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Review

Application of Magnetic Separation Technology in Resource Utilization and Environmental Treatment

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Abstract: Magnetic separation technology is a physical separation method that uses the differences in magnetism between matter to separate them from each other by different motion behaviors in a non-uniform magnetic field. It is highly efficient, green, and environmentally friendly, with little change in the physical and chemical properties of raw materials. Magnetic separation technology is commonly used in the field of mineral processing engineering for magnetite, hematite, titanite, and other magnetic ferrous metal oxide minerals. This paper summarizes the application of magnetic separation technology for resource utilization and environmental treatment in different fields, such as non-metal decomposition, valuable metal recovery, use of magnetic carrier chemical separation, biomedical targeted magnetic separation, and use of magnetic species separation in water and wastewater treatment. We seek to review the application and potential of magnetic separation technology in various fields, emphasize their key role, and explore possible directions for their future development.

Keywords: magnetic separation technology; magnetic selection; magnetic minerals; black metal; chemical separation

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1. Introduction

Separation, purification, debris removal, and other processes are indispensable to obtain high-purity materials or to remove harmful substances in the fields of resource utilization [1–3], materials processing [4,5], environmental treatment [6,7], etc. The principle to achieving the above is to separate different substances from each other according to their physical or chemical properties. In mineral processing engineering, for example, gravitational concentration takes advantage of the density differences between substances [8,9]. This is widely used in processing coal, non-ferrous metals, rare metals, and precious metal ores, and also used in processing non-metallic ores such as asbestos and diamond. Foam flotation technology takes advantage of the difference in surface hydrophobicity between substances [10–12]. The main process of this technology is that bubbles carry selective but poorly adhered ore particles at the gas-liquid interface up through the slurry and then scrape away the froth that forms on the slurry surface. The process is simple in concept and complex in detail, and its adaptability and effectiveness have made bubble-scraping flotation one of the most widely used methods for separating complex, low-grade ores. Over 90% of the world's copper, lead, zinc, molybdenum, antimony, and nickel are recovered by froth flotation. Magnetic separation technology utilizes magnetic differences between substances [13–15] and is widely used in the treatment of strong magnetic iron ore and the exclusion of ferromagnetic impurities from the mixture. In addition, it has large-scale application in the separation of fine-grained weakly magnetic iron and manganese ores, non-ferrous metal sulfide ores, non-metallic ores, as well as wastewater, waste gas treatment, etc., especially since the emergence and development of the high-gradient magnetic separator and superconducting magnetic separator, with their reasonable magnetic system structure, mechanical structure, and the excellent performance of the magnetic material for weakly magnetic micro-fine-grained and coarse-grained materials, as well as wastewater, waste gas purification, and comprehensive utilization of the provision of a reasonable method of treatment, technology, and equipment. Chemical mineralization technology takes advantage of differences in chemical properties between substances [16,17]. The application of chemical mineralization technology is an effective method to deal with poor, fine, miscellaneous, and other difficult-to-select mineral raw materials and make unused mineral resources, and its sorting efficiency is higher than the physical beneficiation method. However, the chemical beneficiation process requires the consumption of many chemicals and equipment materials, and the solid-liquid separation requirements are higher than physical beneficiation. Therefore, under normal conditions, the existing physical beneficiation method should be used as much as possible when dealing with mineral raw materials, and the use of the chemical beneficiation process should only be considered when the separate use of the physical beneficiation method cannot deal with or cannot achieve reasonable technical and economic indicators. Technologies based on these principles are also widely used in other fields, including removing hazardous substances in metallurgy, extracting high-purity chemicals in chemistry and the chemical industry, cleaving cells in biopharmaceuticals, and separating proteins, water, and wastewater in environmental engineering.

This paper mainly reviews the application of magnetic separation technology in the field of mixed-phase separation. It has high efficiency, environmental protection, economy, and almost no physical or chemical impact on raw materials. Under the initiative of the concept of energy conservation and emission reduction and green development, it has become an important technology to alleviate energy scarcity, develop a low-carbon industry, and address the increasing waste emissions [18–20]. Magnetic separation technology has been widely used in many fields and is constantly developing.

2. Impurity Removal

2.1. Removing Impurities from Non-Metallic Ores

Non-metallic ores such as feldspar, quartz, and kaolin are important sources of materials for construction materials, chemicals, semiconductors, and other related industries [21,22]. With the overexploitation of high-quality raw materials, the grade of natural non-metallic ore gradually decreased. In fact, iron oxides are the main cause of this situation, which is caused by the mineralizing environment (e.g., temperature, humidity, pressure, and co-associated minerals, etc.), so it is necessary to remove impurities in order to improve the grade. Magnetic separation, due to its simple operation, has little effect on the physical or chemical properties of raw materials and is a common method of purifying or removing impurities from non-metallic ores [23,24].

A wet-belt permanent high-gradient magnetic separator (WBHGMS) for the purification of garnet mines was studied and its magnetic field characteristics were analyzed by Chen L. Z. et al. [25]. The equipment is based on a high-gradient magnetic levitation system. The magnetic field strength is 1.2~1.3 T with high processing capacity and is not easily clogged, as shown in Figure 1. The WBHGMS captures magnetic material in inclined slurry, and the slurry of garnet and magnetic material mixed from top to bottom flows through the surface belt, moving from the bottom to the top in a raised motion. Magnetic material is captured by magnetic forces and vertical downward gravity along the surface of the belt. Garnet mines with relatively low magnetism are almost free from the magnetic field, as the slurry flows downward into the non-magnetic product, thus achieving the purpose of removing impurities. In this work, the key operating factors affecting the processing capacity of the equipment were carefully investigated, and it was found that the tilt permanent magnet panel and the speed of the belt were significant in removing iron impurities from garnet ore.

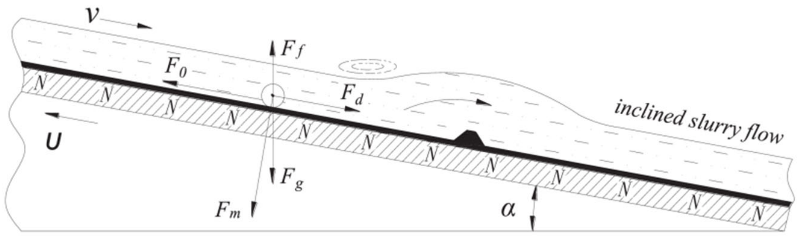

Figure 1. WBHGMS captures magnetic material in inclined slurry. F_m—magnetic force. F_g—gravity. F_f—buoyant force. F_0—friction force. F_d—hydrodynamic resistance [25].

In 2004, Changsha Institute of Mining and Moscow Mining University developed the CRIMM double-box reciprocating permanent magnet high-gradient magnetic separator [26] to improve the overweight of the equipment, which consists of a removable magnetic conductive media heap and two parallel boxes. Only one of the boxes has a background magnetic field on the outside. When sorting, the slurry passes through the conductive medium under the action of gravity and fluid force, where magnetic particles adsorb onto the surface of the medium under the action of the magnetic field. Non-magnetic materials, such as feldspar, quartz, and kaolin, are not affected by the magnetic field and move into the non-magnetic product hopper (a and b in Figure 2). The feed is stopped when a sufficient quantity of magnetic particles is captured on the surface of the conductive medium, and the medium is pushed under the action of a pneumatic component into another chamber that is not covered by a background magnetic field. Magnetic and non-magnetic material separation is achieved by flushing the surface magnetic particles into the magnetic particle product hopper (c in Figure 2). The sorting principle of this device is shown in Figure 2. The magnetic system uses a rare earth permanent magnet large-cavity volume polar window frame magnet structure, where the strength of the uniform background magnetic field is above 0.8 T, the magnetic induction strength of the magnetic conduction medium surface is 1.3 T or more, and the magnetic field gradient exceeds 10^6 Gs/cm. The ore can be treated with different properties by using materials such as stainless steel rods, steel wool, steel plate mesh, and other conductive media. The advantages are low cost and energy consumption. The disadvantage is discontinuous operation, and with the adsorption of magnetic particles, the drastically reduced ability of the magnetic media to capture leads to poor performance.

Stronger background magnetic field strength is conducive to the purification and decomposition of ultra-fine non-metallic ore. Superconducting technology and pulsating high-gradient magnetic separation technology were used in kaolin purification and low-grade brass mine sorting for the first time by Xu J. Y. et al. [27]. Figure 3 shows the physical and structural diagram of the SLon-CD100 SPHGMS separator. This magnet needs to be cooled to 4 K to achieve a magnetic induction strength of 9.0 T. The energy consumption measured under this working condition is as low as 1.5 Kwh. This work used a superconducting SLon-CD100 SPHGMS sorter and a traditional pulsating high-gradient magnetic separator (SLon-100 PHGMS) for super-fine kaolin and brass mine purification. Plenty of experiments show that the purification capacity of the superconducting SLon-CD100 SPHGMS sorter is much higher than that of traditional equipment. When the magnetic field strength is 3.0 T, the iron removal rate could reach 39.52%. In low-iron products such as Fe_2O_3, the grade is 0.442%. In brass mine purification experiments, the SPHGMS sorter also performs well. At the maximum magnetic induction strength of 9.0 T, copper recovery is 90.74% and the concentrate grade is 3.19%, although the specification of superconducting magnetic separation for brass ore is not entirely superior to flotation [28]. However, it is environmentally friendly and has a large processing capacity. Thus, superconducting magnetic separation still has development potential.

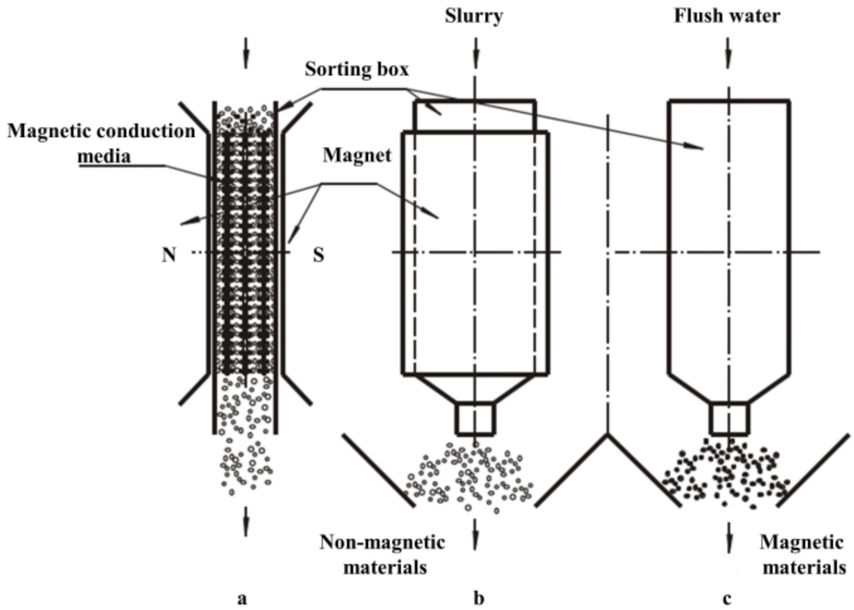

Figure 2. Principle of sorting CRIMM double-box reciprocating permanent magnet high-gradient magnetic separator [26].

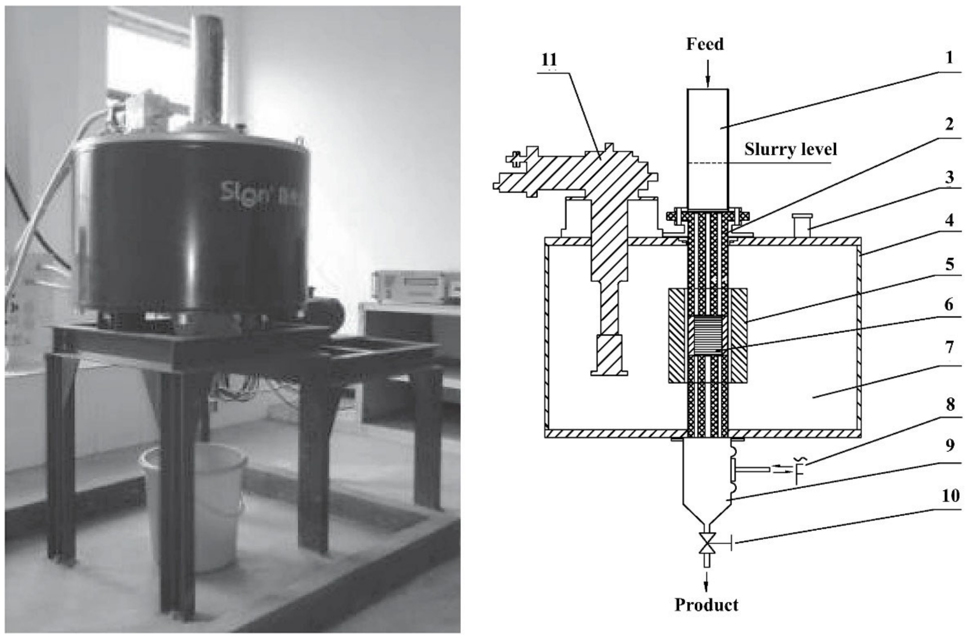

Figure 3. SLon-CD100 SPHGMS separator's physical and structural diagrams. 1—feed box; 2—nylon sleeves; 3—vacuum insulating valve; 4—cryostat; 5—superconducting magnet; 6—magnetic matrix; 7—vacuum chamber; 8—pulsating mechanism; 9—product box; 10—valve; 11—cryocooler [27].

2.2. Removing Impurities during the Metallurgical Process

Although mineral processing processes have maximized the concentrate grade and reduced impurities, the purity of most materials, such as steel, copper, aluminum, metallurgical-grade silicon, and other non-metals, still does not meet the demand as researchers have very high requirements for the purity of their materials. Effective depth removal is the removal of small inclusions from the molten matter during the metallurgical process. Density differences between materials and impurities are largely ineffective when the particle size is small, making it difficult to efficiently remove very small solid particles using conventional methods such as settlement, filtration, or centrifugal separation. This can be avoided by using magnetic separation technology. Studies have shown that micrometer impurities can be removed under the action of electromagnetic fields [29,30]. As shown in Figure 4, the magnetic field is not in contact with the melt, so the safety coefficient is high [31] and the separation and removal operation can be achieved continuously [32–34]. Most importantly, the magnetic field can achieve stirring of the melt to improve the impurity removal rate. At present, based on electromagnetic separation technology proposed by Leenov [32] and Fautrelle [35], this is a quite an effective method. Electromagnetic forces can be created in the molten matter by applying an alternating current [36], an AC magnetic field [29,37,38], and by simultaneously applying an AC magnetic field [39,40].

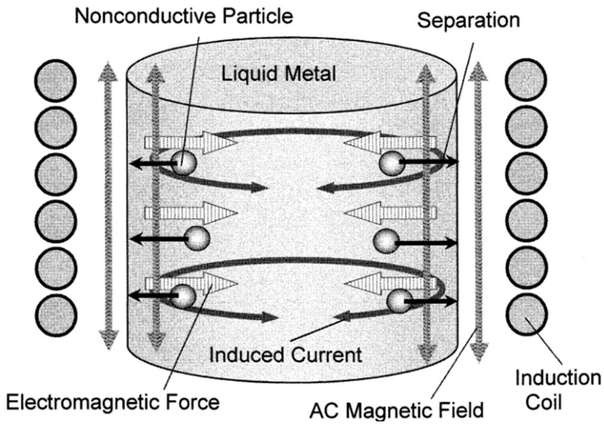

Figure 4. Electromagnetic separation of nonconductive particles from a cylindrical liquid metal in an induction furnace [41].

Shu D. et al. [42] set up a laboratory-scale device for the continuous treatment of aluminum melts using a high-frequency alternating magnetic field. Although it has been reported that this magnetic field is used to separate impurities from alumina in non-continuous liquid metals up to 20 µm [43], there are few reports of continuous separation. The device works as shown in Figure 5, and the molten material consists of pure aluminum and Al5% Si-6% Al_2O_3 particles. The final alloy contains 3~4% Si, 1.5~2.5% Al_2O_3, and the rest is Al. The molten material flows through the runner through a separator wound by a seven-turn copper pipe, and power supply with IGBT induction heating generates 8.3 or 15.6 kHz of alternating current. The resulting magnetic field can repel inclusions in the separator from being captured on the wall [43]. Experimental results show that the maximum effective magnetic field strength is 0.175 T when the AC frequency is 8.3 kHz, the removal rate of 6 µm alumina inclusions was as high as 96.8%, and a changing magnetic field was found to facilitate efficient separation of the stirring melt.

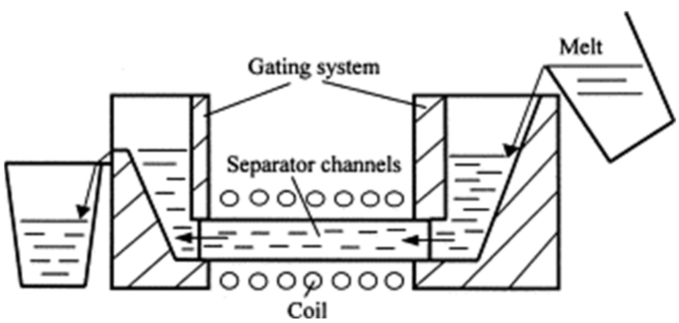

Figure 5. Continuous electromagnetic separation of molten metal [42].

3. Metal Recovery

Nowadays, modern technology brings convenience to life, and numerous advanced technology products are updated every day. This leads to more and more obsolete waste, such as cars, batteries, circuit boards, and so on. These huge quantities of waste not only burden waste disposal, but also cause incalculable harm to the environment [44]. At the same time, as mineable ore resources continue to deplete, recycling useful substances from waste is advantageous in terms of environmental protection and resource sustainability. Lithium batteries such as $LiFePO_4$ (LFP) [45–47] are rich in iron and lithium [48], and recovery techniques including hydrometallurgy [49,50], mechanical chemistry [51], and electrochemistry [52] have been studied in the closed loop from LIB production to recycling and beyond as shown in Figure 6. When recovering Li and Fe from LFP, it is proposed to oxidize Fe^{2+} to Fe_3O_4 using Na_2CO_3 or NaOH, applying a magnetic field to separate it from the slag. The metal is recovered by baking and reduced to iron [53].

Figure 6. Closed loop from production to recycling of LIBs and beyond [52].

While recovering metal materials from silica-rich electronics (IC), Barnwal et al. [44] ground the pending ICs to 100~500 μm and applied a 1500 Gs (0.15 T) magnetic field to recover the black metal. Several experiments show that this method can obtain 120 g of black metal with 57.4% Fe and 26.0% Ni from 1 kg of discarded ICs.

4. Separation during the Chemical Process

Oil is the most important energy source involved in production and life [54]. Spills in the exploration, extraction, transport, and processing of petroleum are inevitable and a total of 5.87 million tons of crude oil leakage has been reported [55] in only 50 years, causing serious environmental hazards [56–62]. Traditional in situ incineration methods such as curing agents, chemical dispersion, and bioremediation remedies are difficult to deal with effectively and may pose other hazards to crude oil leaks [63,64], and the process is complex and expensive. The more efficient solution is to use special adsorption materials, using the surface hydrophobicity or characteristic structure of the material to combine with the oil. Examples include (MS/PDA/SiO_2) made by Xie A. T. et al. [65], and the 3D network carbon nanotube aerogel prepared by Wu Z. Y. et al. [66]. However, most adsorption materials cannot be recycled efficiently, so adding magnetic material to the material and recovering it through the magnetic field is a simple, reliable, and recyclable strategy.

Renjith, P. K. et al. [67] added magnetic foam aerogel composites with ultra-paramagnetic properties to silica aerogel-melamine formaldehyde foam composites for petroleum adsorption (MFAC), which allows for the adsorption of oils and most organic solvents with its very large porosity, excellent oiliness, and hydrophobicity. Optical microscopy images of the oil-absorbed MFAC are depicted in Figure 7, which amply displays the oil retention capabilities of MFAC. As shown in Figure 8a,b, MFAC is significantly more hydrophobic, with a contact angle of 142°, compared to MF. In Figure 8c,d, EDX images confirm the presence of silica and magnetite particles in the composite. Magnetic nanoparticles inherent to the interior of the material can be used in addition to the background magnetic field to achieve recovery of the already adsorbed material, as shown in Figure 9.

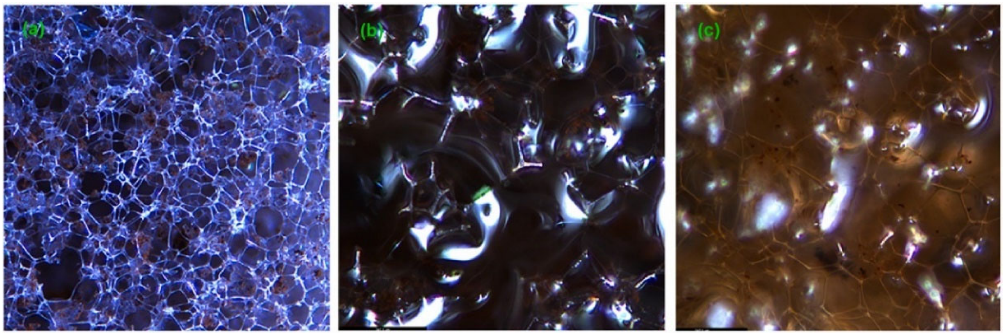

Figure 7. (**a**) MFAC composite; (**b**) oiled MFAC with engine oil; (**c**) oiled MFAC with light oil [67].

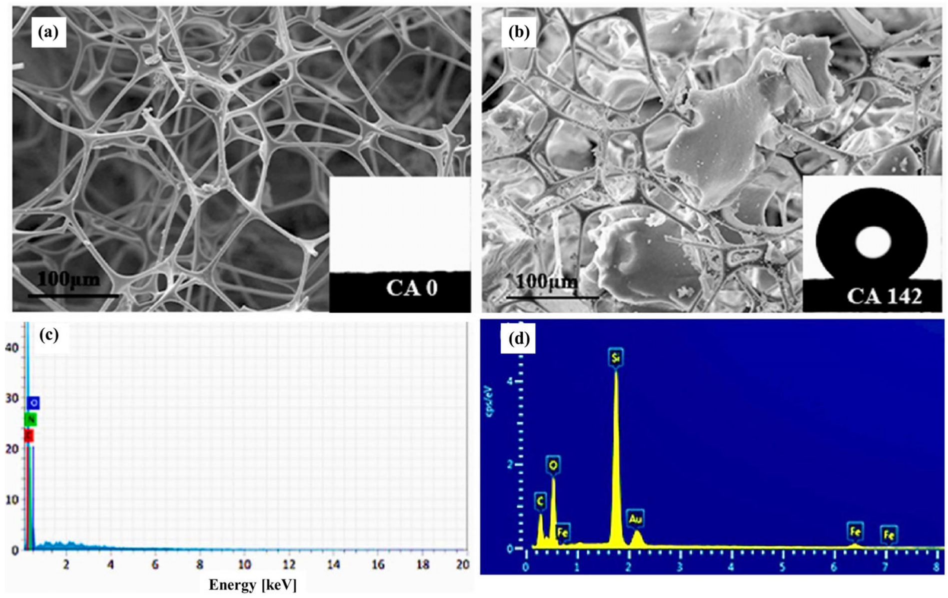

Figure 8. SEM images of (**a**) neat MF; (**b**) MFAC composite; energy-dispersive X-ray spectra (EDX) of MF (**c**); and MFAC composite (**d**) [67].

Wu S. Y. et al. [68] added magnetic Fe_3O_4 material to an ultra-hydrophobic polyurethane sponge (Octadecyl-trichloro-silane (OTS)) for oil-water separation and oil spill recovery. Synthetic Fe_3O_4@SiO_2-OTS possesses super hydrophobic properties, as shown in Figure 10a. Figure 10b,c shows that magnetic Fe_3O_4 is encapsulated in a SiO_2 shell with a thickness of 115~239 nm. OTS on the shell surface enables oil capture with hydrophobicity when adsorption occurs. The adsorption capacity is 48.6~62.3 g/g, as shown in Figure 10d,e. The SiO_2 shell provides rich anchoring points for silanized functional groups and increases the stability of Fe_3O_4 nanoparticles. SEM images confirm the high uniformity and dispersion of Fe_3O_4@SiO_2. It is recovered by applying an external magnetic field when adsorption is complete.

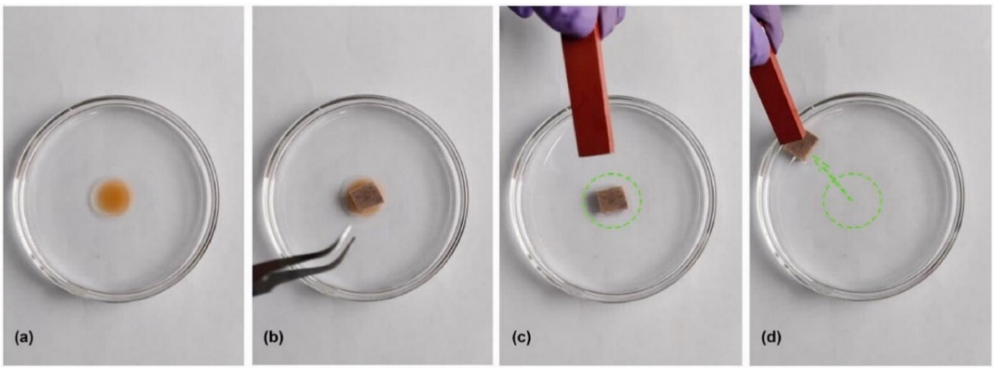

Figure 9. Material adsorption, magnetic field recovery process: (**a**) adsorbed oil; (**b**) process of material adsorption; (**c**,**d**) recovery of materials using magnetic fields [67].

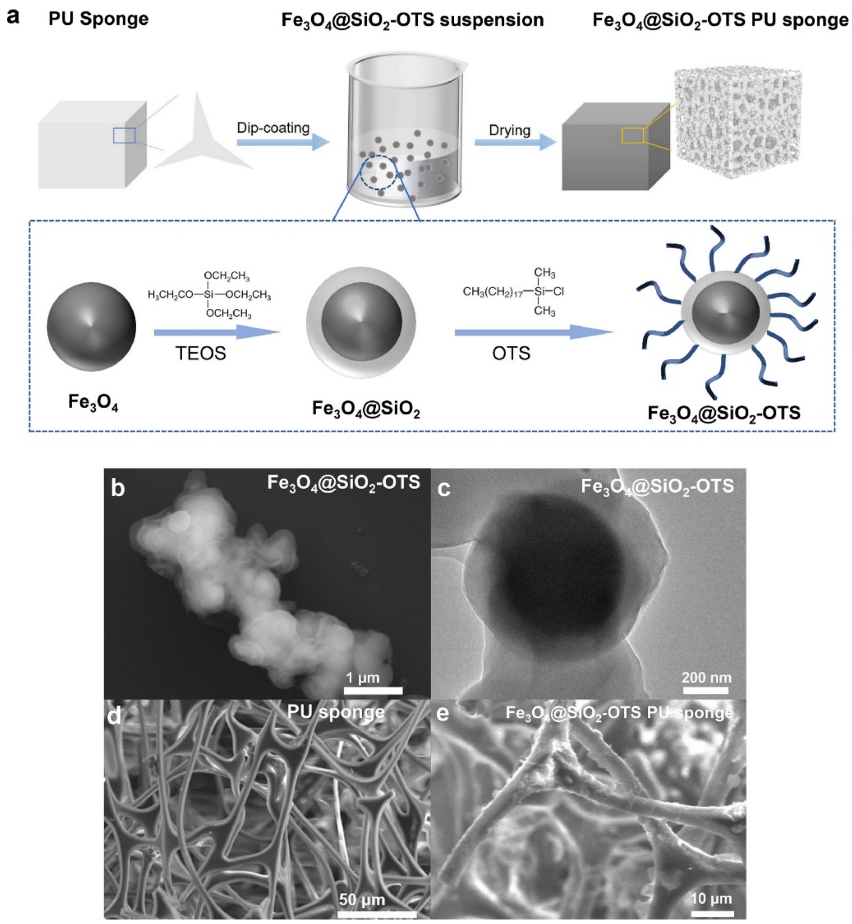

Figure 10. (**a**) Schematic of the preparation of the Fe_3O_4@SiO_2-OTS PU sponge; (**b**) Scanning electron microscopy (SEM) image of Fe_3O_4@SiO_2-OTS; (**c**) High-resolution transmission electron microscopy (HRTEM) images of Fe_3O_4@SiO_2-OTS; (**d**) SEM image of the bare PU sponge; (**e**) SEM image of the Fe_3O_4@SiO_2-OTS PU sponge [68].

5. Magnetic Separation in Biomedical Targeting

It is often necessary to isolate or purify specific proteins, cells, or bacteria in research involving biology or pharmaceuticals. Traditional solutions often require complex pretreatment, such as the use of physical or chemical methods to cleave cells and the removal of cell fragments and contaminants by centrifugal or additive agents. These methods usually take a lot of time and may not work well [69]. With the development of markers and targeted selection, researchers have discovered an effective strategy for the separation of magnetic fields by specific adsorption of targeted proteins, cells, or bacteria using structures, drugs, and organic molecules that carry magnetic materials [70]. Xu C. J. et al. [71] made FePt and Co/Fe_2O_3 magnetic nanocrystals modified with nickel nitrogen triacetic acid (Ni-NTA), which can be used to orientate the adsorption of proteins with multi-histidine affinity labels and purify them using magnetic separation. The Au-Ni-Au nanorubes were prepared using anodized aluminium film for the separation of characterized proteins [72]. Lee I. S. et al. [73] used Ni/NiO nuclear shell-structure nanoparticles to selectively bind to the characterized protein using magnetic field separation. Deng Y. H. et al. [74] prepared a new type of sandwich structure with a mesoporous silica microsphere with a diameter of about 500 nm, as shown in Figure 11. This contains ultra-paramagnetic high magnetization (53.3 emu/g), and the magnetite core structure is coated with silica and a uniform mesopore (2.3 nm), as shown in Figure 12. As a highly effective adsorbent, large microcystic toxins can be removed quickly in liquid environments, and then the microsphere can be recycled and reused by magnetic separation technology [75,76]. Therefore, feature tagging and targeted adsorption co-magnetic field separation is a reliable way to capture and recycle micro-size objects such as proteins and cells.

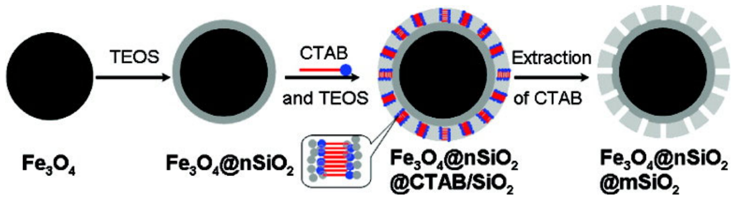

Figure 11. The Formation of Fe_3O_4@nSiO_2@mSiO_2 Microspheres [74].

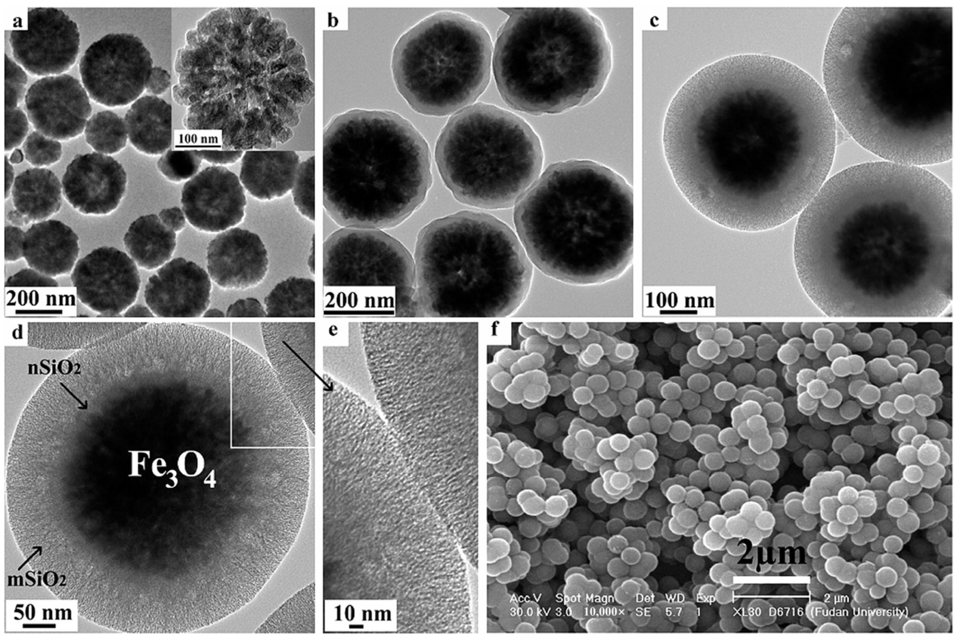

Figure 12. TEM images of (**a**) Fe_3O_4 particles; (**b**) Fe_3O_4@nSiO_2; (**c**–**e**) Fe_3O_4@nSiO_2@mSiO_2 microspheres; (**f**) SEM image of Fe_3O_4@nSiO_2@mSiO_2 microspheres [74].

In fact, the researchers used magnetic fields to capture or separate the targeted individuals from structures, drugs, or organic molecules containing magnetic materials while expecting high reusability from these functional materials. This is because functional processes often take a lot of time and money, but some magnetic materials such as Ni/NiO shell structures have been utilized several times. As magnetic Ni is oxidized, the material's magnetic properties are reduced. A magnetic nanocomposite, MNS-NiO, containing magnetite nanoparticles was synthesized [77] in order to enhance the magnetic properties of the material. The work begins by forming a layer of dense silica shell on the α-Fe_2O_3 surface by a sol-gel reaction. Then, micro-perforation is formed by series functionalization, as shown in Figure 13. Finally, hematite is reduced to magnetite in proportion to H_2:N_2 = 1:1 at 500 °C, and MNS-NiO-saturated magnetization with magnetic reinforcement can reach 82.1 emu/g. It can be used to target the adsorption of His-labeled proteins. After binding to the protein, the saturated magnetization strength is 79.1 emu/g. Magnetic separation technology can be used to achieve material recovery under magnetic field action [73,78,79], as shown in Figure 14.

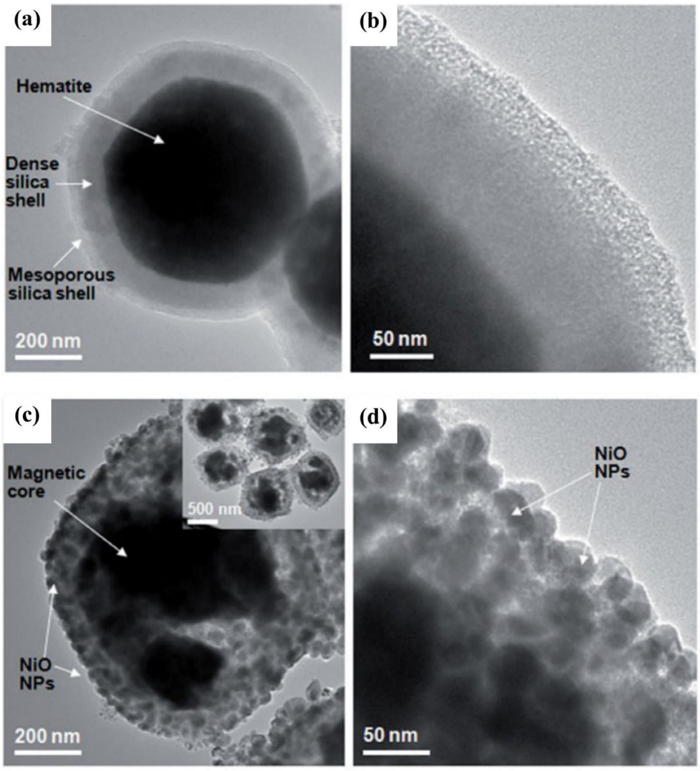

Figure 13. TEM images of mesoporous silica-coated hematite particles (**a**,**b**) and MNS-NiO (**c**,**d**) [77].

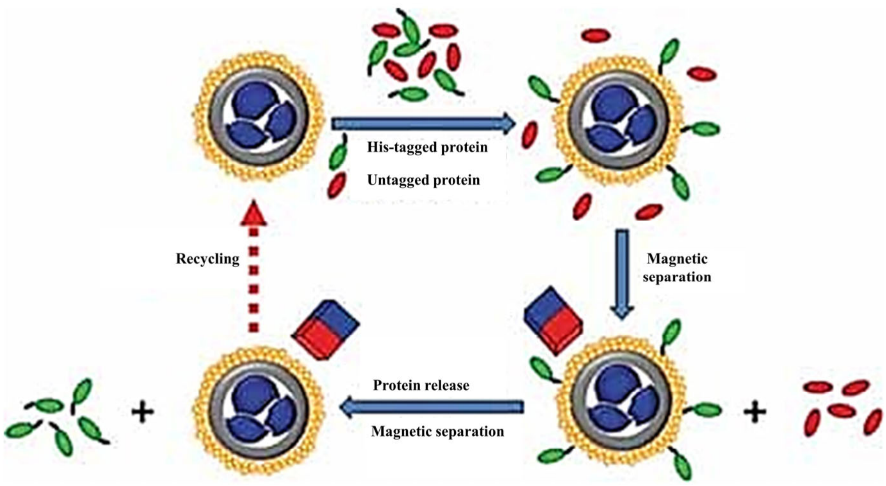

Figure 14. Magnetic MNS-NiO-targeted adsorption protein and magnetic separation process [77].

6. Separation with Magnetic Species in Water and Wastewater Treatment

The use of water is indispensable for both production and life. With the increasing number of people, the risk of contamination of water resources is increasing. According to reports, around 30,000 people worldwide die every day from inadequate water supplies or poor water quality [80]. Thus, achieving efficient, low-cost water and wastewater purification is an important initiative for the benefit of humankind, especially in poor countries and regions where water is scarce.

Previously, a large number of nano-adsorption materials with high selectivity and high adsorption properties showed that they had great application prospects in wastewater treatment [81,82]. Magnetic materials demonstrate the advantages of low-cost and efficient recovery of magnetic fields in microbiology, sensing, and magnetic medicine applications [83–85]. Combining the excellent adsorption properties of nanomaterials with the reliability of magnetic materials, Agasti N. et al. [86] believe that magnetic nanomaterials with high saturation magnetization can be used as carriers of pollutants in water and wastewater, as shown in Figure 15. Purification of water and separation of contaminants by using a magnetic field are more efficient and may be less expensive than conventional methods such as precipitation.

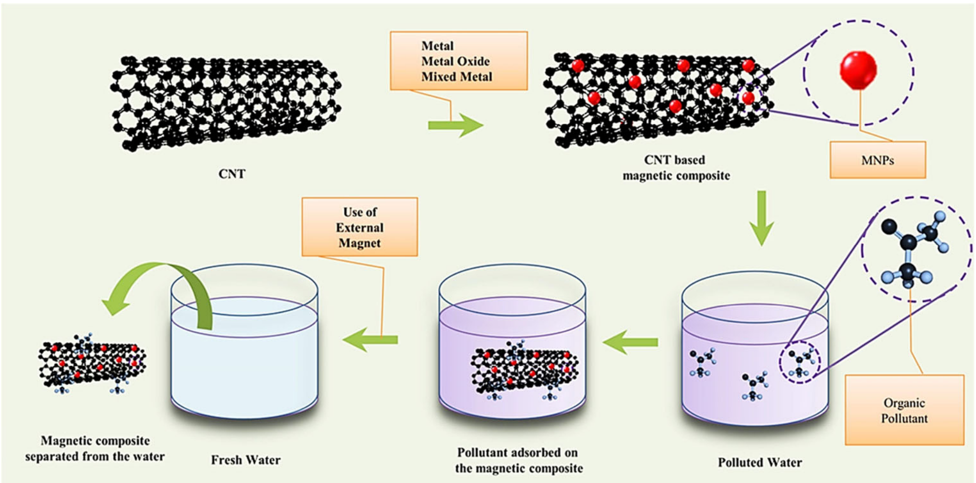

Figure 15. Magnetic nanomaterials with high saturation magnetization [86].

Gao H.R. et al. [87] showed that graphene oxide (GO) has a large specific surface area which contains a large number of oxygen-containing functional groups that can be used for the treatment of heavy metals or organic pollutants in water. It also has the super magnetism of magnetite nanoparticles. Fe_3O_4/GO magnetic nanomaterials were synthesized for the treatment of dye wastewater. As shown in Figure 16a,b, the flaky structure is GO. The surface folds increase the adsorption capacity of heavy metals or organic pollutants. The dispersed white spherical particles on the fold are Fe_3O_4 nanoparticles with a particle size of 30~60 nm. Figure 16c shows Fe_3O_4/GO. The probability of adsorption decreases when the liquid can be dispersed sufficiently uniformly in the absence of an external magnetic field without settling too quickly, as shown in Figure 16d. Regarding Fe_3O_4/GO, the magnetic field can be fully captured after the magnetic field is applied to the outside, which shows that the composite material is recycled well and does not easily cause secondary contamination. Eventually, this work reported that Fe_3O_4/GO magnetic nanomaterials could be used to adsorb six dyes in dye wastewater. The most powerful removal was the removal of gentile purple, where the effective removal rate at 20 °C was 91.06% and adsorption was 34.35 mg/g.

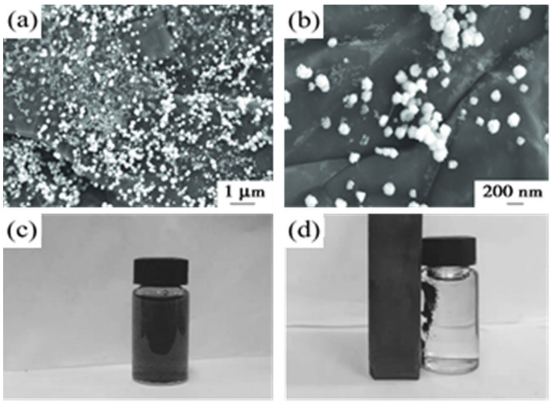

Figure 16. (**a**,**b**) the SEM image of Fe_3O_4/GO; (**c**,**d**) magnetic separation performance test of Fe_3O_4/GO [87].

7. Conclusions

Magnetic separation technology has the advantages of high efficiency, environmental protection, economy, and virtually no physical or chemical effect on treated substances. At present, the separation and purification process in some traditional chemical methods has been replaced by magnetic separation technology. This paper reviews the role of magnetic separation technology in different fields and its unique advantages, such as the use of magnetic separation technology to remove certain metals that can be magnetized in non-metals or the recovery of some valuable metals, which can be achieved while avoiding environmental pollution or the use of chemical agents which can change the chemical properties of materials. In the metallurgical process, this technology can be used to separate certain substances in the molten matter, in addition to achieving greater separation of fine particles when compared to traditional technology. The alternating magnetic field can also increase melt stirring to improve the sorting effect, reducing manual operation and improving safety. In addition, in chemical and biomedical applications, as well as in water and wastewater treatment, more and more functional materials carrying magnetic substances have been used and reported, thanks to magnetic separation technology recovery or precise control. The above cases demonstrate that magnetic separation technology has the advantages of relatively simple operation, large processing capacity, reusability, and low costs of resource utilization and environmental treatment. However, as mentioned, only a portion of minerals and substances can be treated with this technology as it has a small range of treatment objects, and the development of biomedical and water treatment in the field of markers targeting selection and other strategies is very useful. Thus, we believe that magnetic separation technology also has the potential and the need for continuous development.

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Conflicts of Interest: Author Qian Wang is employed by Shandong Huate Magnet Technology Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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