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Iron and manganese removal from groundwater: comprehensive review of filter media performance and pathways to polyfunctional applications

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Drinking water quality is a key factor in public health and the long-term operation of water supply systems. This article considers topical issues of iron and manganese removal from underground water, since exceeding the maximum permissible concentrations of iron and manganese negatively affects the organoleptic properties of water and causes corrosion of pipelines and clogging of water supply systems. This work covers the main criteria for selecting filter materials, including their physicochemical parameters, resistance to pollution, and durability. An analysis of existing filter media of natural, synthetic, and modified origin, such as quartz sand, activated carbon, anthracite, zeolite, and catalytic materials with manganese oxides, is carried out. Particular attention is paid to modern methods of modifying materials that improve their adsorption properties and increase the efficiency of iron and manganese removal. The findings emphasize the promise of using modified filter materials made from inexpensive or recycled waste. Such technologies can reduce water treatment costs and environmental impact and ensure high purification efficiency. The presented results and recommendations may be useful in developing new materials and technologies for water treatment.

Water impact

This paper explores innovative approaches to the removal of iron and manganese from underground water sources, emphasizing the development and application of modified filtering materials. The findings highlight the importance of using eco-friendly, cost-effective technologies that ensure high water purification efficiency while minimizing environmental impact. By proposing advanced solutions for groundwater treatment, this work addresses critical challenges in providing safe drinking water and improving the sustainability of water supply systems worldwide.

1 Introduction

The use of clean drinking water is an important aspect of human life. There are many standards for regulating the quality of drinking water supply.[1,2] The absence of a reliable source of drinking water supply, as well as the consumption of water of inadequate quality, entails a deterioration in public health. The most optimal source of drinking water supply is underground water (aquifers). This is due to the stability of its temperature, minimal pollution, and the microbiological safety of the water composition.[3] The presence of certain contaminants in underground water is determined by local hydrogeological conditions as well as anthropogenic impact. This may include pollution with heavy metals,[4,5] nitrates, chlorides, and so on.

A significant problem in the treatment of groundwater sources in many countries is the excess of the maximum permissible concentration of iron Fe(II) and manganese Mn(II) in the original water supply source.[6,7] The presence of contaminants results in clogging of water supply systems, corrosion,[8,9] and deterioration of the organoleptic parameters of water. According to ref. 2, the concentration of iron and manganese in drinking water should not exceed 0.2 mg L^{-1} and 0.05 mg L^{-1}, respectively. Another article[10] also found that the Fe/Mn ratio in underground water depends on nitrates entering shallow aquifers. At the same time, due to the higher redox potential of manganese, its oxidation by Mn^{2+} is more problematic than that of Fe^{2+}.[6]

Traditional methods of iron and manganese removal from underground water include simplified aeration followed by filtration,[11] dry filtration,[12] iron removal on frame filters, introduction of coagulant reagents or introduction of oxidizing agents[6] (chlorine and sodium hypochlorite, potassium permanganate ($KMnO_4$), ozonation), alkalization of water by adding lime,[5] and oxidation based on catalytic loading.[13,14] The use of non-traditional methods (ion

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exchange method,[5,15] *in situ* iron removal,[16] membrane or biological filtration) is justified only when complex underground water purification is required.

When considering iron removal processes, fundamental differences can be identified in the operating mechanism of inert and modified filter media (Fig. 1). In the case of using unmodified materials (Fig. 1a), the process occurs sequentially in two stages. At the first stage, homogeneous oxidation of dissolved divalent iron occurs in the water volume, resulting in the formation of colloidal iron hydroxide. As $Fe(OH)_3$ accumulates on the surface of the grains of the filler, an active sediment layer is formed, which initiates the second stage – heterogeneous sorption–catalytic oxidation and accelerated removal of iron. In contrast, the use of modified filter materials (Fig. 1b) ensures the occurrence of both stages simultaneously. The presence of a catalytically active coating on the surface of the grains contributes to the direct inclusion of sorption–catalytic mechanisms from the moment the filtration is started, which leads to increased efficiency and stability of the iron removal process already at the initial stages of filtration.

When considering all the presented methods of iron removal and demanganization, it can be seen that these water treatment technologies should be completed by the filtration stage.[14] In this case, the main element of the filtration unit's operation is the filter bed. Therefore, the correct parameters for selecting the catalytic and filter materials determine the method of removing iron and manganese in general. It is important to note that modified filter beds can be used as a catalytic material.[14,17,18] For modification, production methods can be used as an inert carrier or a source of metals to remain on the surface. As a result of modification, changes and improvements in the parameters of the original materials occur. All this will allow for a more detailed consideration of the characteristics of the water supply source and reduce the costs of water treatment plants and the cost of underground water purification. Based on the above, this article i) describes the criteria for selecting filter materials, ii) presents a comparative analysis of filter materials used at underground water iron removal stations, iii) provides an analysis of external coatings and methods for modifying filter materials, and iv) considers promising directions in the development of modified filter materials.

2 Analysis of existing iron removal filter loadings

2.1 Selection criteria and characteristics of filtering materials

The efficiency of Fe and Mn removal from underground water by filtration depends on many factors. These include the characteristics of the water supply source, the physicochemical properties of the impurities contained in it, and the parameters of the filter media, as well as the chemical and biological interaction of water with these materials.[19]

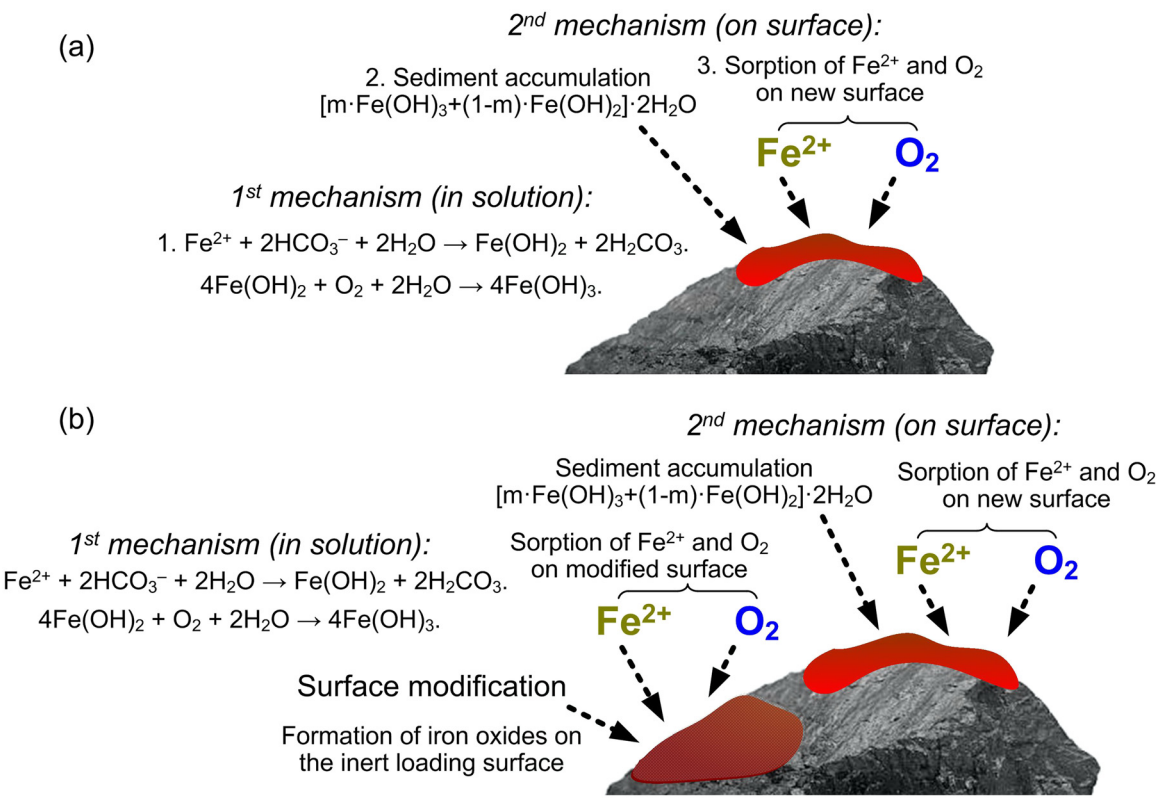

Fig. 1 (a) Mechanisms of iron removal on inert filter media; (b) mechanisms of iron removal on modified filter media.

The choice of granular filter media parameters according to the requirements[20,21] affects both the quality of the filtrate and the efficiency of the filtration process. The selection of the filter material should include the determination of the operational and sanitary-hygienic parameters of the material. Next, the hydrodynamic conditions of filtration, regeneration, the period of the filtration cycle, and the need for reagent treatment of the media are determined. The presented technological filtration parameters must be selected in such a way that the filter is washed upon reaching the maximum pressure loss without deteriorating the quality of the filtrate. If there are several commercially available filter materials, the final choice of loading is made considering technical and economic calculations, costs of transportation, and crushing and screening of the material, as well as the possibility of using screening waste.

In water treatment practice, when selecting filter media, the following material parameters are considered:[22] fractional composition (size) of the media grains, grain shape factor, degree of homogeneity of the media, porosity of the material and intergranular porosity, bulk density, hydraulic size of the media, angle of repose, specific surface area of the material, chemical resistance and mechanical strength of the material, cost, and durability. Some of the presented parameters can be determined based on the results of the sieve analysis. To perform it, a certain volume of the filter material is sifted through a system of calibration sieves, and the percentage of the material remaining on each sieve is determined.

Fractional composition (size) of grains. The use of a filter material of small size can lead to a decrease in the filtration cycle period, an increase in the consumption of wash water, and, as a result, an increase in the cost of water treatment. Meanwhile, the use of a material with a large size and a low specific surface area can lead to an increase in the thickness of the filter layer, an increase in the cost of the filter design, and a decrease in the quality of the filtrate.

Grain shape coefficient (GSC). This coefficient is defined as the ratio of the grain surface to the surface of a sphere of equal volume. Sharp, angular media produce larger voids and remove less sludge than rounded media of equivalent size. Also, materials with a high specific surface area and a high GSC have better adhesion properties, which improve the quality of the filtrate. At the same time, a high GSC leads to faster attrition of the filter media.[23]

Degree of homogeneity of the load.[24] It is characterized by the coefficient of heterogeneity of the material (K_U), which is defined as the ratio of the 80% to the 10% diameter of the filter material. When selecting a filter load, it is necessary to choose more homogeneous granular materials ($K_U < 2$). This will ensure deeper penetration of contaminants into the filter layer (with top-down filtration) with more complete use of the filter's dirt capacity and also create better conditions for backwashing the material. When using materials with high heterogeneity values, it is necessary to reduce the intensity of backwashing to avoid the removal of small grains of the load, which will lead to a decrease in the efficiency of backwashing.

Porosity of the material. It is defined as the degree of filling of the total volume of the material with pores. Filters with highly porous materials have a higher dirt capacity and a longer filtration cycle period.

Intergranular porosity. It is determined by the shape and structure of the pore space, the degree of interaction of the pores with each other, and the distribution in the layer of the filter material. An increase in intergranular porosity and specific surface area allows for an increase in the dirt capacity of the filter layer. This will increase the filtration rate and the duration of the filter cycle.

Bulk density

This parameter characterizes the amount of uncompacted mass in a container of known volume, considering the gaps (voids) between the grains of the material. Based on this parameter, the required intensity of filter washing is determined.

Hydraulic size of the bed. This parameter characterizes the rate of sedimentation of particles in stagnant water. The higher the sedimentation rate, the lower the concentration of suspended matter after passing through the filter bed. At present, the Stokes formula is used to determine this parameter. The calculation is made with a fairly large margin due to the imperfection of the determination technology. This affects the increase in the laid-out dimensions of treatment facilities and increases their cost.

Angle of repose. It characterizes the resistance of the material to shear. The factors affecting this parameter are the shape of the material particles, their mineral composition, the presence of surface films and the roughness of the surface of the bed, the density of the particles, friction, and adhesion forces.

Specific surface. It is determined by the ratio of the total surface of the porous body to its volume or mass. Materials with a developed specific surface allow the grain size of the bed to be increased without changing the height of the filter layer.

Chemical resistance of the material. A filtering load with satisfactory chemical resistance prevents the enrichment of the material with harmful impurities from the source water (AAS or ICP analysis at different pH levels of the leaching solution). This indicator is determined in alkaline, acidic, and neutral environments by the increase in dry residue and oxidizability of water as a result of contact of the granular material with these solutions. In practice, contact of the filtering load with a low pH value is possible when chlorinating the load after repair work or during unfavorable seasons of the year. It should be borne in mind that the permissible frequency of such contact is 2–3 times a year for 7–10 days. The increase of dry residue in water and oxidizability should not be more than 20 mg L^{-1} and 10 mg L^{-1}, respectively. At a typical increase in dry residue of 20 mg L^{-1}, full destruction of the filter material is achieved only after 28 years.

Mechanical strength of the material. Abrasion and grinding of the load as a result of friction and cracking of grains lead to clogging of the filter layer with the crushed material. As a result, the hydraulic resistance of the filter material and the energy consumption of the water treatment plant increase. A significant portion of the destroyed grains is also removed with the wash water. A mechanically strong material is considered to be one whose grindability does not exceed 4%, and whose abrasion is 0.5%.[25] Full destruction of such a material will be observed within 22 years. According to practical experience of operating filtering units, the loading has increased grindability in the first year. This is caused by the destruction of the sharp edges of the material during the filter backwash. Later, the grindability index decreases.

Durability of the material. It is a technical and economic indicator and is determined based on chemical resistance and mechanical strength. According to ref. 25, 7–10% additional loading of material per year is provided, which corresponds to a complete replacement of the material in 14–10 years. Also, after 10 years, unloading of the filter material is required for routine repairs of the drainage and distribution system. It should be noted that it is possible to use a less durable filter material, provided that greater filter performance is ensured.

In addition, filter materials used in domestic and drinking water supply must undergo sanitary and hygienic assessment for microelements passing from the material into water (Be, Mo, As, Al, Cr, Co, Pb, Ag, Mn, Cu, Zn, Fe, Sr). It is not always possible to meet all existing requirements for filter loading, since an increase in some characteristics can lead to a deterioration in others. An example of such dependencies is the hydraulic characteristics and size of the filter material, the ratio of the strength of the filter material, and the economic indicator. Therefore, the choice of filter material is carried out for specific conditions of use with the fulfillment of the most important indicators and the most complete fulfillment of the rest.

2.2 Types of filter materials for iron and manganese removal stations

All filter materials are divided into natural, synthetic, and modified natural by their origin. Among the most commonly used materials applied in underground water iron removal stations are quartz sand,[26] activated carbon (AC), pyrolusite[6] (manganese dioxide), anthracite (AN), expanded clay, shungite, and zeolite.[6,27] An article[15] found that the highest adsorption capacity of Fe was observed in basalts, anthracite, magnetite, sand, pumice, and limestone.

2.2.1 Filter materials of natural origin. Quartz sand (silicon dioxide) is the most commonly used retention layer in drinking water treatment.[25] Quartz sand has the smallest specific surface area compared to other mineral filter media. The material is resistant to various chemicals and durable,[28] and has a low cost and satisfactory efficiency of heavy metal removal. The effect of quartz sand on the chemical composition of water is insignificant. It is widely used in reagent-free removal of Fe^{2+} and Mn^{2+} from underground water by aeration followed by filtration.[19] The effective grain size of the sand is 0.15–0.35 mm,[22] the porosity is 42% and the density is 2.6 g cm^{-3},[19] the specific gravity is 2.66 g cm^{-3}, the bulk density is 1.55 g cm^{-3}, the uniformity coefficient is 1.38, and the specific surface area is 0.64 m^2 g^{-1}.[27,29] The sand has a high silica content and a low content of soluble Ca, Mg, and Fe compounds.[15] Sand with a silica content of at least 96% is chemically resistant and mechanically strong.[25] According to ref. 19, more than 95% of the removal of dissolved Fe^{2+} in the filter is due to the formation of Fe oxides in the upper part of the filter (0–50 cm). Alternating layers of Fe and Mn oxides are also observed on sand grains throughout the filter. The Mn oxide layers are more porous compared to the denser Fe oxide layers. In filters with high oxygen concentrations (O_2 > 250 μM), dissolved Fe^{2+} precipitates in the upper part of the filter (0–50 cm) *via* homogeneous, heterogeneous, or biological oxidation, in this case, with low crystallinity, for example, ferrite ($Fe_{8.2}O_{8.5}(OH)_4{\cdot}3H_2O$).[28] Mn^{2+} removal in rapid sand filters is achieved *via* heterogeneous and/or biological oxidation.[19] At a depth of 50 cm, 52% of the incoming Mn is removed in the filter. Mn(III) or Mn(III)/Mn(II) oxides are formed, including hausmannite, manganite, or feitknechtite. Mn^{2+} removal can be complicated by high concentrations of Fe^{2+} or ammonium (NH_4^+) in the feedwater.

Gravel filters are used to remove suspended solids and heavy metals. Gravel is also used as a support layer in other types of filters. Similar to sand, it has a high silica content and a low content of soluble Ca, Mg, and Fe compounds.[15] According to ref. 30, the height of the gravel filter layer should be 0.3–0.5 m and up to 1.5 m. About 50% of the incoming heavy metals are retained in the upper 30 cm of gravel. A trial filter for biological Mn removal was used.[31] The supporting material was gravel with an average loading diameter of 1.9 mm. The specific surface area was 3105 m^2 m^{-3}. The layer height was 143 cm, and the filter porosity was 0.38. The gravel provided a high specific surface area for the filter. Experiments showed that single-stage filtration was sufficient to simultaneously remove these pollutants. Also, in the study, a two-layer filter with gravel loading was used for the simultaneous biological removal of Fe, Mn, and NH_3. The upper layer is gravel with a diameter of 3.9 mm. The specific surface area is 1385 m^2 m^{-3}. The layer height is 70 cm, and the filter porosity is 0.38. Fe and NH_3 were removed on this layer. The lower layer was filled with gravel with an average diameter of 1.9 mm and immobilized manganese bacteria.

High-purity limestone can remove more than 90% of heavy metals due to the high carbonate content in limestone environments. According to ref. 5, at pH 8.5, limestone can remove up to 95% of Mn ions. Limestone characteristics: Ca content 36.2% and Mg 1.21%; pH = 6.62. The average diameter is 8.5 mm. The density is 1.54 mg m^{-3}. The specific surface area is 0.46 m^2 g^{-1}. The porosity is 0.432. Ref. 32 and 33 found that limestone (0.5–1 mm) in combination with

quartz sand treatment removes Fe from 1.5 mg L^{-1} to less than 0.1 mg L^{-1} (93%). According to ref. 33, the Fe(II) removal rate for limestone is 8.83 mg m^{-2}. In the article,[33] limestone successfully reduced the Fe(II) concentration (>99.4%) (<0.3 mg L^{-1} filtrate concentration). The removal efficiency is 4.06 g Fe per kg limestone. When treated water came into contact with limestone, the pH increased and siderite, goethite, and $Fe(OH)_3$ precipitated on the limestone surface.

Anthracite is a fossil solid fuel classified as a sedimentary organogenic rock. It has the highest carbon content compared to other types of fossil coal. It has a low specific surface area, density, and specific gravity.[28] Anthracite can be combined with other filter media in multi-layer filters.[15,28] Anthracite can also act as a carrier for biofilm development in biosphere filters.[28] Compared to equivalent sand-bed filters, it has a longer filtration cycle and lower pressure losses. The backwash rate is also reduced. According to ref. 34, anthracite has the following parameters: effective grain size of 1–1.1 mm, specific gravity of 1.65 g cm^{-3}, specific surface area of 1.833 m^2 g^{-1}, pore volume of 0.004 cm^3 g^{-1}, and pore diameter of 9.305 nm. According to ref. 29, the bulk density is 0.78 g cm^{-3}, the particle density is 1.56 g cm^{-3}, the average porosity is 43%, the uniformity coefficient is 1.33 and the specific surface area is 0.38 m^2 g^{-1}. In the article in ref. 35, the maximum Fe removal using anthracite (pH = 7) was 67%. The article in ref. 17 describes a study that is devoted to the use of anthracite as a catalytic material for iron removal from natural water. Anthracite granules were coated with iron oxide (Fe_2O_3) by exothermic combustion in solutions. The paper presents regression equations describing the relationships between the concentrations of Fe_{total} and Fe(II) in the filtrate depending on the time of filtration and the iron concentration on the surface of the modified anthracite. Activated carbon is obtained from natural materials (almonds, coconut,[17] nuts,[36] wood species, and coal). The material has increased adsorption properties, porosity, and surface area. In the article in ref. 17, coconut-based activated carbon (AC) with granules of 0.5–2.5 mm in size was used for modification. The bulk density was 0.49–0.53 g cm^{-3}. The specific surface area of AC can be 500–1500 m^2 g^{-1}. In the article in ref. 37, AC had the following properties: bulk density of 415 g L^{-1}, mechanical strength of 98%, and external surface area of 2235 m^2 m^{-3}. In the article in ref. 38, AS had a density of 0.44–2.5 g cm^{-3}, a specific density of 1.47 g cm^{-3}, and a porosity of 55%.

In the studies in ref. 39 and 40, low-cost sugarcane-based AC (SBAC) and rice husk-based AC (RHAC) were developed for the removal of Fe and Mn ions. By passing water containing Fe and Mn ions through both filter media, up to 100% removal of both Fe and Mn was observed. The removal efficiency of Fe(II) using modified coconut-based activated carbon was 95%. In the article in ref. 41, it was proven that the adsorption of Fe ions is faster and more preferable on peanut shell AC compared to Mn ions, where the maximum sorption efficiency of Fe and Mn ions is 90% and 84%, respectively. According to ref. 37, the adsorption of Fe and Mn ions on the AC surface is hampered by the presence of ammonia in the water. The removal efficiency depends on the concentration of these compounds, as well as on the pH and filtration rate.

Zeolite is a crystalline aluminosilicate of Na, K, Mg, and Ca with a porous structure. This material has lower hardness and mechanical strength than quartz sand. They are used as adsorbents and ion exchange materials. Natural zeolites (clinoptilolite, chabazite, phillipite, analcime, and others) are used for water treatment. They contain pores of uniform size in the range of 0.3–1 nm. The porosity of clinoptilolite is 0.50–0.55.[28] According to ref. 27, clinoptilolite has the following parameters: specific gravity of 2200–2440 kg m^{-3}, bulk density of 800–900 kg m^{-3}, porosity of 64.8%, grain diameter of 0.3–2.5 mm, effective grain diameter of 0.4 mm, abrasiveness of 8.2%, and specific surface area of 500–1000 m^2 g^{-1}. To effectively remove zinc from drinking water, a study of zeolite-based sorbents was conducted in the paper in ref. 42. The material was used to remove zinc cations by modifying the feedstock with $Fe(NO)_3{\cdot}9H_2O$ + KOH (to produce iron oxyhydroxide FeO(OH)) and $KMnO_4$ + NaOH (to produce manganese dioxide MnO_2). The results showed that modification of natural clinoptilolite with FeO(OH) and MnO_2 significantly improved the adsorption capacity of zinc cations. The increase in the concentration of Zn(II) on the surface of MnO_2 crystals and amorphous FeO(OH) indicates that these compounds lead to an increase in the capacity of the modified material. The developed sorbents improved their performance compared to their unmodified counterparts, with an increase in Zn(II) adsorption up to 99.65% in the case of MnO_2-modified clinoptilolite.

2.2.2 Manganese oxide coated catalytic materials. Materials with a MnO_x coating of natural or artificial origin (MTM, GreensandPlusTM, Greensand, Birm) allow the removal of dissolved Fe, Mn, and H_2S from underground water. GreensandPlusTM also allows the removal of arsenic and radium.[28]

MTM is a catalytic material (75% silicon dioxide, 10% quartz) coated with a manganese dioxide film (MnO_2). The chemically active coating of MTM is the lowest among the materials listed above (MnO_2 < 1%).[28] Conditions for using MTM according to the manufacturer:[28] pH 6.2–8.5. Lower pH leads to the destruction of the material. It can be used at manganese levels up to 5 mg L^{-1} and iron levels up to 15 mg L^{-1}. A regenerative solution of $KMnO_4$ (ranging from 28.35 to 56.7 g of dry $KMnO_4$ per 28.3 L loading) is employed to regenerate the MnO_2 layer. Material properties: effective grain size of 0.43 mm, bulk density of 720–800 kg m^{-3}, specific gravity of 2 g cm^{-3}, and uniformity coefficient of 2.0.

Manganese Greensand is a glauconite sand enriched with manganese oxides. It is widely used to remove Fe, Mn, and H_2S from underground water.[43] Manganese Greensand, as well as MTM, and GreensandPlusTM loadings can be used in slightly acidic underground water (pH = 6.2).[28] The material size is from 0.3 to 0.35 mm, the density is 2400–2900 kg m^{-3}, the bulk density is 1380 kg m^{-3}, and the uniformity

coefficient is 1.6. The MnO content is about 3–4%.[28] The filter efficiency increases at pH < 6.8.[44] Manganese sand is recommended for use when the combined concentration of Fe and Mn is in the range of 3 to 10 mg L^{-1}.

In a study,[43] the composition of five different commercial green sand materials was investigated. The largest differences were related to the nature of the base materials and the surface characteristics of MnO_2. Two samples were silica-coated with MnO_2, and the other three were different grades of MnO_2. Piispanen and Sallanko[45] demonstrated that an installed green sand layer used for underground water treatment reduced the concentration of iron and manganese by up to 98%.[43] The composition of the green sand did not have a significant effect on the adsorption of Mn(II) and Fe(II). The specific surface area of the material was considered as the main criterion for efficiency.[43] Manganese sand requires periodic regeneration of the MnO_2 layer with NaOCl or $KMnO_4$ solution. The continuous regeneration mode, where an oxidizer is added to the feedwater stream, is also considered. According to ref. 46, 1.29 mg Cl_2 per mg Mn(II) or 1.92 mg $KMnO_4$ per mg Mn(II) of oxidizer is needed to oxidize one milligram of Mn(II). The green sand bed is kept active during the treatment procedure by using a higher concentration of the oxidizer. Because the oxidizer eliminates the majority of the Mn(II) and Fe(II), and the filter bed eliminates any remaining Mn(II), this approach works well for high concentrations of Fe(II) and Mn(II).[43] The adsorption–oxidation method is considered to be compatible with the continuous regeneration mode, where dissolved manganese is eliminated by manganese green sand.[43]

$$Mn^{2+} + MnO(OH)_{2(s)} \rightarrow MnO_2MnO_{(s)} + 2H^+$$

$$MnO_2MnO_{(s)} + HOCl \rightarrow 2MnO_2 + H^+ + Cl^-$$

The oxidation of the adsorbed metal ions on the surface of the green sand reduces its productivity. The oxidized Fe(III) that results from the removal of Fe(II) blocks the active sites on the surface of the green sand.[43] Additionally, it was discovered that certain Fe(II) species considerably decreased the removal of Mn(II) when reacting with both Fe(II) and Mn(II) by leaching large amounts of Mn(II) through reductive dissolution. According to the material study, the process of Mn(II) removal is not dependent just on Mn(II) adsorption and is not associated with a phase shift of the MnO_2 surface. The dissolution process is displayed in the equation below, which illustrates the effects of the reductive dissolution of MnO_2 by Fe(II) that was investigated.[47]

$$MnO_{2(s)} + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$$

Birm is a natural aluminosilicate with an artificially applied catalytic layer of MnO_2. The Birm material contains several times more MnO_x compared to MTM, GreensandPlusTM, and Greensand manganese filter media.[28] It catalyzes the oxidation reaction of iron compounds with oxygen dissolved in water. No chemical reagents are required to restore the material. Backwashing is necessary to remove the accumulated oxidized sludge.

Birm is designed only for the removal of dissolved iron and manganese. The presence of hydrogen sulfide, polyphosphate, and organic matter in water leads to the destruction of the catalytic coating.[27,28] Water to be filtered through Birm media must be saturated with oxygen at 15% iron content and 29% manganese content at pH 6.8.

Depending on the manufacturer, this material has an effective particle diameter of 0.48 mm, a density of 2000 kg m^{-3}, a bulk density of 580–610 kg m^{-3}, and a uniformity coefficient of 2.7. The percentage of MnO_2 on its surface is 25–45%.[44] To restore the material's activity for manganese removal, water should be free of oils, organic matter, and chlorine.[44] For effective Fe removal using Birm media, the feed water pH should be 6.8–9.0, and for Mn removal, the pH should be 8.0–9.0. To achieve this pH, aeration is necessary to compensate for the low oxygen content in underground water. The chlorination process significantly increases the removal efficiency of Birm but does not increase its ability to remove manganese. In the presence of Fe and Mn, the pH should be 7.5–8.5.[15]

In the article in ref. 44, the efficiency of Fe removal during water purification (pH = 7.92, contact time = 30 min, and water temperature of 27.2 °C) was 76.4% when filtered through zeolite, 83.1% through manganese sand, and 92.4% through Birm. The efficiency of Mn removal under the same conditions was 68.5% for zeolite, 71.8% for manganese sand, and 87.5% for Birm media. Below is a comparison table of filter materials (Table 1). According to the table, the most optimal materials for filter operation are anthracite and activated carbon. These natural materials are the most common, accessible, and widely studied. Meanwhile, the catalytic materials available on the market are modified inert materials. The methods used to modify such materials are energy-intensive (long-term multi-stage heat treatment) and time-consuming (the synthesis process can take a day). Considering the long stages of thermal treatment, a significant impact on the environment can be expected. For this reason, the search for and development of new approaches to obtaining modified loads are relevant.

From Table 1, it can be seen that filter media perform with varying degrees of reliability depending on the raw water composition and treatment conditions. For example, quartz sand and Birm provide consistent performance under neutral to slightly alkaline conditions, but the material may lose some of its catalytic effectiveness under highly acidic pH conditions due to surface dissolution or oxide layer degradation. Greensand or MTM media based on manganese oxide surface coatings may perform well under slightly acidic conditions, but prolonged exposure to low pH conditions may significantly affect the durability of the coating. Limestone may perform well under alkaline conditions due to its ability to modify pH, but acidic conditions mean excessive dissolution and reduced

Table 1 Comparison of different filtering materials for deironing and demanganization of underground water

Filter loading parameters	Quartz sand	Gravel	Limestone	Anthracite (AN)	Activated carbon (AC)	Zeolite	MTM	Manganese greensand	Birm
Effective grain size, mm	0.15–0.35 (ref. 22)	5		0.6–0.8, 1–1.1 (ref. 34)	0.4–1.7	0.4	0.43 (ref. 28)	0.3–0.35	0.48 (ref. 28)
Porosity, %	42 (ref. 19)	36	40–45 (ref. 33 and 38)	43 (ref. 29)	55 (ref. 38)	50–55	—	—	—
Density, g cm^{-3}	2.6–2.75 (ref. 19, 38 and 28)	2.8	1.54 2.5 (ref. 38)	1.6 (ref. 29) 1.4–1.8 (ref. 28)	1.47 (ref. 38)	2.4 (ref. 28)	2 (ref. 28)	2.4–2.9 (ref. 28)	2.0 (ref. 28)
Specific gravity g cm^{-3}	2.66			1.65 (ref. 34)		2.2			
Specific surface area, m^2 g^{-1}	0.64 (ref. 29) 0.05–1.8 (ref. 28)	0.93–1.33	0.46	1.8 (ref. 34) 0.38 (ref. 29) 2.2–6.4 (ref. 28)	1.47 (ref. 38)	14–60 (ref. 28)			
Bulk density, g cm^{-3}	1.55–1.6 (ref. 27 and 28)			0.8 (ref. 29) 0.73–0.9 (ref. 28)	0.45–0.48 (ref. 37)	0.8–1.1 28	0.72–0.8 (ref. 28)	1.36 (ref. 28)	0.58–0.61 (ref. 28)
Homogeneity coefficient	1.38 (ref. 29)			1.33 (ref. 29)			2.0 (ref. 28)	1.6 (ref. 28)	2.7 (ref. 28)

performance and efficiency (Table 3). Highly porous media, such as zeolite or activated carbon, have greater adsorption capacity, but such characteristics may negatively impact backwash frequency (Table 2).

Removal of iron and manganese is highly dependent on the media's physical and chemical properties. More porosity increases more surface area for catalytic oxidation and adsorption operations. Grain size influences hydraulic performance and where the oxidation reactions take place. Smaller grains tend to have higher specific surface areas and greater removal efficiency, but may have higher headloss. The chemical stability of the media is a factor that provides long-term stability of the media under a combination of pH and oxidizing conditions and prevents degradation of the catalytic layer when the media are in operation for long periods of time.

Regeneration of filtering media for Fe and Mn removal is necessary to restore catalytic activity and ensure its continuous, reliable operation. The method of regeneration depends on the type and composition of the filter media, as well as the operating conditions and limitations. Chemical regeneration can involve the use of a strong oxidizing agent such as potassium permanganate or sodium hypochlorite, which can re-oxidize the reduced forms of manganese on the media surface. Chemical regeneration is common for Greensand, MTM, and other manganese-coated media, but excessive oxidizing agents can damage the media coating. Backwashing with aerated water is a common practice for silica sand used in filters, Birm, or zeolite media to remove deposits that have accumulated on the silica sand and media. Combination regeneration methods, *e.g.*, backwash and oxidizers, can provide higher recovery rates.

3 Synthesis of modified filter materials

The use of effective and moderately resource-intensive modification methods is an important aspect of the synthesis of modified filter media. These materials have the following benefits: i) the ability to modify and enhance the original material's properties; ii) the use of inexpensive original materials or recycled industrial waste for modification.

3.1 Classification of methods for modifying filter materials

The classification of methods for modifying filter materials is presented in Fig. 2.

Table 2 Fe and Mn removal efficiency by different loadings

Material	Fe removal, %	Mn removal, %	Test conditions	Notes
Quartz sand	>95 (Fe^{2+} in the upper 0–50 cm layer)	52 at 50 cm depth	High O_2 (>250 μM), pH ≈ 7	Mn is removed heterogeneously/biologically
Limestone	95 ± 3	52 ± 5	pH 8.5	Raises pH, forms siderite/goethite
Anthracite	96 ± 3	93 ± 4	pH 7	Long filter cycle, low resistance
Activated carbon (modified coconut)	67 ± 5	—	—	High sorption of Fe and Mn, but NH_3 interferes
Zeolite	95 ± 2	98 ± 3	pH 7.92, 30 min	Low strength, but high porosity
Manganese sand	76.4 ± 3.5	68.5 ± 3.0	pH 7.92, 30 min	Requires MnO_2 regeneration by layer
Birm	83.1 ± 4.0	71.8 ± 3.5	pH 7.92, 30 min	Optimum pH: Fe – 6.8–9.0, Mn – 8.0–9.0
Greensand	92.4 ± 2.5	87.5 ± 3.0	pH 6.2–6.8	Requires an oxidizer (KMnO4 or NaOCl)
MTM	—	—	pH 6.2–8.5	MnO_2 < 1%, $KMnO_4$ regeneration

Table 3 Operating conditions and loading requirements

Material	Optimum pH	Oxidizer/regeneration required	Features
Quartz sand	>6.5	No	Easy to operate
Limestone	>8.0	No	Increases water pH
Anthracite	6.5–8.5	No	Long cycle, low pressure loss
Activated carbon	>6.5	No	High sorption, sensitive to NH_3
Zeolite	>6.5	No	Ion exchange, low strength
MTM	6.2–8.5	$KMnO_4$	Low MnO_2 content
Greensand	6.2–6.8	$KMnO_4$/NaOCl	Works in acidic water
Birm	Fe: 6.8–9.0, Mn: 8.0–9.0	No (but O_2 is required)	Destroyed by H_2S, organics
Manganese sand	6.5–8.0	$KMnO_4$/NaOCl	High efficiency during regeneration

These methods can be divided depending on: i) processing temperature (drying (<105 °C), calcination (>105 °C)); ii) processing time (from several minutes to several days); iii) reagents used (non-reagent processing: increases the surface of the material and improves the structure of the material; processing with acids (hydrochloric (HCl), sulfuric (H_2SO_4), nitric (HNO_3), phosphoric (H_3PO_4), *etc.*): allows removal of metal impurities and increases the content of acid-containing groups on the surface of the material; processing with alkalis (sodium hydroxides (NaOH), potassium (KOH), calcium ($Ca(OH)_2$), copper ($Cu(OH)_2$), *etc.*): allows the surface area to be increased, reduces the hydrophilicity of the material, and changes the functional groups to increase the catalytic capacity and magnetic characteristics of the modified material; processing with metal salt solutions: increases the adsorption and catalytic properties and improves the magnetism of the material). The following are used as salts: i) nitrates of iron ($Fe(NO_3)_3{\cdot}9H_2O$), manganese ($Mn(NO_3)_2{\cdot}6H_2O$), lanthanum ($La(NO_3)_3{\cdot}6H_2O$), silver ($AgNO_3{\cdot}9H_2O$) and others; ii) sulfates of iron ($FeSO_4{\cdot}7H_2O$), copper ($CuSO_4{\cdot}5H_2O$) and others; iii) chlorides of iron ($FeCl_3{\cdot}6H_2O$), manganese ($MnCl_2{\cdot}6H_2O$), lanthanum ($LaCl_3{\cdot}6H_2O$), calcium

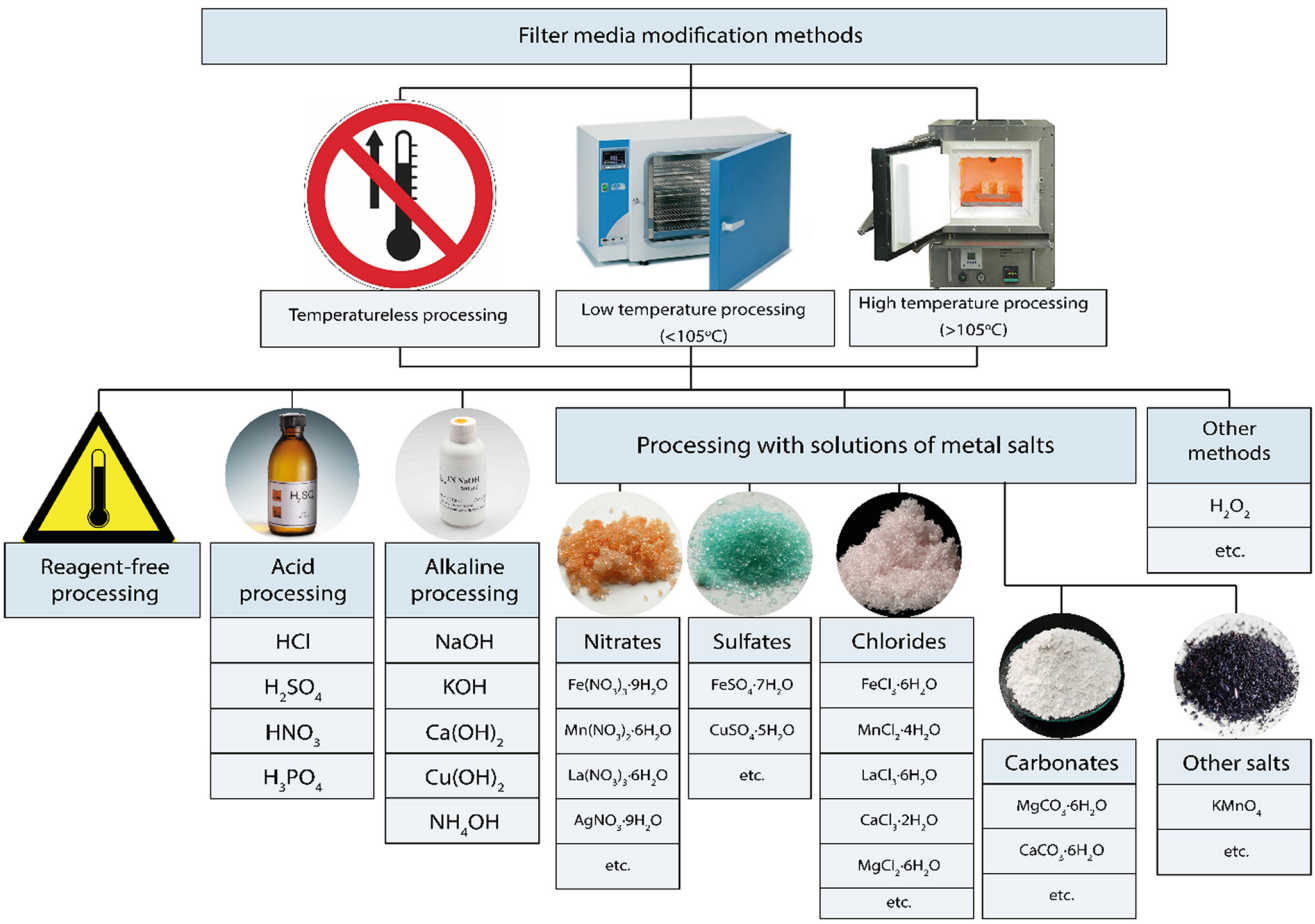

Fig. 2 Classification of methods for modifying filter materials.

($CaCl_3 \cdot 2H_2O$), magnesium ($MgCl_2 \cdot 6H_2O$) and others; iv) carbonates of magnesium ($MgCO_3 \cdot 6H_2O$), calcium ($CaCO_3 \cdot 6H_2O$) and others; v) other metal salts: potassium permanganate ($KMnO_4$) and others; vi) treatment with other reagents (hydrogen peroxide (H_2O_2)): increases the content of oxygen-containing functional groups (carboxyl groups), decreases pH, increases the sorption capacity of the material depending on the adsorbate, and increases the surface area of the material.[48]

3.2 Methods of modification of filter materials depending on the purposes of synthesis

According to the classification presented in section 3.1., the initial materials can be modified by physicochemical, chemical, or thermal treatment. These kinds of treatments enable the initial material to acquire new characteristics. Changing the morphological characteristics of the starting material, such as texture, roughness, mechanical strength, and chemical resistance, is achieved using physicochemical methods. To increase the specific surface area of the material, acid modification methods using potassium permanganate $KMnO_4$ or aluminum chloride ($AlCl_3$), magnesium ($MgCl_2$) or zinc ($ZnCl_2$),[49] magnetic,[50] and alkaline can be used.[49] Also, steam activation[51] and acid[49] and magnetic[50] modifications lead to the formation of a porous structure or micropores with an increased average pore diameter. Using acid[52] and magnetic[50] modification or chemical modification using potassium hydroxide (KOH) and hydrogen peroxide (H_2O_2),[53] an increase in adsorption properties and adsorption capacity and an increase in the ability to adsorb heavy metals are achieved. Through heat treatment[51] or steam activation,[51] acid ($KMnO_4$, $AlCl_3$, $MgCl_2$ or $ZnCl_2$)[49] or alkaline modification,[49] the formation of hydroxyl, basic functional, or oxygen-containing groups on the surface of the material is achieved. The formation of a positive charge on the surface of the starting material for the adsorption of negatively charged ions[49] is achieved by alkaline modification.

Chemical modification techniques involving chemical reactions on the original material's surface are appropriate if it is necessary to alter the surface's chemical composition. The original material is soaked in a solution of salts, chlorides, carbonates, and sulfates to create coatings for the removal of metal ions. The steps of drying, heat treatment, and washing come next. Such treatment results in the formation of a surface coating. The deposition of metal oxides on the surface of the material in the form of separate phases can be achieved using acid[49] and magnetic modifications[50] or the method of exothermic combustion in solutions (solution combustion synthesis, SCS).[13,17]

A promising method for modifying granular filter materials may be the method of exothermic solution combustion in solutions (SCS).[54] This method is characterized by short synthesis time, low environmental impact, and low reagent and energy consumption.[55–58] To carry out the chemical reaction, the starting material is soaked in a stoichiometric mixture of metal salts (oxidizer) and organic compounds such as urea and citric acid (reducing agent). Afterward, the material is filtered and placed in a muffle furnace at a temperature of 600 °C.

A number of laboratory and pilot-scale studies have shown that the processes of Fe^{2+} and Mn^{2+} removal on catalytically active loads obey kinetics close to pseudo-first order, where the reaction rate depends on both the concentration of dissolved oxygen and the initial pH value, and on the degree of preliminary surface activation. In this case, heterogeneous oxidation occurs in parallel with the adsorption of hydroxide forms of metals on active centers, and the formation of $Fe(OH)_3$ and MnO_2 precipitates additionally increases the sorption capacity due to the formation of new surface areas. Experimental data indicate that under optimal conditions (pH 7.5–8.5, the presence of free $O_2 > 2$ mg L^{-1}), 80–95% of iron is removed during the first 10–15 minutes of contact, and manganese in 20–30 minutes. Economic assessment shows that when choosing the optimal loading and operating mode, the total operating costs for reagents and maintenance are reduced by 15–25% compared to traditional iron and manganese removal schemes, which is especially noticeable in systems with combined oxidation and periodic regeneration of the catalytic layer.[18]

3.3 Analysis of coating varieties for modification of filter materials

As described above, in addition to the main pollutants, such as iron and manganese, underground water may also contain other pollutants that have a negative impact on their removal from underground water during the purification process. During the modification of the source material, various types of coatings can be used depending on the purpose of water treatment. In addition to Fe and Mn, groundwater typically contains associated contaminants such as phosphate, ammonium, and possibly pathogens, which can negatively impact the catalytic activity and service life of Fe/Mn removal materials. Therefore, additional modifications, such as zinc, silver or copper oxide,[59] will help inactivate microorganisms or prevent biofouling. In multifunctional coatings, both the main catalytic layer and other functional components may be present to provide additional functions. These include the inactivation of microorganisms, removal of nitrates and phosphates, and removal of other heavy metals from underground water (Fig. 3).

Along with the main contaminants of underground water, such as iron and manganese ions, they often contain associated substances, including phosphates, ammonium, nitrogen, and other ions, as well as possible pathogenic microorganisms. In this regard, various types of coatings designed to remove such contaminants and inactivate microorganisms will be discussed below.

3.3.1 Modification of filter media to remove nitrates and phosphates. Animal waste products, malfunctioning home

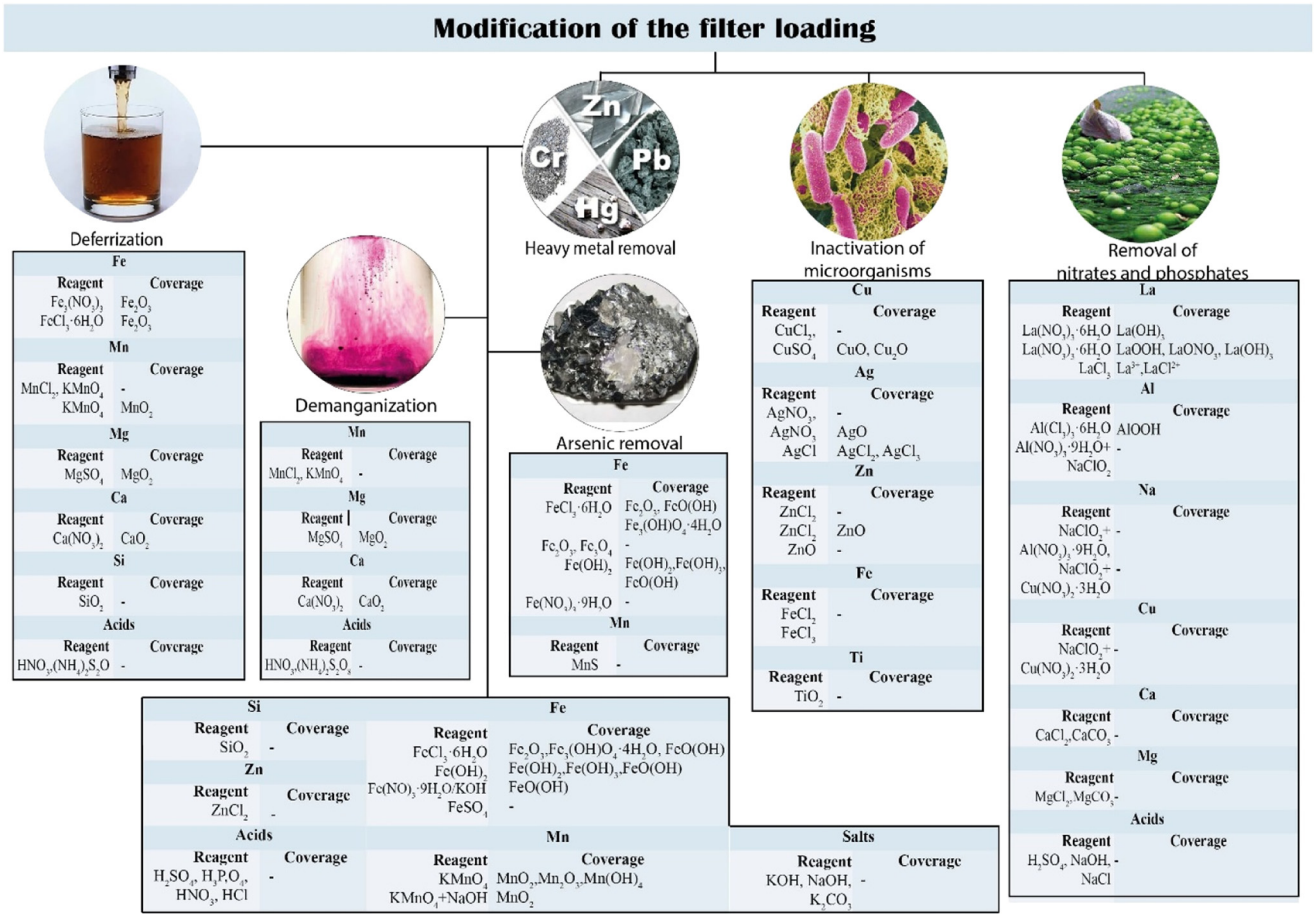

Fig. 3 Types of filter material coatings.

wastewater treatment systems, and contamination of the water supply source with dead plant and animal particles can all contribute to the presence of nitrates in natural water.[11] When organic nitrogen compounds mineralize, such as when protein breaks down into amino acids, nitrates are created in water. The bacterial ammonium is first oxidized to nitrites and subsequently to nitrates in this process. The surface water body exhibits eutrophication when the nitrate concentration rises. On agricultural land, eutrophication can also happen when fertilizers and household waste are present. Consequently, this causes land erosion, phosphate concentrations in natural water to rise, photo- and zooplankton to increase, and dead biomass to increase. To remove nitrates from treated water, the article in ref. 49 used modified natural zeolite. The treatment was carried out using acids, bases, and salts (H_2SO_4, NaOH, and NaCl), calcination, and ultrasound for the subsequent removal of nitrite from the treated water. The most effective modification method was the treatment of zeolite with H_2SO_4 acid. As a result, an increase in the specific surface area and adsorption properties of the material was observed. In the article in ref. 60, lanthanum chloride ($LaCl_3/La^{3+}$, $LaCl^{2+}$) was applied to the surface of a porous zeolite using hydrothermal synthesis. The research results also established the high efficiency of the material for phosphate adsorption (95%) in a wide pH range of 3–7.

Also, in the article in ref. 61, a new lanthanum-based magnetic adsorbent was developed for the removal of phosphates from wastewater. For this purpose, natural magnetite (Fe_3O_4) was partially dissolved in a hydrochloric acid (HCl) solution. The resulting suspension was then mixed with an alkaline solution (NaOH) and calcined to obtain a ferrihydrite coating of natural magnetite. The sample was also treated with lanthanum nitrate $La(NO_3)_3{\cdot}6H_2O$. As a result of the study of the adsorption and desorption cycle, a high adsorption capacity of the synthesized material was demonstrated. Also, when it interacted with real wastewater, the phosphate concentration was reduced from 1.7 mg L^{-1} to less than 0.02 mg L^{-1}. A similar method for obtaining a sorbent for phosphate removal is described in the article in ref. 62. The modification consisted of the chemical deposition of lanthanum composites ($La(NO_3)_3$/LaOOH, $LaONO_3$, $La(OH)_3$) on the surface of activated carbon. This treatment contributed to the reduction of negative charges and the surface area of biochar. In addition, in the article in ref. 63, high adsorption efficiency of nitrates and phosphates was achieved using modified biochar with different aluminum contents on the surface of the filter material

($AlCl_3 \cdot 6H_2O$/AlOOH). Also in the article in ref. 64, 99.6% phosphate removal was achieved using a carbon fiber modified with copper ($Cu(NO_3)_2 \cdot 3H_2O$) and aluminum ($Al(NO_3)_3 \cdot 9H_2O$). The reuse of the sorbent and the regeneration potential showed the high recycling capacity of the material.

3.3.2 Modification of filter media for inactivation of microorganisms. To reduce the activity of pathogenic microorganisms in purified water and on the surface of the filter material, water supply facilities are disinfected.[65–68] Most methods for preventing biofouling (using chlorine or hypochlorite) do not prevent the re-formation of biofilms. Also, the use of classical methods of treatment with ozone, chlorine, heavy metal ions, ultraviolet, and ultrasound significantly complicates the water treatment process. This entails an increase in corrosion,[66] reagent consumption, economic and environmental costs[68] and the cost of water treatment. These expenses will be decreased by using modified filter materials. Zinc treatment of the filtering load is one of the efficient ways to change the filter material and prevent biofouling. Therefore, the impregnation and heating approach was used in the article in ref. 69 to modify activated carbon with zinc oxide (ZnO). Oxide was evenly distributed across the activated carbon's surface. As a result of the research, the safety of using zinc was confirmed, and it was also found that modified activated carbon is capable of reducing the content of *E. coli* in the treated water by up to 91%.

The patent in ref. 70 discusses the development of nanoparticle-modified SiO_2 treated with $CuCl_2$, $AgNO_3$, $ZnCl_2$, $FeCl_2$, and $FeCl_3$. The modified nanoparticles bind various gases and/or aromatic compounds, which allows for the removal of these compounds from air and water. Metal ions are also attached to the surface of the nanoparticles and are bound to the surface of the material. Also, in the article in ref. 71, activated carbon was modified using titanium dioxide (TiO_2). This led to a decrease in the level of bacteria in drinking water. There are cases when the same type of modification of the filter material coating can meet several water treatment tasks at once. For example, silver ($AgNO_3$) modified zeolite promotes the removal of heavy metals (Pb, Cd, and Zn) and the elimination of *E. coli* bacterial cells.[72] As a result, complete inactivation of microorganisms and removal of Cd and Zn were achieved over 1080 min. No breakthrough of Pb ions was observed until 7920 min due to the high selectivity of the zeolite.

Inactivation of microorganisms can also be achieved by treating activated carbon with copper and silver oxides ($AgNO_3$/Ag_2O, $CuSO_4$/CuO, Cu_2O). For this purpose, the article in ref. 73 studied the purification of bacterial suspensions using filters with the obtained material. As a result, the high efficiency in bacteriophage inactivation and the high inactivation capacity of the modified material without significant transfer of silver and copper into the filtrate were confirmed. Interest in the use of silver-based disinfection is due to its safe and effective bactericidal effect. For example, in the article in ref. 74, a material with a chlorinated silver coating (AgCl/$AgCl_2$, $AgCl_3$) was used for bactericidal action on the treated water. Modification was carried out by a chemical or electrochemical method. This coating contributed to a significant increase in bactericidal effect compared to the original material. Deterioration of such properties was observed only at high values of hardness and the amount of organic matter.

Some types of clays and clay minerals can be effective and easily accessible starting materials for modification. Thus, in the article in ref. 75, a mixture of clay–polymer composites using bentonite and commercial polymers was used to remove *E. coli* from treated water. In addition, a new bacteriostatic hybrid clay composite was synthesized from a combination of kaolinite, *Carica* seeds, and papaya. Zinc chloride $ZnCl_2$ was used to obtain a modified ZnO coating. Such a composite is used to effectively remove cholera vibrios and *Salmonella* from water. Kaolinite clay mineral modified with chitosan also turned out to be effective in removing bacteria from water.

A significant problem in the operation of membrane filters for water purification is the unwanted adsorption of biological materials on the filter surface. As a result, the permeability and service life of the membrane are reduced. Therefore, biofouling prevention is an important aspect of membrane filter performance.[69,76–78]

3.3.3 Modification of filter media for removal of heavy metals. Metals with a molar mass above 40 are classified as heavy metals. These include iron (Fe), manganese (Mn), zinc (Zn), arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), nickel (Ni), copper (Cu), chromium (Cr), strontium (Sr), thallium (Tl) and other metals. The presence of increased concentrations of heavy metals in drinking water leads to mutations and changes in metabolism in the human body, disruption of the structure and permeability of cell membranes, *etc.* Modified filter materials can also be used to effectively remove these components from water.

For example, effective removal of Zn^{2+} was achieved in the article in ref. 42 using modified zeolite materials. The modification was carried out using $Fe(NO)_3 \cdot 9H_2O$ and KOH (to obtain iron oxyhydroxide FeO(OH)) and $KMnO_4$ + NaOH (to obtain manganese dioxide MnO_2). The combination of MnO_2 crystals and amorphous FeO(OH) contributed to an increase in the capacity of the modified material and the adsorption efficiency of zinc cations (99.7% compared to the original material).

Activated carbon, which is modified by forced hydrolysis with iron chloride ($FeCl_3$),[79] can be an effective filter material for removing arsenic (As) from water. As a result of a 6-hour reaction, iron oxides (Fe_2O_3, $Fe_3(OH)O_7 \cdot 4H_2O$, FeO(OH)) are formed on the surface of the material. In this case, the modification does not change the structure of the material, and the efficiency of arsenic removal from underground water reaches 94%. In the article in ref. 80, arsenic removal was carried out using activated carbon coated with $Fe(NO_3)_3 \cdot 9H_2O$. This coating was obtained by oxidation with HNO_3/H_2SO_4 or $HNO_3/KMnO_4$. As a result, the amount of

iron on the surface of the material and the arsenic sorption rate were increased. An alternative method for removing arsenic from natural water can be adsorption on iron oxide (Fe_2O_3, Fe_3O_4)-treated brown algae (*Sargassum muticum*).[81] Despite significant leaching of iron in the solution, arsenic removal from contaminated water reaches 100%.

Modified materials can also be used in the complex removal of heavy metals. The article in ref. 82 described a method for the combined removal of arsenic and nickel from underground water. For this purpose, granular sorption materials GEH, CFH 0818, CFH 12, and Bayoxide with a coating based on iron oxides and hydroxides ($Fe(OH)_3$, $FeO(OH)$, Fe_2O_3) were used. As a result, contact of water with these materials for 2.5 minutes allowed the nickel concentration to be reduced to the standard requirements. Subsequent interaction did not lead to a significant effect on the removal of nickel. The studies also showed the effectiveness of the material in the adsorption of iron and manganese. The best effect of removing heavy metals from water was achieved using Bayoxide. In the article in ref. 83, a peat-based sorbent with iron oxide on its surface was synthesized. For this purpose, peat powder was immersed in an iron salt solution ($FeCl_3{\cdot}6H_2O$). Experimental adsorption of Cu, Cr, As, and Zn at pH = 5 showed that the iron coating increased the adsorption efficiency of As from 5 to 80% and Cr from 3 to 25% compared to the original material. The SEM/EDX analysis showed the homogeneity of the iron coating and active sorption of Cr on the surface of the filter material. At the same time, the sorption of Cu and Zn on the surface of the modified peat was insignificant.

Comprehensive removal of heavy metals is also possible using composite materials (clay and activated carbon) modified with iron oxide.[84] These materials were used to remove lead Pb, cadmium Cd, and arsenic As from natural water. As a result, the concentrations of these heavy metals are reduced to standard requirements. According to FTIR analysis, the main functional groups responsible for the removal of the presented heavy metals were hydroxyl, carboxyl and Fe–O bonds ($Fe(OH)_2$, $Fe(OH)_3$, $FeO(OH)$).

In the article in ref. 85, modification of quartz sand was carried out for the comprehensive removal of copper Cu(II) and copper Cu(II) from natural water. When treated with manganese nitrate $Mn(NO_3)_2{\cdot}6H_2O$, manganese nanoparticles (MnO_2, Mn_2O_3, $Mn(OH)_4$) were uniformly distributed on the surface of quartz sand. This led to a significant increase in the removal capacity of Cu (II) and Pb(II) and an increase in the surface area of the material. Inexpensive materials or agricultural waste can be used as starting materials to obtain a modified bed. This helps to solve the problem of disposal of this type of waste.[86,87] According to ref. 86, carbon activation is possible from euryale waste, bamboo fragments, cherry pits, tea waste, paulownia flowers, *etc.* The properties of such materials will depend on the pyrolysis conditions and the adopted activation procedure. In the study in ref. 86, biochar was activated using KOH, H_2SO_4, $ZnCl_2$, K_2CO_3, NaOH, H_3PO_4, and HNO_3. The resulting material is a good adsorbent for removing nitrogen oxide NO_2 and hydrogen sulfide H_2S from gas vapor, as well as for removing methylene blue and iodine from the liquid phase. A material was also obtained for removing lead ions Pb from wastewater by activating biochar from sugar cane waste (bagasse) with HNO_3. Similarly, in the article in ref. 87, activated carbon was modified, which was obtained from fruit plant waste. As a result of chemical activation with 85% phosphoric acid solution (H_3PO_4), a cheap and effective material for copper Cu(II) removal was obtained. The article in ref. 88 demonstrated the efficiency of removing chromium Cr(VI) from wastewater using modified activated carbon based on rice husk. Modification was carried out by treating the initial material with a 0.1 M solution of hydrochloric acid (HCl). It was found that with an increase in pH, an increase in the adsorption of Cr(VI) was observed. The removal of iron and manganese ions from water is more effective when phases containing these elements are applied to the surface of the original material. Treatment with iron sulfate and iron oxide, manganese chloride and oxides, potassium permanganate, sodium triphosphate or sulfite, calcium, or magnesium peroxide can accomplish this. Modified materials treated with zinc chlorides and oxide are appropriate if it's required to inactivate microorganisms and save money.[69]

3.3.4 Modification of filter media for iron removal from underground water. Efficient oxidation of Fe^{2+} to Fe^{3+} can be achieved in the presence of an effective oxidizer such as iron on the surface of the modified material. For example, the article in ref. 13 describes a study of anthracite modified with iron oxide Fe_2O_3. Modification was carried out using the method of exothermic combustion in solutions. Additionally, the study explained how the concentrations of Fe_{total} and Fe(II) in the filtrate varied according to the time of filtration and the amount of iron present on the modified anthracite's surface. In ref. 89, deironing and demanganization of underground water were carried out using modified quartz sand. Modification was carried out with sequential treatment with a 0.5% solution of manganese chloride ($MnCl_2$) and potassium permanganate ($KMnO_4$). As a result, the surface of the material was covered with a fine suspension of MnO_2. This contributed to the increased efficiency of manganese and iron oxidation even at lower pH values. To prevent increased $KMnO_4$ consumption, solutions of iron sulfate ($FeSO_4$) and potassium permanganate ($KMnO_4$) were applied to the surface of the material. To fix the resulting film on the surface of the material, the modified material was treated with sodium triphosphate or sulfite (Na_2SO_3).

One of the new catalytic materials for water deironing is "activated pink sand", Institute of Mining SB RAS.[90] The material was modified by infiltration and stepwise heat treatment with salt solutions. As a result, coatings of manganese (MnO_2) and iron (Fe_2O_3) oxides were formed on the surface of the original material (argillite rocks). The paper in ref. 91 reported on the use of modified biosand filters (MBSF) to remove *E. coli* and different concentrations of nickel Ni, iron Fe, copper Cu, and zinc Zn from treated water.

These filters were filled with iron oxide-treated gravel and three layers of soil. The following water treatment efficiencies were achieved: 99–98.2% for Cu, 99.12–99.06% for Zn, 98.17–94.03% for Ni, 95.27–92.33% for Fe(II), and 94.21% for total coliform bacteria. The filter performance after regeneration was also demonstrated. In the article in ref. 92, the modification of coconut-based activated carbon was carried out. To activate the carbon, the coconut shell was heated at a temperature of 900 °C for 4 hours. Also, the calculated amount of $KMnO_4$ was added to the carbon to form 1.0 mg L^{-1} MnO_2 in the structure of the material. Then the material was dried at a temperature of 60 °C for 1 hour. The obtained material allows removal of iron from water to values below 0.3 mg L^{-1} without increasing the pH.

3.4 Promising directions for creating new loadings

Based on section 3.2, filter media modification methods can be divided into three main classes: chemical, thermal, and physicochemical. Each approach has its advantages and limitations, especially in Fe/Mn removal. Chemical modifications (*e.g.*, acid–base treatment and metal salt impregnation) can effectively increase the surface area and add active oxide coatings such as MnO_2 or Fe_2O_3. Simple-to-implement chemical modification methods have the limitation of continuous leaching of the active phase under acidic conditions, and material regeneration is often required. Thermal modifications (*e.g.*, calcination and thermal activation) can increase the stability of the structure, remove volatile impurities, and improve the crystallinity of the catalytic phase, increasing the service life, but they can also affect the surface hydroxyl groups important for particle adsorption. Thermal modifications often require large energy costs. A promising method here is exothermic combustion in solutions, where the temperature is only needed to initiate a self-propagating reaction. Physicochemical modifications (*e.g.*, hydrothermal coating, sol–gel deposition, and plasma treatment) allow precise control over the composition and morphology of the catalytic layers and provide unique and often multifactorial characteristics. This method is characterized by initially high adhesion of the active phase and a specific pore structure, but, as a rule, it is more complex, requires special equipment, and is more expensive than other modification methods. The optimal modification method will depend on the desired improvement in productivity, operational stability, and cost-effectiveness under specific water treatment conditions.

A promising direction in the field of creating new catalytic materials for iron and manganese removal from underground water is the synthesis of polyfunctional filter materials. There are many examples where combining different processes in one leads to synergy in efficiency.[93] This type of material, in addition to improving the characteristics and morphology of the material, will increase the efficiency of water treatment in several directions at once. For example, by changing the chemical composition of the material, simultaneous removal of iron and inactivation of microorganisms can be achieved (for example, a coating based on iron and zinc). In addition, the use of cheap granulated natural materials or waste as an inert matrix will also reduce the cost of water treatment. In this case, there will be no significant changes in the operating modes of the filter.

4 Conclusions

All methods of iron and manganese removal require a filtration stage through granular loading. The use of catalytic filter materials for these purposes without the addition of oxidizing reagents is the simplest and most accessible. Meanwhile, the problem of iron and manganese removal may arise in the presence of organic films on the surface of the material. Modified materials with a microorganism-inactivating layer are used to solve these problems. Modification allows changing and improving the parameters of the original loading. For modification, anthracite and activated carbon can be used as the original materials as they are the most studied and widely used materials. Inexpensive granulated natural materials or recycled industrial waste can also be the basis for modification. Polyfunctional filter materials are of particular interest since their use allows for solving several water treatment problems at once, in particular, iron removal and microorganism inactivation.

Author contributions

Dmitry Propolsky: validation, formal analysis, visualization, data curation, writing – original draft. Valentin Romanovski: supervision, conceptualization, methodology, validation, formal analysis, data curation, writing – original draft, writing – review and editing.

Conflicts of interest

The authors declare no competing interest with any previous work.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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