



Review

Water purification using magnetic assistance: A review

Ritu D. Ambashta^{a,b,*}, Mika Sillanpää^{a,c}^a Laboratory of Applied Environmental Chemistry, University of Eastern Finland, Patteristonkatu 1, FI-50100 Mikkeli, Finland^b Backend Technology Development Division, Bhabha Atomic Research Centre, Mumbai 400085, India^c Faculty of Technology, Lappeenranta University of Technology, Patteristonkatu 1, FI-50100 Mikkeli, Finland

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ABSTRACT

Water is a major source for survival on this planet. Its conservation is therefore a priority. With the increase in demand, the supply needs to meet specific standards. Several purification techniques have been adopted to meet the standards. Magnetic separation is one purification technique that has been adapted from ore mining industries to anti-scale treatment of pipe lines to seeding magnetic flocculent. No reviews have come up in recent years on the water purification technique using magnetic assistance. The present article brings out a series of information on this water purification technique and explains different aspects of magnetism and magnetic materials for water purification.

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* Corresponding author at: Laboratory of Applied Environmental Chemistry, University of Eastern Finland, Patteristonkatu 1, FI-50100 Mikkeli, Finland.

Tel.: +358 40 355 3710; fax: +358 15 355 6363.

E-mail addresses: Ritu.Ambashta@uef.fi, aritu@barc.gov.in (R.D. Ambashta), Mika.Sillanpaa@uef.fi (M. Sillanpää).

1. Introduction

The major drinking water sources include ground water, lakes and reservoirs, canals, atmospheric water generation, rain water harvesting, fog collection and sea water. Their contamination could be varied depending on the source of pollutant [1–6]. Management of water can be divided based on source of water which could be further classified as natural source water management, domestic waste water management, and industrial waste water management. Depending on quality of water, each scheme needs a separate plan of action for re-use or disposal. In case of water remediation biological, chemical and physical methods are commonly adopted. The biological treatment refers to degradation of organic compounds by breaking and transformation of inorganic compounds by bio-aided reactions. Some of the chemical treatment methods include coagulation, oxidation, electron beam irradiation, radiocolloid treatment and sorption to organic/inorganic substrates. Some physical treatment methods include air-sparging/air-stripping and incineration [7,8].

The techniques in water purification can be classified into six methods:

- Adsorption
- Biotechnology
- Catalytic processes
- Membrane processes
- Ionizing radiation processes
- Magnetically assisted processes.

In addition, nanomaterials based processes are emerging as promising options to the currently practised water treatment schemes.

The adsorption technique is the most frequently studied and industrially adopted technique [9–12]. Activated carbon from various sources such as coconut coir, jute stick, rice husk etc is the most popular of the adsorbents. The treatment of water includes adsorption methods using specific ion exchangers or extractants and combination of adsorption with catalytic treatment methods, redox processes and magnetic processes. Recently, a new technique in adsorption is reported by the application of carbon nanotube clusters [13]. The unique property of this cluster is in the removal of bacteria from water by adsorption method.

In the area of biotechnology, plants as sorbents and microbes for contaminant destruction or transformation are widely studied [14,15]. In case of water purification for degradation of organic pollutants, Simpson gave an account on biologically active carbon biofilm capable of degrading a significant fraction of entrapped water-borne nutrients and dissolved organic matter adsorbed on granular activated carbon (GAC) surfaces and other contaminants, minerals and microorganisms contained in source water [16]. Another method for water purification termed as Soil Biotechnology, or SBT, uses a formulated soil environment wherein fundamental processes of nature, viz. respiration, mineral weathering and photosynthesis bring about the bioconversion. The system consists of a medium of suitable mineral constitution, culture containing native microflora, geophagus worm *Pheretima elongata* and bio-indicator plants [17].

Catalytic processes for oxidation or reduction of both organic and inorganic pollutants are widely adopted [18–25]. Solar-assisted oxidation, photo-assisted oxidation, heterogeneous catalytic ozonation, electro catalysis, electro-Fenton methods, photo-electro-catalysis process and photo-electro-Fenton process applications are a few areas of catalytic applications to water purification.

High pressure-membrane methods for water purification apply to seawater desalination, brackish water desalination, groundwater

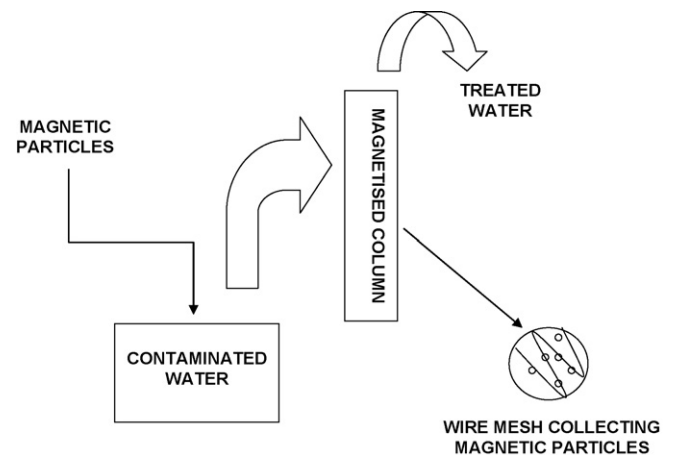


Fig. 1. A typical high-gradient magnetic separation facility.

softening, surface water treatment, and municipal water reclamation [26,27]. For water treatment micro- and ultra-filtration, membrane bioreactors and RO find application. In order to overcome biofouling aspects of organic membranes, Phelps et al. demonstrated the application of metallic membranes with less than micron sized pores [28]. Another article by Macedonio cites the application of membrane distillation in improvising efficiency of process [29].

An emerging field in waste water treatment is in the application of ionizing radiation sources for water purification [30]. This technique also finds application in sterilisation of sewage waste source.

Recently, Yavuz et al. reviewed the scope of magnetic separations in diverse industries: clay decolorisation, steel factories and power plants, enrichment of ores-mineral beneficiation, food industry, water treatment and metal removal [31]. This article only cites examples of advancement in the area of magnetic separations. There has been no review so far on the role of magnetism for water purification. This article is an attempt to present the different aspects in the area of magnetism and magnetic materials for water purification.

2. Magnetic separation for water purification

Magnetism is a unique physical property that independently helps in water purification by influencing the physical properties of contaminants in water. In addition, its combination with other processes enables an improvised efficient purification technology. Before discussing on the technological advancement of this subject, we may refer to Appendix A that introduces definitions of a few terms of magnetism and units of commonly used variables of magnetic separators [32].

High-gradient magnetic separation (HGMS) is a commonly used term in magnetic separations [33–45]. An HGMS device comprises of a bed of magnetically susceptible wires placed inside an electromagnet, as shown in Fig. 1. When a magnetic field is applied across the column, the wires dehomogenize the magnetic field in the column, producing large field gradients around the wires that attract magnetic particles to their surfaces and trap them there. The collection of particles depends strongly on the creation of these large magnetic field gradients, as well as on the particle size and magnetic properties. For successful collection of magnetic particles by HGMS, the magnetic force attracting particles toward the wires must dominate the fluid drag, gravitational, inertial, and diffusion forces as the particle suspension flows through the separator.

Table 1
Variables of magnetic separator.

Characteristics of impurity	Parameters of separator
Solid or solution type	Filter matrix spacing design for examples as arrangement of mesh or wires or balls.
Concentration of solid or solution	Intensity of magnetic field and its orientation based on design and type of matrix.
Size of solid	Resistance of magnetic force towards competing forces.
Magnetic susceptibility	Magnetic field strength and magnetic filter volume.

2.1. Parameters of magnetic separator

The magnetic filter capture processes involve magnetic force expressed as

$$F_m = \mu_0 V_p M_p \text{grad } H \quad (1)$$

where μ_0 denotes permeability constant of the vacuum, V_p is the particle volume, M_p is the particle magnetisation and $\text{grad } H$ is the gradient of magnetic field strength at the position of the particle.

The particle magnetisation may be expressed by the magnetic volume susceptibility χ and the magnetic field strength H where the volume susceptibility is a constant for diamagnetic and paramagnetic substances and a function among others of particle shape and size as well as field strength for the ferromagnetic or ferrimagnetic substances.

$$M_p = \chi H \quad (2)$$

The competing forces in a magnetic separator include gravitational forces

$$F_g = (\rho_p - \rho_g) V_p g \quad (3)$$

where, ρ_p is spherical particle density, ρ_g and g are density of fluid and acceleration due to gravity.

The centrifugal force can be expressed as

$$F_c = (\rho_p - \rho_f) \omega V_p r \quad (4)$$

where r is the radial position of the particle and ω is the angular velocity.

The hydrodynamic drag force can be obtained from Stokes' equation

$$F_d = 6\pi\eta b(v_f - v_p) \quad (5)$$

where η is the dynamic viscosity of the fluid and v_f and v_p are velocities of the fluid and particle respectively.

Many important performance equations of magnetic separator including other interacting forces can be referred from the works of Watson [46], Lubrowsky [47], Clarkson [48], Uchima [49], Birss [50], Sandulyak [51], Abbasov [52] and Eskandarpour [53].

Table 1 summarises a qualitative picture of the variables of impurities and magnetic separators. Impurity here refers to either the pollutant as a stand alone magnetic entity or nonmagnetic pollutant associated with magnetic entity. When impurity is a solid or solution type, the filter matrix spacing designs need to be matched to trap the contaminant. When the amount of impurity is low, the intensity of magnetic field strength required is high. For example solids can be handled using permanent magnet-based separators which generate relatively low intensity magnetic fields while ions require high intensity magnetic field sometimes generated from superconducting magnet types. When comparing millimeter sized impurity to nanosized impurity then resistance of magnetic forces towards competing forces need to be accounted for when making a choice for a separator type. The most important parameter

magnetic susceptibility which is actually related to each characteristic discussed above guides both the magnetic field strength and magnetic filter volume requirement.

2.2. Types of magnets

The intensity of magnetisation of a separator can be enhanced by variation in magnet type used. There are three categories of separators based on magnet type: permanent magnet-based, electromagnet-based and superconducting magnet-based.

Permanent magnets have been prepared from ferromagnets of iron-based, nickel-based, cobalt-based or rare earth element-based compounds. Traditionally permanent magnets were considered weak intensity magnetic forces generating fields of less than 1 T however with the advancement in materials development and shape design parameters information; high intensity magnetic field strengths could be generated [54–60]. In this regard multipole magnets find considerable advantages since it can generate fields greater than 2 T per unit length. The developments in this field helps to offer reduction in operational cost related to other types of magnets since no electricity would be utilised for generation of magnetic field.

In case of electromagnets, there is a solenoid of electrical conducting wires which generate magnetic field within their cavity on passage of electric current [61–63]. The space of solenoid for linear, annular and different shape designs have been developed depending on the application. The electromagnets generate maximum field of 2.4 T.

The third category of magnetic separators is based on superconducting magnets which generate the highest intensity magnetic field [64–65]. Superconducting magnets are capable of generating magnetic field from 2 to 10 T. More references on this magnet have been discussed in the direct purification method described below.

Some commercial suppliers of the different types of magnetic separators include JONES (separators using air-cooled coils with an iron yoke), ERIEZ/SALA (separators water-cooled coils surrounded by a closed iron circuit) and CAPRO (super conductive magnetic separators with coils cooled with liquid helium the magnetic induction attains values up to 5 T).

2.3. Industrial advancement

The industrial usage of magnetic water treatment can be traced back to more than 100 years. Non-chemical water treatment devices were first proposed as a means of scale control by Porter [66]. Faunce and Cabell used electric means for preventing boiler incrustation [67]. They invented an electromagnetic device to treat boiler feed water. In 1873, Hay received the first US patent for a water treatment device that employed a magnetic field [68]. Friedman et al summarised that the stages of development have been from process water treatment to advances in materials development and instrumentation for capture of feebly magnetic particles. Later magnetic particle carrier based separators were developed for pollutant separations [69].

The first full scale HGMS device for steel mill water treatment was installed at the Chiba Plant of the Kawasaki Steel Corporation (Japan). Recently Hitachi Plant Technologies, Ltd. and Mitsubishi Heavy Industries, Ltd. were granted the first formal approval by the Japanese government for their jointly developed Hitachi Ballast Water Purification System. This system utilises principle of coagulation and water purification using magnetic means. Besides the steel industry power industries employ HGMS for coolant pipe lines cleaning. Details on this aspect of cleaning are discussed further in subsequent section.

Table 2
Anti-scale magnetic treatment experiments.

S. no.	Work	Remark	Reference
1.	Reduction of soluble mineral concentrations in CaSO ₄ saturated water using a magnetic field.	NMR was used to create a varying field. Under rotation using field, the total dissolved solids increased by 22%.	[72]
2.	Review paper: magnetic amelioration of scale formation.	The description on configurations of separations, physicochemical properties of water, effects on crystallinity, and proposed mechanisms is covered.	[73]
3.	Anti-scale magnetic pre-treatment of reverse osmosis feed water.	Magnetic pre-treatment generates deposits on RO membrane filters therefore improvises purification.	[74]
4.	Laboratory studies on magnetic water treatment and their relationship to a possible mechanism for scale reduction.	Magneto-hydrodynamics and shape of magnetic poles have direct influence on the scale formation.	[75]
5.	Magnetic treatment of calcium carbonate scale-effect of pH control.	Calcium carbonate scale formation in heat exchanger in re-circulatory system under controlled pH is reduced by 50% by magnetic treatment.	[76]
6.	Rapid onset of calcium carbonate crystallisation under the influence of a magnetic field.	During crystallisation, the rate of nucleation is proportionate to the intensity of applied field. The number of crystals and size of crystals could be controlled using applied field.	[77]
7.	Magnetic water treatment for scale prevention.	Scaling depends on materials of construction of pipe. The electrokinetic influence in control of mechanism is indicated.	[78]
8.	Adhesion of in situ precipitated calcium carbonate in the presence and absence of magnetic field in quiescent conditions on different solid surfaces.	SS, Cu, Al, glass showed difference in scaling behaviour. Maximum deposition under given conditions were observed on glass.	[79]
9.	Effect of a magnetic water treatment on homogeneous and heterogeneous precipitation of calcium carbonate.	Magnetic field presence promotes the homogeneous precipitation of calcium carbonate scales.	[80]
10.	A spectrophotometer-based study of magnetic water treatment: assessment of ionic vs. surface mechanisms.	Experimental evidence concludes that crystallisation in the presence of magnetic field was due to surface mechanism.	[81]
11.	Quantitative study of the effect of electromagnetic field on scale deposition on nanofiltration membranes via UTDR.	Using ultrasonic time domain reflectometry tool it was shown that an anti-scale magnetic pre-treatment followed by nanofiltration increased the purification rate by 6–10%.	[82]

2.4. Economy considerations

The cost effectiveness of the separation technology has been effectively evaluated by a few workers. For example in a study, Yano et al have applied HGMS to the filtration of steel mill waste water streams [70]. They found that while the installation of the HGMS and sand filter are almost the same HGMS surpasses the sand filter with regard to operating costs and space requirements. For a 150 mg/L solid waste the flow rate through sand filter required was 8×10^{-3} m/s as against 6×10^{-2} m/s flow rate required for HGMS. The feed time was 20 min for HGMS as against 8 h for sand filter. The space requirement was 4.5 m² as against 8 m² for sand filter. The relative operating cost is 0.7:1 for HGMS with respect to sand filter though the installation cost is 1.1:1 with respect to sand filter. In another example, Vedavyasan has evaluated a cost estimate for RO application in combination with magnetic separator technique [71]. The killers of RO plants are colloidal solids and biological fouling devices. By incorporating turbulence generating flow distributors and EMF device, fouling is reduced and efficiency is improvised. The calculations showed that capital cost of RO plants with EMF is higher by 13% as compared to conventional ones. However, the down time is reduced by 30% on account of saving in membrane cleaning and there is overall 20% reduction in trans-membrane pressure drop. Combined savings and improvised technology enabled a better feed water quality. The examples discussed suggest that magnetically assisted techniques have considerable advantages with respect to time saving as well as cost savings for the purification of water.

Based on the difference in adoption of physical process, magnetically assisted water purification can be primarily classified as

- Direct purification
- Seeding and separation of magnetic flocculant
- Magnetic sorbent application in organic and inorganic contaminants including radionuclides
- Combination processes supported by magnetic assistance.

Through the discussion of each technique examples of applicability to various waste stream sources have been cited.

2.5. Direct purification

In the direct purification method, there is no carrier magnetic component added. Instead, the basic properties of ions or solids response to magnetic field is utilised for purification.

Magnetic field aides in inducing crystallisation and when magnetic filter is introduced before water distribution the filter picks up all the salts and prevents salt ions to lead through the distribution pipelines. In this manner the scaling by deposition on pipelines is prevented. In direct purification method, anti-scaling technique is most commonly practiced. In case of boilers, heat exchangers and pipelines, the salt deposition leads to damage of equipment with time. Table 2 lists some of the work reported in the area of anti-scale magnetic treatment [72–82]. The most common constituents of scale are CaCO₃, CaSO₄·2H₂O and silica, while other potential scaling species are BaSO₄, SrSO₄, Ca₃(PO₄)₂ and ferric and aluminum hydroxides. Anti-scale effect results from the changes in crystallisation behaviour prompting bulk solution precipitation rather than formation of adherent scale. The magnetic effect also appears to be enhanced under conditions of supersaturation and high ionic load of process water. Salt concentration, anion present in salt, material of construction of pipe, physicochemical properties of water, intensity of magnetic field, duration of field application, are among few parameters that affect the mechanism of de-scaling. Different configurations of equipments as permanent magnets and electromagnets or single-pass mode and re-circulatory-mode have been employed for this application. The classification of magnetic devices for the application is also based on magnetic field orientation that could be parallel or perpendicular to fluid flow directions. Each configuration is expressed as commercially successful by the designers. The designers of single-pass mode confer flow rate control as reason for improved de-scaling while designers of re-circulatory mode confer turbulence factor responsible for

Table 3
Molar susceptibility of the elements and inorganic compounds.

Name	Formula	χ_m (10^{-6} cm ³ /mol)
Barium	Ba	20.6
Barium oxide	BaO	−29.1
Barium nitrate	Ba(NO ₃) ₂	−66.5
Barium hydroxide	Ba(OH) ₂	−53.2
Cerium	Ce	2500
Cerium oxide	CeO ₂	26
Caesium	Cs	29
Europium	Eu	30900
Europium oxide	Eu ₂ O ₃	10100
Iron	Fe	Ferromagnetic
Iron oxide	FeO	7200
Hematite	α -Fe ₂ O ₃	Antiferromagnetic
Iron nitrate nonahydrate	Fe(NO ₃) ₃ ·9H ₂ O	15200
Maghemite	γ -Fe ₂ O ₃	Ferrimagnetic
Magnetite	Fe ₃ O ₄	Ferrimagnetic
Lanthanum	La	95.9
Lanthanum oxide	La ₂ O ₃	−78
Plutonium	Pu	525
Plutonium oxide	PuO ₂	730
Rhodium	Rh	102
Rhodium oxide	Rh ₂ O ₃	104
Rubidium	Rb	17
Rubidium nitrate	RbNO ₃	−41
Rubidium oxide	Rb ₂ O	1527
Ruthenium	Rh	39
Ruthenium oxide	RuO ₂	162
Strontium	Sr	92
Strontium hydroxide	Sr(OH) ₂	−40
Strontium nitrate	Sr(NO ₃) ₂	−57.2
Strontium oxide	SrO	−35
Thorium	Th	97
Thorium oxide	ThO ₂	−16
Uranium	U	409
Uranium oxide	UO ₂	2360

de-scaling. Owing to several parameters responsible for de-scaling, the superiority of one mode of operation over another is therefore difficult to predict.

In case of separation of feebly magnetic or paramagnetic materials, superconducting magnetic filtration finds extensive application [83–85]. A superconducting magnet is an electromagnet that is built using coils of superconducting wire. It must be cooled to cryogenic temperatures during operation. Its advantage lies in the production of stronger magnetic fields (2–10 T) than ordinary iron-core electromagnets (2 T), and can be cheaper to operate, since no power is lost to ohmic resistance in the windings. Another technique of direct purification in magnetic separation is magnetophoresis where separation is carried out with the assistance of magnetic field application. The particles with differing susceptibility can be separated gravimetrically [86]. In a study on separation efficiency of 0.1 μ m haematite (α -Fe₂O₃) and 1 μ m copper oxide (CuO) particles using background field of 7 T, the migration velocity of CuO was an order higher than α -Fe₂O₃. In magnetophoresis, differential magnetic classification is a new term coined to classify magnetic particles by classes of magnetic susceptibility. This is useful for defining the limits of separation factors [87]. Development in the area of design of bench scale superconducting magnetic separator and warm bore superconducting magnet designs has enabled high temperature application in separation of paramagnetic ions [88–90].

An important application of superconducting magnets is in the remediation from plutonium, a radio toxic hazard that forms compounds carrying paramagnetic properties. Direct plutonium colloid capture was carried out using specially designed steel wires as magnetic filtration bed material. The use of nickel dendrites grown on SS wires enabled reduction in background field requirement from 7 to 2 T for the capture of particles [91,92]. Table 3 gives a list of volume susceptibilities of typical components of radioactive wastes.

Owing to the fact that majority radionuclides in waste sludges are paramagnetic in nature, magnetic separation studies have been undertaken for the radioactive waste composites. Open gradient magnetic separation (OGMS) is a modified version of high-gradient magnetic separation that is suitable for feebly magnetic material filtration. A pre-treatment with HGMS aided in preventing clogging of OGMS owing to separation of strongly magnetic materials in the first stage and then utilising OGMS for remaining feebly magnetic constituents [93].

The corrosion products from pressurised water nuclear reactor can be directly removed using HGMS [94]. This technology has been adopted at different stages in the nuclear program of United Kingdom, France, Japan, Germany, Russia and USA [95].

Another application of direct purification was shown by passing sea water solutions through a permanent magnetic device which increased its conductivity and pH. More salt was removed from the solution hence further purification through membranes was not desirable [96].

Magnetic pulse compressors as alternative to pulsed electric field is emerging as a promising technology for disinfection for purification of water [97]. The fundamental principle behind magnetic switching is to utilise the changes in the permeabilities displayed by the saturable magnetic materials during saturation to generate large changes in the impedance. A typical magnetic modulator system consists of the capacitor charging high-voltage power supply, the commutator with a compression stage and a pulse transformer and compression head with the last stage of compression. The short duration electrical pulses from the magnetic pulse compressor have been used for inactivation of spores, bacteria and viruses in drinking water. A 4 log reduction was seen for bacteria *E. coli* at field strengths of 110 kV/cm and 70 pps, with a total energy consumption of 40 J/cm³.

Magnetic pre-treatment to water alters its chemistry with respect to pH, ionic composition and microbe mutation which impacts the quality of drinking water in a positive and negative manner [98–100]. In one study, double distilled water samples were exposed for 48 h to 50 Hz powerline electromagnetic field (EMF) strength of 51.2 μ T (36.2 RMS). This EMF exposed water was made available to experimental adult Charles–Foster male rats for drinking ad libitum for 30 days. On gross examination, no anomaly was observed in the kidney of the exposed group. On histological examination, marked spongiform changes leading to degeneration and compensatory proliferation of the glomerular tufts and degeneration of the lining epithelia of the tubules was observed. This study adds a link in demonstrating that powerline exposure induces stable changes in water structures and affects biomechanisms of tissue fluid. In another experiment, a regular water pipeline supplying a group of milking cows was treated magnetically at fields lower than 5 mT. A control group of cows received untreated water. The group on treated water yielded more milk with the same percentage of fat. The influence of a constant magnetic field with an intensity ranging from 0.4 to 0.6 T was determined on physicochemical parameters of water and on rearing of larvae of the European sheatfish *Silurus glanis* L. larvae. In the experiment, feeding brood of European sheatfish was reared in two groups. One was kept in tanks supplied with magnetically treated water. The second group was kept in tanks supplied with water without treatment with a magnetic field (control). The fish tanks were supplied with circulating river water. Rearing was conducted for 15 days at an initial stocking density for both groups of 8 fish/L. The mean fish mass obtained was 0.46 g, and in the control group – 0.78 g ($P < 0.05$). Stocking mortality was 19.1% in the tanks with a constant magnetic field, and 13.5% in the control group. No changes were observed in water phosphate, ammonium, organic compounds or chloride concentrations. The examples confirm that both water source and magnetic field can impact on drinking water quality.

2.6. Seeding and separation of magnetic flocculant using high-gradient magnetic separation

Seeding method followed by HGMS is also among the older methods, with reviews available from early 1900s, for water purification like the direct purification method. Under the proper chemical conditions, a coagulant cation such as Fe(III) yields an insoluble precipitate that possesses positive susceptibility under applied magnetic field. This property is utilised to trap the coagulant with contaminant on a magnetic filtration assembly. It is an effective means of lowering significantly both the oil and suspended solids of water effluent streams including paper industry and steel industry [101–106]. Some typical areas of application include in the development of continuous low magnetic field filtration system with provision for seeding and flocculating phytoplankton for cleaning of lake water [107]. The removal of algae, biochemical oxygen demand (BOD), total nitrogen (T-N), and total phosphorous was simultaneously observed. Almost 93% phytoplankton could be flocculated out from the lake water at 400 m³/day flow rates using superconducting magnetic filter. Radioactive sludge carrying majority magnetic constituents have been effectively separated using seeding followed by HGMS [108]. This tool finds particular application with respect to actinide carrying sludges due to their compounds being paramagnetic in nature [109]. Specific elements like phosphate and arsenic contaminants have also been removed by seeding method for water purification [110,111]. With 15 mg/L of FeCl₃ solution, without the addition of magnetite, phosphate ion recovery increased from 20% to 80% with increasing magnetic field from 0.8 to 8 T. By the addition of 5 mg/L of magnetite with 15 mg/L of FeCl₃ solution, above 95% recovery was achieved in a wide range of magnetic field ($H=0.8\text{--}8\text{ T}$). It can therefore be concluded that a high magnetic field gradient generated in the vicinity of steel wool caused the enhancement of the magnetic coagulation of the complex with phosphate ion and Fe(III) ion, and the paramagnetic iron phosphate complexes were attracted to magnetite, which resulted in high (>95%) recovery in a wide range of magnetic fields. In another study for phosphate removal with the second prototype of a permanent magnet-based carousel magnetic filter, the flow rate could be increased by a factor of up to ten as compared to the first prototype with the dimensions remaining the same [112].

2.7. Magnetic sorbents

In waste water, there are streams which are difficult to coagulate. Many ionic species tend to polymerise as polyhydroxy complexes, or nitroso-hydroxy, or hydroxy-carbonato or halogeno-hydroxo-carbonato complexes. These by ferric ion seeding do not precipitate with the ferric floc. In addition monovalent ions do not coagulate well with ferric ions. HGMS separations cannot be effective for such waste streams. The alternative to removal of such ions is in the application of adsorbents or ion exchangers or solvent extractants. Conventional application of these sorbents is in the form of column based, membrane based or density based separations. These methods suffer from loss of theoretical exchange value in the practical time period allowed for separation. The magnetic component added to these sorbents enables an effective solid liquid separation; especially in case of low concentration solutes with faster exchange kinetics.

In 1995, magnetic ion exchange resins (MIEX) were introduced for the removal of natural organic matter (NOM) from ambient raw water which was superior to coagulation processes. The name MIEX[®] comes from “Magnetic Ion EXchange”, because the ion exchange resin beads contain a magnetised component within their structure which allows the beads to act as individual magnets. The magnetic component results in the beads forming agglomer-

ates that will settle rapidly or fluidise at high hydraulic loading rates. The very small resin bead size provides a high surface area allowing rapid exchange kinetics of select ions. It was applied for the treatment of humic acid [113], low to moderate organic concentrations over wide range of alkalinities and bromide concentrations [114,115]. Coagulation removed 60% of the dissolved organic carbon (DOC) associated with the 1–10k fraction but had little impact on the DOC concentration of the <1k fraction. Treatment with MIEX removed approximately 80% of the DOC associated with the 1–10k fraction and almost 60% of the DOC associated with the <1k fraction. Mergen Max et al. showed the impact of nature of water and resin type in the MIEX method [116]. The nature of water was varied with respect to differing natural organic matter and passed through MIEX. It was observed that hydrophobicity increase of resin reduced the dissolved organic carbon while the increase in hydrophilicity of resin showed consistency in contaminant removal. MIEX was used for the removal of some specific inorganic ions such as As(V) and Cr(VI) [117]. MIEX also finds application in pre-treatment to catalytic processes such as effective debromination using ozonation [118].

In case of magnetic separations based on the contaminant type removed, the classification of magnetic sorbents can be made accordingly. The sorbents include synthetically functionalised magnetic adsorbents such as silica with extractant or naturally functionalised such as biosorbents like sulphide forming bacteria.

2.7.1. Sorbents for organic pollutants

Magnetic chitosan gel particles, magnetite bearing covalently immobilised copper phthalocyanine dye, magnetic charcoal and magnetic alginates find application in the removal of polycyclic dyes, malachite green, crystal white and other organic dyes and suspensions from water solutions and suspensions [119–123]. Magnetotactic bacteria naturally occur as magnetic sorbent sources in nature. These bacteria have the ability to orient themselves in the direction of the magnetic field. They find application in organic pollutant removal from water by enzymic reactions [124]. Surfactant coated magnetite particles find application in the extraction of organic contaminant 2-hydroxyphenol [125]. Floating magnetic sorbents in the form of polymer coated vermiculite iron oxide composites have been formulated. The composites float on the surface of water and can easily separate spilled oil contaminant on water [126].

2.7.2. Sorbents for inorganic pollutants

A number of iron-based functionalised materials find application in the removal of heavy ions either by exchange or sorption or chemical reaction [127]. A list of functionalised materials with their sorption capability values has been summarised in Table 4 [128–139]. For specific ion separation, functional groups are attached to magnetic substrates. Silica, zeolites, polymers have been used with magnetic materials to form composites with similar apparent sorption capability as the adsorbent without magnetic component. Efficient separation factors have been obtained due to the presence of magnetic field as can be seen from Table 4.

In case of magnetically stabilised fluidised bed, the magnetic materials can be fluidised and retained in magnetic filter column while waste solution can be pumped through the column. Magnetic materials such as titanomagnetite have been suggested as suitable alternatives to fluidised magnetically stabilised filtration beds since the matrix is able to retain functionalised magnetic sorbents and large porosity of matrix enables easy water flow for efficient separation [131].

Heavy metals occur naturally within the environment and are utilised by microbes for metabolic processes. Some of these microbes are also capable of forming magnetic materials such as ferrous sulphides therefore a combination of Fe ions with

Table 4
Magnetic sorbents for application of inorganic contaminants removal.

S. no.	Work	Remark	Reference
1.	Preparation of functionalised mesostructured silica containing magnetite (MSM) for the removal of copper ions in aqueous solutions and its magnetic separation.	Amine functionalised mesostructured silica: 0.1 mmol for Cu per g adsorbent Magnetite based functionalised mesostructured silica: 0.5 mmol Cu per g adsorbent.	[128]
3.	Design and performance of magnetic composite particles for the separation of heavy metals from water.	Recyclable ball-milled composite of acrylate-based polymer with magnetite showed the selectivity as Cu > Cr > Zn > Ni.	[129]
4.	Magnetic zeolites: a new adsorbent for removal of metallic contaminants from water.	The apparent sorption capability of magnetite zeolite composite remained unaltered for Cu, Cr and Zn.	[130]
5.	The use of magnetic bed conditioning and pH control to enhance filtration by natural titanomagnetite.	Natural titanomagnetite as expanded filtration column can be magnetically conditioned and substituted for magnetically stabilised fluidised bed applications.	[131]
6.	Development of a highly magnetic iron sulphide for metal uptake and magnetic separation.	Bacteria are capable of producing magnetic iron sulphide. The same was applied for metal uptake.	[132]
7.	Nickel adsorption by magnetic alginate microcapsules containing an extractant.	A high sorption capability value of 0.52 mmol per g of magnetic alginate was obtained for Ni.	[133]
8.	Synthesis of LDH-type clay substituted with Fe and Ni ion for arsenic removal and its application to magnetic separation.	Layered double hydroxide prepared from Fe ³⁺ and Ni ²⁺ showed good uptake characteristics for As under high-gradient field of 5T.	[134]
9.	Removal of toxic metal ions with magnetic hydrogels.	Recyclable magnetic hydrogels, based on 2-acrylamido-2-methyl-1-propanesulfonic acid was used for removal of Cd(II), Co(II), Fe(II), Pb(II), Ni(II), Cu(II) and Cr(III) from aqueous solutions.	[135]
10.	Separation/preconcentration of trace amounts of Cr, Cu and Pb in environmental samples by magnetic solid-phase extraction with bismuthiol-II-immobilised magnetic nanoparticles and their determination by ICP-OES.	Recyclable BSCMNPs showed the static adsorption capacities of 8.6, 5.3 and 9.4 mg/g for Cr, Cu and Pb, respectively. Improvised sensitivity in analytical detection, and so further confirming the advantage of using magnetic assistance.	[136]
11.	Selective adsorption and separation of chromium(VI) on the magnetic iron-nickel oxide from waste nickel liquid.	Recyclable magnetic iron-nickel oxide adsorbent showed a maximum of 30 mg/g uptake capability for Cr(VI).	[137]
12.	Characteristics of magnetic separation for magnetic particle and ion by magnetic chromatography with novel magnetic column.	For separation of magnetic materials differing in magnetic susceptibilities the fractionation column can be designed based on magnetic particle size, magnetic susceptibility, magnetic material mobility and height of column.	[138]
13.	Preparation and characterisation of magnetic chelating resin based on chitosan for adsorption of Cu(II), Co(II), and Ni(II) ions.	A case of supported magnetic carrier on chitosan.	[139]

microbes can be made use of for removal of heavy metals [140].

2.7.2.1. Sorbents for radioactive pollutants. Of the inorganic pollutants, the radioactive elements are major sources of concern owing to their long-term hazard impacts. It is preferred to have a zero discharge of these materials into the environment. The high efficiency of magnetic separations has led to a separate field of environmental research under the scope of magnetically assisted chemical separation of radionuclides [141–143]. A comparison is drawn between experimental results using the conventional column filter, with bone char as the adsorbent medium for plutonium uptake. In order to treat 3.22 m³ of solution containing 8 ppm of ²³⁸Pu and to remove the ²³⁸Pu, HGMS method helped in removal of nearly two orders higher concentration than conventional column method in the same given time [144]. The partition coefficients for various actinides were determined to be between 3000 and 30,000 using recyclable magnetic polymer microparticles adsorbed with solvents. These values are larger than those projected for transuranics removal by traditional liquid/liquid extraction [145]. Dendrimers with terminal amino groups attached to the magnetic particle surface showed a 50–400-fold increase of the distribution coefficients for europium and americium in comparison to the reference particles without the dendrimers [146]. Magnetic microparticles containing embedded silicotitanate powders for uptake of ¹³⁷Cs from HEDPA solution showed that the distribution coefficient was between 3000 and 10,000 mL/g (90–98% ¹³⁷Cs removed) depending on particle mass-to-solution volume ratios [147].

Along with synthetic magnetic sorbents, bio sorbents with capability to form magnetic compounds also find application in decontamination of effluents from radioactivity. Microbiologically

produced, strongly magnetic iron sulphide is a good adsorbent effective over a wide range of metal ion concentrations from 30 g/L to ng/L levels and below [148]. The same gives significant sorption characteristic towards technetium and actinides from aqueous wastes [149].

Using a 10 T superconducting high-gradient magnetic separator, 10 ppb uranium ions in sample solution could be reduced to less than 1 ppb level successfully with the 100 ppm magnetic adsorbent addition [150].

The magnetic susceptibility of particle guides the background field requirement for uptake behaviour. The macroporous polymer composites showed higher magnetic susceptibilities than microporous therefore lower background field could be utilised using macroporous polymer composites for recovery of radionuclides [151].

In order to remove contaminated oil in radioactive aqueous waste using HGMS, seeding principle was successfully implemented [152].

2.8. Combination applications using magnetic assistance

The landfill water contains a number of contaminant species including nitrogen, phosphorous and organic compounds [153]. In combination applications, the magnetic separation technique has aided in the improvisation of efficiency of separation. The advances in this category include electrolytic reactions, catalytic reactions, membrane separations and biotechnology.

Watanabe [153] used electrolysis and HGMS combination for water purification. The system was composed of two different types of electrolysis reactors and a superconducting magnetic separation apparatus. The first iron electrolysis reactor produced iron

phosphate and the paramagnetic iron hydroxide particles that absorb some organic compounds. These were separated using high-gradient magnetic separation. The second lead dioxide electrolysis reactor treated the nitrogen and resultant organic compounds by electrochemical oxidation. The flow rate of tested water was 100 L/h. The total removal efficiencies of this system was as follows; 88% for total phosphate, 77% for total nitrogen, and 62% for COD (chemical oxygen demand). These removal efficiencies were observed to be same as or greater than those of the conventional landfill water treatment system. Ihara et al. demonstrated the combination of electrocoagulation and electrochemical oxidation to HGMS for the treatment of landfill leachate [154]. The electrocoagulation using iron electrodes was used as magnetic seeding method for organics and phosphorus in landfill leachate. Magnetic substances generated by electrocoagulation were removed with magnetic separation using a superconducting magnet. The residuals in the effluent of magnetic filter such as ammonium nitrogen and refractory organics were destroyed by electrochemical oxidation using Ti/PbO anode. Song et al. demonstrated the cleaning of this coolant water using magnetic filter-electrodeionisation hybrid system [155]. This study showed the effective performances of a hybrid system for the removal of magnetite and nickel ions from the primary coolant. Continuous electrodeionisation helped in nickel ions removal while magnetic separator helped in magnetite precipitate removal.

The studies on effects of magnetic fields on biological and biochemical systems suggest the potential application of static magnetic fields to enhance microbial degradation of environmental pollutants such as paraoxons [156–158]. For in vivo applications, the biocompatibility of magnetic iron oxide based minerals is known. The magnetic Fe₂O₃ cores allow the nanocatalysts to be facilely concentrated and recovered for repeated uses via applying an external magnetic field. Enzyme based biocatalysts find application in environmental remediation. Key requirements for a bio-magnetic separation material are biocompatibility, suitable linkers, functional layers on magnetic core, protective layer, antigen detection, shape recognition, fluorescent signaling. In case of bio-applications, the shape, size and magnetisation behaviour of magnetic materials is very critical. The bead form is ideal shape desired. In case of size, as size decreases the magnetic susceptibility gets lowered as compared to bulk magnetic susceptibility, therefore; a compromise between active surface and sufficient magnetic properties is made for beneficial applications [159].

Mineralisation of organic compounds such as formic acid can be enhanced by application of magnetic photocatalyst. Most studies have focussed on the comparison of magnetite and titanium oxide based photocatalysts [160,161]. Polyoxometallate-based magnetic photocatalyst was assessed and compared to the conventional suspended fine particles and supported TiO₂ photocatalysts with respect to the degradation of formic acid. Though lower than fine suspensions, the apparent quantum efficiency of the magnetic photocatalyst was 2.7–3.8 times higher than quartz sand supported TiO₂, depending on the pH of solution.

Gold nanocatalysts on magnetic oxide based supports also showed improvisation in degradation efficiency for organic compounds such as phenols and amines as compared to other support based systems [162].

3. Nanomaterials based water purification processes

The unique surface reactivity of nanoscale materials has led to advancement in application and model development of nanoscale magnetic separations. Magnetic materials when scaled down to nanosize show different magnetisation behaviour than bulk magnetic material. On account of this the magnetic separation

characteristics would be affected. If scaling down the size generates hard magnetic material then the magnetic filter regeneration would be difficult. Soft magnets with low magnetic remanence and superparamagnetic materials with zero magnetic remanence are preferred for magnetic separation applications. The magnetic nanoparticles could be separated based on their nanostructures since the ease of direction of magnetisation would vary depending on the ordering of atoms in the magnetic structure [163]. Considering the extensive influence of hydrodynamic drag forces on nanoscale materials, the magnetic nanocarrier properties could be altered by designing materials to application point of view. The intrinsic interaction of magnetic nanoparticles with applied magnetic field gradients makes these particles attractive for directing transport and separation of attached material that can range in size from molecules to cells. As a result, magnetic nanoparticles have garnered widespread attention in recent years to develop and understand synthetic means to control their size, magnetic behaviour, and chemical reactivity. Simultaneously tuning surface chemistry and physical properties enables preparation of functional magnetic nanoparticles that can be specific to contaminant type [164,165]. The nano-adsorbents of gamma ferric oxy hydroxide, and nano oxides of magnetite incorporated on charcoal aided in the removal of fluoride and arsenate [166]. A series of magnetic nano-adsorbents were used for the removal of metallic ions such as Cr(VI), Cu(II), Co(II), Cd(II), As(V), As(III) and Hg(II) from water and it was found that in most cases nanoparticles show better efficiency for the removal of metallic pollutants [167,168]. Iron oxide as nano-adsorbent is able to remove arsenic 5–10 times more effectively than their micron size counterparts. For nanoscale γ -Fe₂O₃ of surface area 200 m²/g at pH 3, the maximum absorption was 50 mg/g while at pH ~9 it was lower by 3%. The removal efficiency was observed as dependent upon surface area, surface charge (pH) and applied background magnetic field. Dong et al. designed a novel functional composite for environmental remediation using magnetic component (Fe₃O₄), molecular sieve matrix (zeolite) and silver nanoparticles and studied mercury extraction properties [169]. These could serve for multifunctional application such as adsorption, redox alteration and improvised efficiency of separation using magnetic assistance.

The properties of mesoporous magnetic adsorbents have opened a new field in engineering separations applications. Several types of functionalised materials have been prepared by grafting of chelating ligands (i.e., mercapto, amine, etc.) on to the surface of the supports to remove metal ions from aqueous solution. However, their irregular pore structures limit their access to the chelating ligands. This, in turn, lowers the metal loading capacities and specificity of ligand towards ion. To overcome these drawbacks, mesoporous molecular sieves, prepared by a self-assembly of inorganic precursors in solution containing structure-directing surfactants were proposed as adsorbents. Mesoporous magnetic MCM-41 was grafted with aminopropyls and studied for exceptionally high uptake behaviour for As(V) and Cr(VI) and nil for Cu(II) confirming the specificity aspects of the material [170]. Tailoring the size of magnetite to 8 nm generated adsorbents with sorption capability for Ni(II), Cd(II) and Cr(VI) of values around 35 mg/g. This value was experimentally observed as about seven times higher than for coarse particles [171]. In a third study it was demonstrated that mesoporous gamma iron oxide works as a better sorbent for Cr(VI) removal as compared to gamma iron oxide of less than 10 nm size under magnetic field [172].

In recent years, the study on nanoscale metallic materials for water treatment is being researched extensively. The application of nanoscale iron particles, a strong ferromagnet, has been extensively researched and reported [173–176]. The nanoscale iron particles are very effective for the transformation and detoxification of a wide variety of common environmental contaminants,

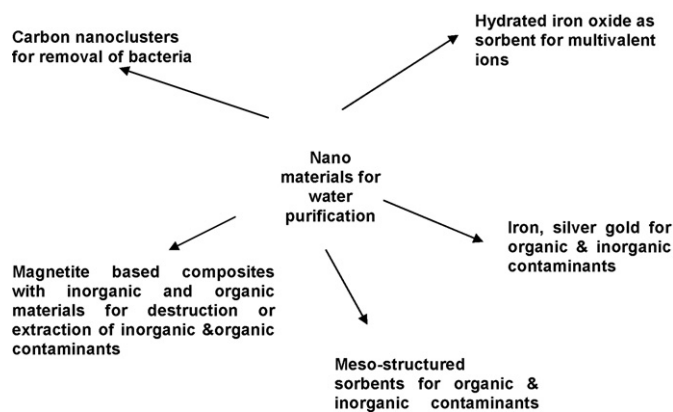


Fig. 2. Application of nanomaterials in areas of contaminant destruction/sorption.

such as chlorinated organic solvents, organochlorine pesticides, trinitrotoluenes, phenols, and herbicide molinate, amino carboxylic acids and p-hydroxybenzoic acid. Almost all halogenated hydrocarbons can be dehalogenated. It was demonstrated that along with organic contaminants, the inorganic anionic contaminants such as NO_3^- , $\text{Cr}_2\text{O}_7^{2-}$ could also be degraded using iron nanoparticles [177–182]. Modified iron nanoparticles, such as catalyzed and supported nanoparticles have been synthesized to further enhance the speed and efficiency of remediation [183,184]. In case of application under magnetic field, it has been reported that the magnetic particles would tend to aggregate and therefore there would be a loss of surface reactivity when the magnetic field is applied [185]. However, the aggregation is dependent on the intensity of applied magnetic field and the direction of arrangement of the nanoparticles. Also, steric barrier provided in case of supported iron-based catalysts, would aide in prevention of aggregation. More detailed investigation is desirable in the role of nanoscale iron-based materials for the study on contaminant destruction under magnetic field.

While discussing on nanomaterials, the toxicity factors cannot be ignored. Major drinking water systems are distributed mainly through iron-based tubes. The colloids formed as a consequence of corrosion are potential superparamagnetic carriers of potentially hazardous species. While the chemistry of nanomaterials is unique for removal of many contaminants, the same properties interfere with cellular processes [186–188]. Nanoparticle wastes should be stored in a way that prevents interaction of nanoparticles with water. Iron oxide is experimentally observed as least toxic therefore, purification systems based on this magnetic material is desirable [189].

4. Conclusions and scope for further work

Magnetic separation offers a common technology adoption for purification of water which could be from oil removal to inorganic ion removal to organic contaminant removal to bacteria removal. To each technique whether adsorption, catalytic processes, membrane processes, it has been demonstrated that addition of magnetic component aides to improvisation in efficiency of separations. Referring to Fig. 2 on role of nanomaterials for contaminants removal except for role of carbon nanoclusters all other areas can be in the scope of iron or iron-based materials. Mesostructured iron oxides could be a scope for research for bacteria trapping or removal. Nanoscale iron for degradation of contaminants under magnetic field can be converted to magnetic oxide wastes that could be effectively separated using magnetic assistance. In the area of nanomaterials for water decontamination, magnetic separation system designs need to be in the frontier area of research. From the waste management point of view of handling

least toxic substance and owing to high saturation magnetisation of iron, nanoscale iron-based catalyst and magnetic assistance based separations would provide long-term benefits.

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Appendix A.

A.1. Magnetism

Magnetism arises from the relative motion of electric charge (orbital/spin motion) and observer. It is used to characterise the magnetic phase of materials. In case of ferromagnetism, the interaction is strongly attractive towards magnetic pole due to intrinsic magnetic moment in material. In case of paramagnetism, the interaction is weakly attractive towards magnetic pole. In case of diamagnetism, the interaction is weakly repulsive from a magnetic pole. In case of antiferromagnetism, the interaction is strongly repulsive from a magnetic pole. In case of ferrimagnetism there is no intrinsic magnetic moment in material, however the interaction is strongly attractive towards magnetic pole.

A.2. SI units related to magnetism

Symbol	Name of quantity	Derived units	Unit	Base units
B	Magnetic flux density, Magnetic induction	tesla	T	$\text{Wb/m}^2 = \text{kg/s/A} = \text{N/A/m}$
Φ	Magnetic flux	weber	Wb	$\text{Vs} = \text{kg m}^2/\text{s}^2/\text{A}$
H	Magnetic field strength	ampere per metre	A/m	A/m
μ	Permeability	henry per metre	H/m	kg m/s/A
χ	Magnetic susceptibility	Dimensionless	–	–

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