliminate manganese (Mn) from water has grown owing to the progress made in molecular techniques for studying microorganisms found in biological Mn elimination systems. This study aims to contribute to the existing research on Mn occurrence and highlight the historical and current removal strategies used in drinking water treatment. The main objective is to assist future researchers in developing more efficient technologies and clarify the subject matter.

Keywords: manganese; efficient; potable water; microorganism

Introduction

Drinking water from groundwater is an essential source. However, this groundwater gets contaminated due to certain species of elements such as manganese. This contamination can be produced by both organic and inorganic contaminants released by humans. With an approximate quantity of 0.095% in the Earth's crust, manganese, a gray-white element, is the 12th most prevalent substance in the universe. Because of the magnetic qualities of its parent mineral, pyrolusite, its scientific name comes from the Latin word magnes, referring to the magnet [1]. Mn(III) and Mn(II) are the forms of manganese that actually matter the most for biological systems although it has some other valance forms. The distribution, accumulation, and excretion of Mn all appear to be significantly influenced by its oxidation state. Manganese in its Mn(II) form is quickly removed from the bloodstream and excreted efficiently in the bile. However, through the membranes, Mn(III) moves slower and takes longer to eliminate. The exchange and balance between the Mn(II) and Mn(III) states is crucial in determining the spreading of manganese in the body and any potential neurotoxic effects. Mn(III) is only stable when bonded to other molecules since Mn(VI) and Mn(V) are unstable in ordinary solutions. Additionally, permanganate ion (MnO_4^-) is a highly oxidizing purple substance and Mn(VII) exists in this form and the formation of it in normally available waters is unusual [2]. Even though manganese is a vital micronutrient for human life and numerous enzymes utilize its redox abilities, chronic exposure to this constituent is detrimental to both humans and water bodies. Extremely high manganese (Mn) levels can cause damage to the neurological system, manifesting as symptoms similar to Parkinson's disease, and impair human intelligence. Neurobehavioral impairments among kids were observed in response to water-manganese interaction, even at modest concentrations that are prevalent in North America [3–8]. Plumbing fixtures or laundry may become stained if water has a high iron or manganese content. Water may contain black particles from

manganese solids that break off from deposits inside pipes and give it a terrible taste and look. Manganese can be harmful when consumed in high doses through oral intake or drinking water [9]. Although manganese is necessary for human life, manganese makes an unpleasant taste to drinks and stains clothing and other items when it is present in water supplies in amounts more than 0.1 mg/L. The bioaccumulation of manganese may be caused by its presence in drinking water. The health-based value of manganese is 0.4 mg/L, which is higher than its tolerance level of 0.1 mg/L. According to European Community Directive 98/83/EC Annex 1 Part C-indicator parameters the parameter value for Mn is 50 g/L [1,10]. According to the European Union Directive and the United States Environmental Protection Agency, the maximum manganese content that may be found in the water supply of residential property is 0.005 mg/L [11]. Groundwater has a higher concentration of many chemicals because these chemical species are mainly generated from different ore or rock-subsurface fluid interactions in-temperature geothermal formations [12]. Shallower groundwater has less minerals because these types of ore are mainly found in high depth, manganese is a common pollutant among this chemical species which also generates due to aging and leaching of Mn-ore [13]. Certain minerals, such as manganese, dissolve when groundwater percolates through soil and rocks [14]. This review article focuses to provide an outline of the available treatment techniques for the elimination of Mn. The principal focus of this article is to demonstrate a comprehensive overview of various removal methods and relevant features, based on multiple studies.

Treatment techniques for Manganese Removal

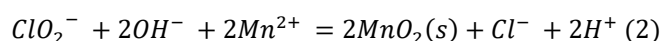
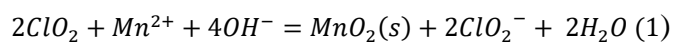
There are several biological, chemical, physical, and hybrid approaches for removing manganese from groundwater sources. Different physicochemical treatment methods have been discussed in several recent and thorough review studies for the elimination of heavy metals from groundwater and wastewater [11,15–17]. This review article discusses the many technologies that have been employed over time to extract manganese ions from groundwater and wastewater. These methods include ion exchange, membrane filtration, oxidation-filtration, adsorption, biological operations, precipitation, and electrochemical operations. A thorough analysis of all relevant research done up to date on this area has been used, and an end assessment has been conducted to determine the most effective techniques for manganese removal.

Oxidation and Filtration

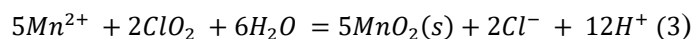
For remote locations, oxidation, and filtering are the best techniques because they may be used without power [15]. Conventional physical and chemical methods for elimination are more flexible and effective for certain smaller treatment facilities or in emergencies, like a sharp increase in manganese concentration in source water at the time of summer, even though plenty of treatment attempts have been used to extract soluble Mn(II) from water [18]. Oxidation and filtration are low-cost technologies that are effective and practical for rural locations because they work without electricity. The main negatives are that the oxidant is difficult to hoard and transport, that system components corrode, and that solid manganese compounds may form that could affect how the system functions [19]. The oxidation method may be followed by filtration and precipitation and works more accurately [20].

Oxidation

Even at low pH, by using ClO_2 , Mn(II) can be oxidized to generate insoluble precipitates. The insoluble residue is then removed using a further filtration-separation technique. Mn(II) and ClO_2 react quickly, and the result of that reaction, chlorite (ClO_2^-), might continue to react with Mn(II).



The final reaction equation stands as



Based on Equation (3), the ratio of $[\text{ClO}_2]$ to $[\text{Mn}^{2+}]$ should be 0.5. To enhance the efficiency of removing manganese from water, increase the pre-oxidant dose, reduce flow velocity, and use smaller sand particles, and thicker filter beds. Experiments show that with these settings: DO = 0.99 mg/L, particle size = 0.6–1.2 mm, H = 60 cm, and Q = 282.6 mL/min, more than 95% of Fe and Mn can be eliminated. The progress of self-catalytic oxidation in Mn sand can be accelerated due to the pre-oxidation of ClO_2 [18].

Aeration or the application of powerful oxidizing chemicals such as hypochlorite, ozone, potassium permanganate, or chlorine dioxide can be applied to achieve oxidation [20]. As an oxidant potassium permanganate (KMnO_4) is employed to precipitate Mn^{2+} , and it can remove 96% of Mn^{2+} from groundwater [21,22]. Potassium permanganate is used to oxidize synthetic groundwater to remove Mn(II). Kan et al. conducted a study to examine how characteristics such as the amount of oxidant used, the presence of co-ions (Mg^{2+} , Ca^{2+}), and additional alum affect the extraction of Mn^{2+} . The aeration process resulted in a 30.6% reduction of Mn^{2+} in one metal system. In the dual metal approach, the reduction of Mn^{2+} by aeration was 37.2%. A rock-bottom oxidant dosage of 0.603mg/L KMnO_4 is essential to get Mn^{2+} below its maximum contamination level [23]. Boost the removal efficiency of manganese by using higher oxidant doses, thicker filter beds, smaller sand particle diameters, and lower liquid flow rates [18].

Filtration

Filters may remove materials using a variety of processes, including gravity-settling, adsorption, physical trapping, straining, impaction, interception, and flocculation. Slow sand filtering removes just the first few millimeters from the sand surface. When body feed is used, pre-coat and deep bed granular filters utilize a filter medium, and filtering fruitfully eliminates the bulk of metal precipitate particles that would otherwise settle.

Mondol [24] observed that the manganese removal increases as the amount of manganese in the supplied water increases. Through the use of filtration, 80–89% of the manganese was removed. It was shown that the Down-flow Roughing Filter (DRF) alone contributed significantly (around 37%) to manganese removal. Aeration, flocculation, and sedimentation each contribute around 33% to manganese removal. Up-flow roughing filter (URF) has a modest (15%) role in manganese removal.

Ali et al. [9] found that only around 20% of the manganese was removed from the iron-coated sand layer under testing conditions, which is not sufficient. Aziz et al. [25] talked about filtration using inexpensive coarse media, such as limestone. They discovered that 95% of the Mn(II) was removed, compared to 60% for gravel, 82% for broken brick, and less than 15% for no media input.

Shafiquzzaman [26] investigated a simple and economical household-based filter for removing biological manganese (Mn) from water. From the investigation, it was found that from tubewell water, the filter was able to produce less than 0.1 mg/L of effluent manganese content, and the average Mn content of the raw tubewell water was 0.36 mg/L. The observed Eh-pH values in each filter suggest that the iron bacteria, *Leptothrix* group also oxidizes Mn which is then removed via filtration.

Athirah et al. [27] applied different flow rates to filter groundwater using marble column filters made of pebble-sized and sand-sized marble. The highest percentage removal from a pebble-sized marble column filter is 58.15% at a flow rate of 0.007 L/s. However, when the flow rate is 0.017 L/s, the marble column filter with sand size has the maximum percentage removal at 97.26%. Compared to pebble-sized marble particles, sand-sized marble particles demonstrate an effective manganese removal in groundwater.

Feng et al. [28] inquired into the use of a manganese sand filtration column device to remove Mn^{2+} over the long term from simulated geothermal water and encountered that in produced water with intake temperatures of water of 25, 50, and 70 °C, the average Mn^{2+} elimination rate was 87.4%, 96.2%, and 99.0% during the length of the 90-day trial. They also identified that the average Mn^{2+}

removal rates were 94.0% and 99.8%, at input rates of 10.4 mL/min and 5.2 mL/min, respectively. A microbial trickling filter is employed for eliminating Mn(II) from drinking water, and it has been revealed that combined biological and chemical oxidation account for 94% of elimination. It enhances around 6% filter efficiency and the required filter depth is reduced approximately. It improves filter performance by roughly 6% and decreases the necessary filter depth by roughly 40% [29–31]. Rapid sand filters (RSF) are a widely established method for treating groundwater [32].

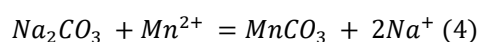
However, it is necessary to modify the use of chemicals in the oxidation treatment processes due to secondary effects which mainly result from residuals and by-product generation, besides the growth of plant running expenses also needs to be reduced [22]. Oxidation can be done in the presence of air which does not require any economical support and high technology. Spreading Mn-contaminated water through the air oxidizes manganese, producing MnO_2 that can be absorbed by filtration.

Chemical Precipitation

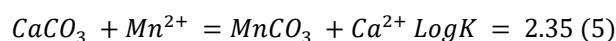
A highly efficient and widespread approach for eliminating heavy metals from various wastes is chemical precipitation. In order to significantly reduce manganese by precipitation, this method requires converting soluble manganous ions to an insoluble precipitate [15]. The three primary precipitation methods used are sulfide, carbonate, and hydroxyl [33].

Carbonate Precipitation

During the process of high-pH lime-soda precipitative softening, which is used for removing hardness, the pH is raised to a level where Mn(II) is eliminated. This process not only removes hardness but also removes Mn, without oxidizing Mn(II), as the pH of the procedure ranges from 10 to 11. At this pH, CO_3^{2-} and Mn^{2+} are combined and form the $\text{MnCO}_3(\text{s})$ precipitate which is relatively insoluble [3].



Another precipitant limestone is also used widely because of its low cost and availability [34].



Mn can be precipitated using dolomite, magnesite, and quartzite in addition to limestone. If the solution's alkalinity isn't high enough to cause precipitation, soluble carbonate can be added [35].

Hydroxide Precipitation

The most usual technique of removing metals from solutions in hydrometallurgical processes involves precipitating metal hydroxides from the solution [15]. By adjusting the pH, heavy metal ions can be transformed into less soluble hydroxide compounds via hydroxide precipitation. As the pH rises, solubility decreases and allows the removal of Mn(II) [35].

Using hydroxide precipitation, Zhang et al. [35] recovered Mn(II) from synthetic wastewater. Manganese precipitation was barely at pH 6.0, but throughout the course of 60 minutes at pH 8.0, nearly thirty percent of the manganese was removed. When the pH was higher than 9, the Mn^{2+} concentration in the sample significantly decreased from 2.0 g/L to less than 0.01 g/L. Cu^{2+} , Zn^{2+} , and Mg^{2+} may also be drawn out by hydroxide precipitation in a solution of water.

Sulfide Precipitation

Another crucial step in the hydrometallurgical processing of effluents and metals is precipitation of metal sulfides. Since MnS phases are very soluble, it is uncommon to employ metal sulfide precipitation for Mn(II) because it may cause Mn(II) to be released from sediment into water in a

subsequent manner. Furthermore, there are risks associated with using too much sulfide, which could result in the formation of undesirable byproducts [21].

Although hydroxide precipitation is a common method used in industries to remove metal, sulfide precipitation has some benefits to use. Sulfide precipitation has the capability for particular metal removal, better-settling features, rapid reaction rates, and the ability to recycle sulfide precipitates through smelting. Yet, it is not widely used due to threats about the corrosiveness and fatality of surplus sulfide. Additionally, dosing sulfide can be tough to manage because of the poor dispersibility of the metal sulfides, which makes the process sensitive to the dose. Manganese can be removed along with hardness, without oxidizing the Mn(II) [3,21].

Oxidation Precipitation

In the pH range of 3 to 6, oxidative precipitation provides the highest acceptance for recovering manganese as Mn_2O_3/MnO_2 in comparison to other metals including Zn, Ni, Co, Mg, and Ca.

Ozone (O_3) is another potential oxidant which is used for the oxidation of Mn^{2+} . In the truancy of other demands for oxidants, for oxidizing 1.0 mg Mn(II) around 0.87 mg O_3 is required. The rate constant for the reaction between Mn(II) and O_3 at pH 7 is $2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, indicating that it happens rather fast. Much more O_3 is required in order to totally oxidize Mn(II) in the presence of modest amounts of organic materials [36,37].

Aeration can be used to remediate iron and manganese contaminants before they enter the post-filtration system. A Gravitational Aeration Tower System (GATS) can be used to improve the water pre-treatment process. Radzi et al. found that 14.25% of contaminants can be removed with GATS aeration. Though GATS reduces the contaminants to 0.361 mg/L, water quality standards are not met, hence post-filtration is needed [38].

Zhang et al. [39] conducted an oxidative precipitation process using air, O_2 , and SO_2 /air to separate manganese from magnesium. However, achieving efficient kinetics in practical applications is crucial. The application of O_2 as an oxidant remarkably increased the amount of manganese precipitation while reducing magnesium co-precipitation. In addition, the researchers found that a pH range of 8 to 8.5 was optimal for achieving 99.5% manganese precipitation with less than 10 mg/L Mn(II). On the other hand, oxidative precipitation using SO_2 /air (O_2) in a pH range of 6 to 7 resulted in 99.5% manganese recovery, but with higher levels of Mn(II) presenting in the solution.

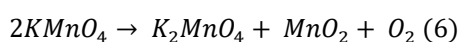
The price of some oxidants, such as ozone, is the main issue with using the oxidative precipitation approach. However, oxidizing using air is regarded as the most potential oxidant for recovering manganese from water since it is a reasonably inexpensive oxidant.

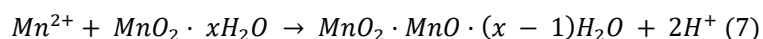
Ion Exchange

One kind of physical activity is the ion exchange method, which means the movement of ions from a solid to a liquid or gas and back again. Ions on solids are linked to functional structures on the solid medium that is submerged in the liquid or gas. Ions displace other ions with the same or similar charges when their concentration is high. On the other hand, even low-concentration ions may shift to lower-valence ions with the same charge [15]. It is a technique for the extraction of manganese from aqueous solution since dissolved manganese exists as the divalent cation Mn^{2+} . Studies on the ability of natural minerals and synthetic polymers, some of which are zeolites, like clinoptilolite, to absorb manganese, have been conducted [3,40].

Manganese greensand is frequently used in treatment facilities to remove manganese and iron from groundwater.

Glauconitic $KMnO_4$ is used to make manganese greensand, which has a thin coating of MnO_2 on the exterior surface of the granular materials [41].





Of all the recovery processes, it is the one with the highest energy and financial efficiency. This is the only system that can effectively treat an extremely diluted solution in ppm levels in a single pass. Ion-exchange resins become exhausted and need to be regenerated using a large volume of chemical reagents. However, treating large amounts of wastewater containing heavy metals in low concentrations can be expensive and cause serious secondary pollution. Therefore, ion exchanges are not suitable for large-scale use [15].

Electrochemical Treatment

Electrocoagulation (EC) is a technique that removes metal by generating a coagulant through anodic dissolution.

Ince et al. looked into how well the EC approach worked to extract iron, phosphate, and manganese from rinse water coming from a Mn-PO₄ (MPO) coating factory. In the initial pH, they employed sacrificial aluminum electrodes. It was discovered that as the current increased, the removal's speed greatly increased. The use of energy and electrodes increased at the same time, though. 20 Am⁻² was found to be the ideal current density for the fastest therapy. The procedure eliminates 97.95% of the manganese at this current density [42].

These methods of treatment are said to be quick and precise, using fewer chemicals, offering high reduction yields, and producing less sludge. Nevertheless, the development of an electrochemical system required high initial capital expenditure and high energy-providing costs.

Adsorption

Adsorption is the buildup of one substance on top of another's surface. At the surface of the adsorbent, the building up of chemical complexes, the attraction due to electrical conditions (Almost all chemical mechanisms involve a characteristic that includes complex formation), and the debarment of the adsorbate from the bulk solution can all be contributing factors to the mechanism of adsorption [15].

Activated Carbon as Adsorbents

Activated carbon (AC) is the adsorbent used most frequently to treat wastewater. Once saturated, activated carbon has to be replaced or renewed. The chemical regeneration can be carried out within a column using either acid or other oxidizing agents.

Granular activated carbon (GAC) filtration of Mn(II) was studied by Chen et al. [6] under various circumstances. The results showed that over a limited ripening time biological GAC filter columns could lower Mn²⁺ from 400 g/L to 10 g/L, unlike sand filter columns which could not clearly exhibit Mn(II) removal capability. It has been shown that activated carbon improves Mn(II) oxidation under chlorine. Granular activated carbon (GAC) filtration was more successful than sand filtration in removing Mn(II), under chlorinated circumstances, nevertheless. Fast chlorine degradation in GAC filter columns made chemical Mn(II) oxidation harder to sustain, hence lowering Mn(II) removal. The investigation showed that for the Mn(II) removal, biological GAC filtration dominated over sand filtration.

Goher et al. [43] used two distinct sorbents Amberlite IR-120H (AIR-120H) and Granular activated carbon (GAC) in the study to remove aluminum, iron, and manganese. They demonstrated that at pH 5 and 10 minutes of room temperature contact time, the two sorbents are most effective at removing aluminum and iron, whereas pH 7 and 30 minutes are best for removing manganese. The highest removal capacity was achieved for both GAC and AIR-120H at a dose of 2 g/L. Al⁺³ > Fe⁺² > Mn⁺² was the removal trend at ideal circumstances, while GAC and AIR-120H had metal removal rates of 99.2, 99.02, 79.05, 99.55, 99.42, and 96.55%, respectively.

Manganese, iron, and ammonium nitrogen were eliminated using impregnated activated carbon. According to Okoniewska et al. [44] discovered that the impregnated activated carbon's surface area dropped to 658 from 725 m²/g (or nearly 9%) following impregnation. Iron, manganese, and ammonium nitrogen starting concentrations in treated water were all impacted by pH, and adsorption increased with both a rise in pH and a drop in the beginning concentration. Independent of starting concentration and filtration speed, impregnated activated carbon from compounds investigated consistently had the greatest adsorptive capacity for manganese. The choice of process parameters is crucial for high manganese removal.

According to Wedasingha et al.'s [45] research, graphene oxide quantum dots (GOQD-MnO₂) are a superior adsorbent for Mn (II). Over 85% of the waste can be removed under ideal circumstances. The ideal adsorption conditions are an initial concentration of 0.6 mg/l, a dose value of 1.0×10^4 mg l⁻¹, and a pH of 8.0.

Agro/Plant-Derived Adsorbents

Because of its affordability, ease of manufacturing and use, eco-friendliness, and capacity to treat aqueous solutions, biochar has recently gained interest as an adsorbent from a multitude of sources [46,47]. The specific surface area, porosity, and the abundance of functional groups on the surface of biochar are physical and chemical characteristics that have a significant impact on how well it removes contaminants from aqueous solutions. These characteristics are influenced by the sources of the feedstock used to make biochar, the heating rate, temperature, and residence time during the pyrolysis process [48–51]. Additionally, adsorption parameters including the initial pH, concentration, and biochar dose affect how well biochar removes substances. The research found that the adsorption of manganese is greatly influenced by the circumstances under which it occurs. This was shown by utilizing biochar made from banana peels that were either untreated (BPB) or modified with phosphoric acid (PBPB) [52].

In recent research, Yayah et al. [53] detected that a modified cashew nut shell-derived biochar in the fixed-bed column could remove manganese with an efficiency of 53.09% and an adsorption capacity of 9.82 mg/g at an influent concentration of 20.3 mg/L, a flow rate of 5 mL/min, and a biochar bed depth of 10 cm.

Fseha et al. [54] discovered that adsorption capacities and high removal efficiencies (94.94%, q_e : 4.18 mg/g for nitrate and 73.20%, q_e : 3.57 mg/g for manganese) were achieved at pH 6 using a dose of 0.1 g biochar which was made from an amalgamation of 50/50% date palm leaves and fronds that were pyrolyzed at 500°C.

Esfandiar et al. [14] utilized sugarcane bagasse (SCB) and activated carbon (AC) to remove Mn(II). Response surface methodology (RSM), utilizing the Box-Behnken design, was employed to investigate the influence of three variables on the adsorption of Mn(II). These variables include pH, starting metal concentration (C_0), and adsorbent dose (C_a). The experimental Mn(II) removal efficiencies for AC and SCB were 97% and 63%, respectively. Furthermore, a chemical approach involving hydrochloric acid (HCl) was performed on SCB. The results revealed that this treatment had a significant effect on the adsorption process, leading to a remarkable increase in the highest possible removal rate of up to 99%.

Khajeh et al.'s [55] development of solid tea debris as a reasonably priced adsorbent to extract cobalt and manganese from water samples resulted in removal rates of 92% and 99%, respectively. RSM, a technique for analyzing response surfaces, and a mix of artificial creating predictive models using the neural network-particle swarm optimization (ANN-PSO) process of extracting tea waste using simulation and optimization.

Idrees et al. [56] looked into biochar made from farmyard and chicken dung as affordable adsorbents for extracting manganese from the aqueous media. On the Mn removal effectiveness of biochar, the effects of functional factors, including solution pH, temperature, contact duration, and concentration were assessed. Compared to farmyard manure-derived biochar, poultry manure-derived biochar shows higher adsorption efficiency because of its surface functionality and porosity.

The greatest adsorption was accomplished at 298 K, pH 6, and 3 hours of contact duration. The Freundlich model suited the adsorption isotherm data well, demonstrating multilayer adsorption onto the biochars' heterogeneous surfaces. Thermodynamic simulations show that Mn adsorption onto biochars is a spontaneous, exothermic process, controlled by hydrogen bonding electrostatic interactions.

Natural Minerals, Modified Absorbents, and Industrial Wastes as Adsorbents

As the primary focus of the researchers to search for low-cost adsorbents despite the widespread use of AC, which is relatively expensive, researchers investigated further for low-cost, easily available absorbents, researchers further investigated the available natural absorbent, and waste [57,58]. Based on the property of the absorbents and the required quality they modified the industrially generated waste and natural absorbents.

Belviso et al. [13] investigated zeolite and fly ash made from fly ash as effective adsorbents to extract Mn(II). In their column tests, they found that even with the lowest amount of fly ash, a 99% reduction in Mn concentration was achieved. They also discovered that using synthetic zeolite instead of fly ash resulted in a 97% removal of Mn from the solution using 10g of the zeolite sample. However, to completely sequester Mn from the solution, a sample mass of 30g was necessary. The batch test findings also showed that after only a few minutes, running the solution through fly ash nearly completely (99%) eliminates the pollutant.

According to research by Ashraf Ali [59], the amount of Mn removed using a "synthetic" Mn-coated medium increased from 30% at a flow velocity of 8.0 ml/min/cm² to 100% at a flow rate of around 1 ml/min/cm². The amount of Mn removed was shown to rise when both the influent water's Mn concentration and the filter media's Mn content increased.

Baharudin et al. [60] investigated the Fe and Mn in the subsurface water were eliminated by using 2, 4, and 8 grams of activated carbon derived from banana peels. It has been discovered that increasing the quantity of activated banana peels leads to a more efficient elimination of iron and manganese. The percentage of iron extraction varies from 82.25% to 90.84%, whereas the percentage of manganese removal ranges from 98.79% to 99.43%. Based on the findings, it can be inferred that banana peel-activated carbon is a very efficient and affordable adsorbent for treating groundwater.

Lu et al. [61] conducted research on the extraction of manganese (Mn) from a water-based solution using a permeable reactive barrier that included hydroxyapatite-coated quartz sand. This sand was produced using the sol-gel technique. The researchers discovered that the highest amount of Mn(II) that can be adsorbed is 0.7546 mg/g.

Hassouna et al. [62] assessed the effectiveness of sulfuric and acetic acid-modified powder of sub-micro-kaolin and its natural forms for removing Mn and Fe from raw water samples. They discovered that compared to natural clay, both modified forms had better adsorption effectiveness.

Mohd Sapongi et al. [63] investigated that using 14 g of metakaolin an average of 30.2% of the manganese sample can be removed from groundwater. However, manganese removal can be obtained at about 33.2% with an optimum contact period of 120 minutes.

Kang et al. [64] investigated the adsorption process of modified manganese sand on iron and manganese ions from groundwater. Through single-factor studies, the effects of manganese sand dose, pH, and the starting concentration of Mn/Fe on the removal percentage of manganese and iron ions were examined. To construct the ideal adsorption circumstances, a quadratic polynomial model between the adsorption rate and the aforementioned components was developed based on the three factors mentioned above. According to the response surface study, pH had the most impact on the adsorption procedure. The ideal pH value, manganese sand dose, and starting the Fe/Mn concentration ratio for the adsorption of manganese and iron ions by modified manganese sand were 7.20, 3.54, and 3.80 g/L, respectively.

According to the study of Xing et al. [65], a film of iron Fe-Mn complex oxide is effective in removing over 95% of NH₄⁺-N and Mn²⁺ from water, even at alkalinity level of 30 mg/L and a low temperature of 20°C. This film can stably eliminate up to 3.5 mgL⁻¹ of NH₄⁺-N and 5.5 mgL⁻¹ of Mn²⁺.

In a study conducted by Zhang et al. [39], it was found that MOCS has a high efficiency in removing Mn^{2+} in a large range of hydraulic retention times (15-40 minutes) over a period of 40 days. This indicates that MOCS has great potential for removing manganese from groundwater.

Sharma et al. [66] looked into the possibility of removing manganese from aqueous solutions and wastewater using fly ash, a waste material product from thermal power plants. It was discovered that the removal was very concentration-dependent, with more removal occurring at low Mn (II) concentrations in solutions. The removal rate of Mn(II) was found to decrease when the concentration was increased from 1.5 to 5.0 mg/L at pH 8.0, 298 K, and ionic strength of 1.0×10^2 M $NaClO_4$. The removal rate decreased from 74.2% to 47.2%. In addition, increasing the size of the adsorbent particles from 100 to 250 m resulted in a decrease in the removal rate from 51.3% to 7.2%.

To remove Mn^{2+} from an aqueous solution, Gogoi et al. [67] investigated the effects of contact duration, pH, ionic strength, and temperature on calcium hydroxyapatite (HAP) as an adsorbent. The buffering abilities of HAP were discovered to be responsible for the pH independence of manganese sorption on HAP, which ranged from 4 to 6. At pH 5 and an initial manganese ion concentration of 1 mg/L, 99% of manganese ions were sorbed within 20-30 minutes of contact time.

Polymer as Adsorbents

A few types of polymers, such as polyhydroxy-polyurethane foam, polyvinyl alcohol/chitosan dry mix hydrogel, and poly sodium acrylate-graphene oxide, have been described to be employed as adsorbents for manganese ion removal [68].

In research by Moawad et al. [69], manganese ions were removed using polyhydroxy polyurethane foam (PPF) at different loadings. The dosage ranged from 0.1 to 0.5 g, and it was equilibrated with feedwater that had its pH value set to the ideal level. At a feed solution pH of 6–8, it was discovered that the highest removal of manganese ions was attained in the range of 88–91%. It was discovered that the principal mechanism in the removal of metal ions was electrostatic interaction to create hydrogen bonds, the adsorbent's surface was negatively charged at pH 6-8, resulting in the adsorption of manganese ions. Under pH 5, the surface of polyhydroxy polyurethane foam was positively charged. PPF provides the benefits of rapid extraction kinetics and inexpensive cost for manganese ion removal.

Patil et al. [70] found that PSA-GO gel removed 84% of manganese ions when the initial pH was above 3.

Abdeen et al. [68] conducted research on a binary dry blend consisting of polyvinyl alcohol and chitosan (PVA/CS) for its potential as an adsorbent for the removal of Mn^{2+} ion from aqueous solutions. The outcomes showed that adsorbent dose, pH, and contact duration all affect the removal of Mn (II) ions, with 6.0 being the ideal pH. Additionally, the pseudo-second-order kinetic model and the Freundlich isotherm model both provided good fits for the adsorption equilibrium and kinetics, respectively. The thermodynamic analysis showed that Mn (II) ion adsorption onto PVA/CS was endothermic and spontaneous in origin.

The study conducted by Tang et al. [71] focused on using a poly (sodium acrylate)-graphene oxide (PSA-GO) double network hydrogel adsorbent to eliminate Mn(II) and Cd(II) from aqueous solutions. The research examined the adsorption characteristics under various conditions such as pH, contact time, ionic concentration, and the presence of fulvic acid, as well as the adsorption mechanism. Results showed that the maximum sorption capacities were up to 238.3 mg/g and 165.5 mg/g for Cd(II) and Mn(II), respectively at a temperature of 303K and pH 6, estimated from the Langmuir model. Additionally, the study involved a selective adsorption test, where a mixed solution of metal ions containing Cu(II), Pb(II), Cd(II), Mn(II) Zn(II), and Ni(II) at pH 5.0 ± 0.1 , and all the heavy metal ions were set at ~ 40 mg/L. It was discovered that the adsorption of Cd(II), Pb(II), and Mn(II) ions was higher than the other metal ions. This could be due to the chelation ability of different metal species. Pb(II), Cd(II), and Mn(II) were found to be favored to adsorb onto the surface of PSA-GO gel. Moreover, since Pb(II) easily precipitates at pH>6 under actual conditions, this hydrogel can be a selective adsorbent of Cd(II) and Mn(II) at a wide range of pH values. Adsorption

is till now, the most used method for removing heavy materials. Adsorption can be used in terms of the economy and locally available low cost material can also be used as adsorbent.

Biological Method

Biological treatment using media-supported biofilm (also known as biofiltration) is an effective way of removing Mn with little to no chemical input [3]. Chemically mediated Mn(II) oxidation pathways are distinct from biological oxidation mechanisms. Diverse bacteria have been found on filter grains after chemical oxidation/filtration for the removal of Mn. The majority of them are MnOB, which is connected to Mn(II) oxidation and precipitation [72]. *Leptothrix*, *Hyphomicrobium*, *Crenothrix*, *Bacillus*, *Siderocystis*, *Siderocapsa*, and *Metallogenium* are common bacteria genera that undertake manganese oxidation [73,74]. According to Hameed et al. [41] manganese may be oxidized by iron-oxidizing bacteria if the iron content is higher than the manganese concentration.

Afipia, *Bosea*, and *Reyranella* are three genera of Alphaproteobacteria where Mn(II)-oxidizing bacteria were discovered by Marcus et al. [75].

Pacini et al. [72] observed that *Gallionella* were visible inside significant flocculent precipitates of Fe and Mn upon microscopic examination of the backwash sludge of the roughing filter and the fast filter. In every instance, either a black precipitate covering the free cells or pustules on the filamentous bacteria's sheaths indicated the presence of oxidized Mn, which may have been deposited as MnO_2 .

Saccharomyces cerevisiae was employed by Fadel et al. [76] as a metal bio-adsorbent. It has been discovered that *S. cerevisiae* F-25 when in a live state, is excellent at absorbing Mn^{2+} . It can biosorb 22.5 mg of Mn^{2+} per gram of yeast biomass. The optimal conditions for *S. cerevisiae* F-25 to absorb the most Mn^{2+} in its live state are as follows: 4.8 mg Mn^{2+} /g after 30 minutes at pH 7, 0.1 gm/L of yeast biomass, and 150 rpm of agitation at 30° C. It should be noted that the percentage of biosorbed Mn^{2+} was impacted by the presence of additional heavy metals.

Perez Silva et al. [77] investigated how *Pseudomonas aeruginosa* AT18 absorbed Cr, Cu, Mn, and Zn. They discovered that the ionic strength and pH of the solution had a significant impact on the metal biosorption capability of *P. aeruginosa* AT18 for Mn^{2+} , Cr^{3+} , Zn^{2+} , and Cu^{2+} . From a starting value of 49.0 mg/L, 20% of the manganese was removed which was very low.

Shafiquzzaman investigated [25] that a typical tubewell water content of 0.36 mgL^{-1} was formed by the arsenic (As) removal filter (ARFs), whereas less than 0.1 mg/L of effluent Mn was generated. The Eh-pH values discovered in all filters revealed that the *Leptothrix* group of iron bacteria is largely responsible for the oxidation of Mn and its elimination via filtration.

The study conducted by Yang et al. [78] showed the distribution and genetic diversity of microorganisms in a biofilter for removing arsenic, manganese, and iron from simulated groundwater. According to the study, Iron oxidizing bacteria (IOB), such as *Leptothrix* and *Gallionella*, manganese oxidizing bacteria (MnOB), such as *Leptothrix*, *Hyphomicrobium*, *Pseudomonas*, and *Arthrobacter*, and As(III) oxidizing bacteria (AsOB), such as *Pseudomonas* and *Alcaligenes*, are the most prevalent bacteria in the biofilter. The study showed that the removal of Mn(II), Fe(II), and As(III) happened at different depths of the biofilter. Specifically, Fe (II) removal occurred at a depth of 20 cm, while Mn(II) and As(III) removal occurred at a depth of 60 cm. The corresponding removal efficiencies were 84%, 86%, and 87%, respectively.

Reports suggest that encouraging the growth of manganese-oxidizing bacteria the organic manganese removal in conventional groundwater treatment can expedite the typically lengthy ripening process [79]. Biological oxidation and precipitation are viable alternatives for groundwater treatment, and the biological Mn removal being a cost-effective method that doesn't require additional chemicals [25]. However, at low pH, biogenic Mn oxidation is severely restricted. Additionally, aeration conditions are necessary for biological Mn(II) oxidation [80].

Phytoremediation

The process of phytoremediation uses plants to break down, adsorb, and eliminate pollutants from soil or wastewater [81,82]. In recent years, phytoremediation has emerged as one of the most attractive, affordable, sustainable, and environmentally friendly methods for removing heavy metals [83]. Many researchers around the globe have identified numerous plants as metal accumulators such as Water Bulrush (*Typha*), Bahia grass (*Paspalum notatum* Flugge), Hyacinth (*Eichhornia crassipes*), *Pteris vitata* L., Common reed (*Phragmites australis*), *Arundo donex* L., Water lettuce (*Pistia stratiotes* L.), *Spirodela polyrhiza*. The efficiency of *Vetiveria zizanioides* (*V. zizanioides*) for manganese phytoremediation in hydroponic systems was also investigated [84,85].

In a study, Singh Thakur et al. [84] examined the ability of *V. zizanioides* to remove manganese from a hydroponic system. The researchers studied how pH and treatment time affected the removal of manganese and also calculated the translocation factors and bioconcentration. The results showed that the best pH for removal was 8 and the optimal treatment time was 22 days, resulting in a 99.3% removal of manganese by *V. zizanioides*. The researchers also observed that manganese accumulation was highest in the roots, followed by stems and leaves. Manganese was determined to have a 235.6 and 0.68 bioconcentration and translocation factor in *V. zizanioides*, respectively.

Guittouny-Philippe et al. [86] investigated *Alisma lanceolatum*, *Epilobium hirsutum*, *Carex cuprina*, and *Juncus inflexus* (European meadow rush, Hard rush) for the removal of As, Al, Cu, Cd, Ni, Fe, Mn, Cr, Zn, Sn, Pb and organic pollutants from industrial wastewater.

Spirodela polyrhiza is a freshwater macrophyte that can be used to remove Mn(II), Cu(II), and Zn(II) ions from single, binary, and ternary metal solution systems through adsorption, according to investigation of Meitei et al. [87]. They discovered that under 120 minutes equilibrium was reached also metal adsorption happened quickly. The Langmuir isotherm was found to be the best fit for equilibrium with maximal adsorption capacities for Mn(II), Cu(II), and Zn(II) ions being 35.7 mg/g, 52.6 mg/g, and 28.5 mg/g, respectively.

From investigations conducted by previously discussed researchers, it can be said that phytoremediation is a long-term treatment process hence it is comparatively more suitable for surface water sources. Wastewater containing Mn can also be treated using plants. Where the available space is more phytoremediation may be much more effective.

Membrane Filtration

Membrane technology is a common and effective approach to removing heavy metals. This process uses semi-permeable membranes with different pore sizes that come into contact with the substances you want to separate. These membranes work by allowing the solvent to pass through while trapping the heavy metals, effectively separating them from the mixture [88]. There are three primary kinds of membranes used in extraction processes: liquid membranes, pressure-driven membranes, and hybrid membranes. The efficacy and affordability of various membrane processes might vary based on numerous parameters, including the substances used to produce the membranes, the size of their holes, and their overall composition. Therefore, it's important to consider these factors when choosing a membrane for a separation operation [89,90]. Reverse osmosis, ultrafiltration, microfiltration, nanofiltration, and electrodialysis are the five types of membrane processes, which are frequently used in conjunction with other technologies [88,91–94].

Monica Mirea et al. [95] investigated the behavior of the transport of Fe^{2+} , Fe^{3+} , and Mn^{2+} cations via the bulk liquid membrane in the presence of Aliquat 336 as a carrier. Efficiency levels of less than 10% for the removal of Mn (II), less than 30% for the removal of Fe (II), and around 90% for the removal of Fe (III) were achieved under ideal transport circumstances.

Tang et al. [96] found that gravity-driven membrane (GDM) filtration, which is a novel biofilm-based UF technology. The GDM can effectively treat high concentrations of manganese-contaminated surface water. The study discovered that GDM filtration could rapidly and constantly establish a very high efficiency for both iron and manganese removal up to 90% in average rate by Fe/Mn during treating contaminated water. The UF membrane was also very effective in blocking out active

catalytic manganese oxides, and the rapid growth of iron- and manganese-oxidizing bacteria within biofilms contributed further to successful removal.

Reverse osmosis (RO) is another technique for heavy material removal. RO is notable for its great efficiency, lack of chemical requirements, lack of solid waste generation, and easy and compact automation [70,97,98]. In this method, solutes are extracted from solutions or separated using water that has been pushed across a semi-permeable membrane. The fact that this separation is achieved without a phase shift and requires little energy makes this technology very alluring. The fragility of the membranes is linked to the main issues in using these systems. Still, the production of superior polymers and membrane technologies is effectively overcoming this problem. Membranes have a two-year usable life, but they may be made to last longer by utilizing soft water, filters, and the right pressure and pH levels. Reverse osmosis can be beneficial when combined with other systems or during hot plating procedures [70].

UF is effective at removing species such as colloidal particulates, suspended species, and dissolved macromolecules [99]. During ultrafiltration, water, solvents, salts, and small organic molecules pass through the membrane [70]. Minimal pressure variations occur during ultrafiltration as salts are not detained by the membrane. Because of the comparatively large flux rates across the membranes, lower pressures may be employed.

Haddad et al. [100] investigated the workability of thin-film composite hollow fiber nanofiltration for the removal of dissolved Fe, Mn, and natural organic matter from domestic groundwater sources. The HFNF membranes demonstrated an impressive rejection of all model solutes (manganese, iron, natural organic matter [NOM]): over 90% in each case. The lack of membrane fouling was attributed to the smooth facer surfaces and the controlled hydrodynamic conditions. We observed a decrease in manganese and iron ions removal to different levels with increase water hardness while the natural organic matter was not affected by hardness level.

Kasim et al. [101] studied the effectiveness of UF and NF membranes in treating groundwater for drinking. Using commercial membranes, they found that TS40, TFC-SR3, and GHSP removed up to 60%, 80%, and 30% of manganese, respectively. However, these membranes were efficient in removing iron. Huang et al. [102] looked into employing polymer-enhanced ultrafiltration with polyvinyl amine (PVAm) as a complexing agent to remove heavy metals from water, like Fe (III), Co (II), Zn (II), Cu (II), Mn (II), Ni (II), Cd (II), and Pb (II).

Instead of using the straightforward membrane filtering methods used in previous research, Demirkol et al. [103] explored the removal of Fe^{2+} and Mn^{2+} by aeration with various catalysts and assessed the aerated submerged membrane systems individually. Total oxidation of Fe^{2+} was attained after 27 minutes of $\text{Fe}(\text{OH})_3$ application in the aeration stage, but total oxidation of Mn^{2+} took 76 minutes. However, total oxidation of Mn^{2+} and Fe^{2+} occurred somewhat slowly when MnO_2 was added during the aeration stage (110 and 36 min, respectively). According to the findings from the aerated membrane system, $\text{Fe}(\text{OH})_3$ enhanced the removal of Fe^{2+} and Mn^{2+} via adsorption/surface oxidation. $\text{Fe}(\text{OH})_3$ was found to improve the removal of Mn^{2+} and Fe^{2+} via adsorption/surface oxidation in the aerated membrane system.

Chery Leal et al. [104] focused on evaluating the efficacy of nanofiltration (NF) and ultrafiltration (UF) techniques, following pre-treatment steps for the elimination of manganese, iron, and HS. Nevertheless, while there was a significant decrease in the HS (about 80% after UF and 90% after NF, as measured by DOC, for two different kinds of water), whole method did not achieve satisfactory results (with an efficiency of less than 50%) in eliminating soluble manganese.

Acrylic acid and maleic acid copolymer with polyvinyl butyral (PVB) ultrafiltration membrane were used in Qiu et al.'s [105] investigation into the complexation-ultrafiltration removal of manganese from wastewater. Mn(II) was discovered to have a 99.6% rejection rate.

(RO) is now quite a popular technology used in water purification for drinking purposes. It can be run with the use of a low amount of electricity but the price of this available reverse osmosis technology is high for household use. Besides these nanofiltration and ultrafiltration are still not that popular among the general people.

Conclusion

Despite being a necessary element for human existence, manganese may be dangerous in the environment if its concentration rises over a certain point. Manganese must thus be extracted or recovered from wastewater and other waste materials. In recent times there are numerous technologies available for the removal of manganese due to the need for potable water, all these technologies have some advantages and disadvantages and applicability among the users. The literature study indicates that oxidation filtration can remove up to 99.8% Mn with a flow rate of 5.2 ml/min. Oxidation precipitation with O₂ or SO₂ as the oxidant can remove 99.5% Mn in a neutral pH range of 6-7 which is also very satisfactory. Phytoremediation is a long-term treatment process hence it is comparatively more suitable for surface water sources and further research needs to increase the removal efficiency of phytoremediation. Granular activated carbon also shows great efficiency but natural, waste and agro-based absorbents have immense potential as manganese removal material (solid tea debris, a low-cost agro absorbent can remove about 99% of manganese content from water, a "synthetic" Mn-coated medium can remove 100% of Mn at a flow rate of around 1 ml/min/cm²). Extract heavy metals from aqueous solutions, adsorption is currently the most efficient and cost-effective approach for the treatment of wastewater that contains heavy metals. Adsorption techniques are adaptable in their design and execution, and they typically result in treated effluent with acceptable quality. A competent desorption technique may refill the adsorbent, and adsorption is sometimes reversible. However, regeneration and activated carbon's expensive price restrict its application in adsorption. Additionally, the kind of adsorbents affects the adsorption effectiveness. Adsorption can be used in terms of the economy and locally available low-cost material can also be used as adsorbent. A relatively recent and promising method for removing heavy metals from wastewater is the biosorption of heavy metals from aqueous solutions. Membrane filtration and biological techniques need to be given more attention. Biological procedures can be conducted at low cost and can be applied for longer periods. The application of multiple removal techniques can be very effective and further research needs to be conducted regarding this. The use of multiple methods at a time may give 100% removal of manganese.

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