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MODIFICATION OF DIAMAGNETIC MATERIALS USING MAGNETIC FLUIDS¹

Magnetic fluids (ferrofluids) have found many important applications in various areas of biosciences, biotechnology, medicine, and environmental technology. In this review, we have summarized the relevant information dealing with a magnetic modification of diamagnetic materials using different types of ferrofluids. Special attention is focused on a magnetic modification of plant-derived biomaterials, microbial and microalgal cells, eukaryotic cells, biopolymers, inorganic materials, and organic polymers. Derivatization is usually caused by the presence of magnetic iron oxide nanoparticles within the pores of treated materials, on the materials surface or within the polymer gels. The obtained smart materials exhibit several types of responses to an external magnetic field, especially the possibility of the selective magnetic separation from difficult-to-handle environments by means of a magnetic separator. The ferrofluid-modified materials have been especially used as adsorbents, carriers, composite nanozymes or whole-cell biocatalysts.

Keywords: magnetic fluids, diamagnetic materials, magnetic modification, magnetic separation.

1. Introduction

Magnetically responsive nano- and micromaterials have been efficiently used in many areas of biosciences, biotechnology, (bio)analytical chemistry, medicine, and environmental science and technology. These materials exhibit several types of responses

to external magnetic fields. They can be selectively separated from difficult-to-handle environments by means of a magnetic separator; alternatively, they can be also localized in a specific place using an appropriate magnetic system. Magnetic (nano)particles subjected to a high-frequency alternating magnetic field generate heat sufficient for therapy of cancer

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¹ This article is dedicated to the 75th anniversary of Academician L.A. Bulavin.

diseases. Magnetic iron oxide nanoparticles can be used as a negative contrast agent during the magnetic resonance imaging. Magnetorheological fluids increase their apparent viscosity when subjected to a magnetic field. Recently, peroxidase-like activity was observed in both naked magnetic nanoparticles and magnetoferritin [1, 2].

Different types of non-magnetic (diamagnetic) particulate and high aspect ratio materials including adsorbents, catalysts, chromatography materials, carriers, microbial cells, waste biological materials, etc. are available. In many cases, the application potential of these materials can be improved by their magnetic modification which will enable the simple magnetic separation (see Fig. 8 in [3]²). Many strategies leading to the formation of interesting magnetically responsive materials from diamagnetic precursors have been developed [3, 4].

Ferromagnetic or ferrimagnetic nano- and microparticles (represented, e.g., by magnetic iron oxides magnetite and maghemite, various types of ferrites or metallic iron, cobalt, and nickel) have been successfully used for a magnetic modification of diamagnetic materials. Both biological materials including prokaryotic and eukaryotic cells, plant-derived materials and biopolymers, as well as organic polymers and inorganic materials, have been successfully converted into magnetically responsive materials with important properties and applications [1].

Many procedures for the conversion of non-magnetic materials into their magnetic derivatives have been already described. Magnetic modification is usually caused by the presence of magnetic nano- or microparticles within the pores of treated materials, on the materials surface or within the polymer gels [1, 3, 4]. Efficient magnetic modification of diamagnetic materials can also be achieved using various types of ionically and sterically stabilized magnetic fluids (MF; also named ferrofluids, FF). This specific magnetization procedure leading to the formation of magnetically responsive materials will be summarized in this review paper.

2. Characterization of Magnetic Fluids

Magnetic fluids are stable colloidal suspensions of magnetic nanoparticles in a continuous liquid me-

dium. The nanoparticles are superparamagnetic with sizes often ranging from 3 nm to 15 nm. On the surface, the nanoparticles are coated with a molecular layer of a dispersant. Various mineral oils, water, and other liquids may be used as a carrier medium. Owing to the thermal agitation and Brownian motion, the nanoparticles are kept suspended, and the coating prevents the nanoparticles from the sticking to each other. In this way, the unique combination of fluidity and magnetism may be found in magnetic fluids. There are several experimental methods of the preparation of magnetic fluids. The most common is the preparation of magnetic fluids by the chemical precipitation or by size reduction described in several excellent books [5, 6].

To provide a complex characterization of magnetic fluids, one usually employs the standard experimental methods used in the research of liquid systems with nanoparticles (nanofluids). Thus, to assess the stability and structural properties of magnetic fluids, the experimental methods like UV-VIS and infrared spectroscopies, transmission and scanning electron microscopies, dynamic light scatterings, acoustic measurements, small-angle neutron and X-ray scattering are often utilized. Especially, the application of neutron and X-ray scattering techniques may yield rich information on the morphology, size, concentration, and interaction between the dispersed nanoparticles [7–12].

However, to describe the unique magnetic properties of magnetic fluids, the specific quantities such as magnetization and magnetic susceptibility must be analyzed. The magnetization of magnetic fluids is measured in dependence on an external magnetic field, so obtaining the magnetization curves. At room temperature, the magnetization curve of magnetic fluids often exhibits the zero hysteresis and coercivity (Fig. 1, *a*). This property is a typical manifestation of the superparamagnetic behavior of magnetic nanoparticles dispersed in a base liquid [13]. Below a certain critical temperature, the magnetic moments are not any more able of the free fluctuation around an easy axis of magnetization. The resulting state at which the magnetic anisotropy energy barrier is not overwhelmed by the thermal energy is called a blocked state. The critical temperature is determined by the particle size, and the size distribution is often reflected in the distribution of the blocking temperatures. Thus, this fact is often utilized in revealing the

² https://link.springer.com/chapter/10.1007/978-94-017-8896-0_2

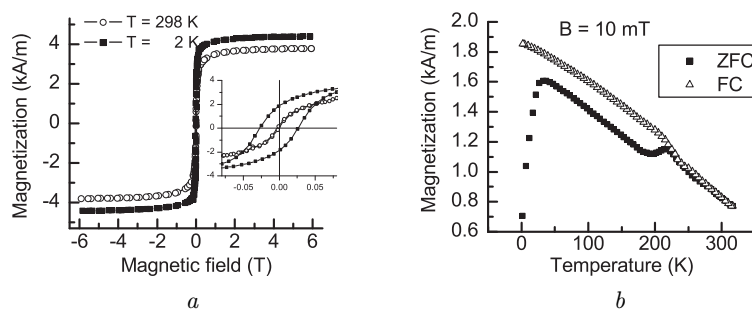


Fig. 1. Magnetization curves measured on a magnetic fluid at room temperature and at 2 K (a). Temperature dependence of the magnetization of a magnetic fluid in ZFC and FC regimes (b). Reproduced, with modification, from [15]

particle size distribution when measuring the temperature dependent magnetization of magnetic fluids in the so-called zero field cooling (ZFC) and field cooling (FC) regimes (Fig. 1, b). On the other hand, one can obtain important information from magnetization curves on the magnetic particle volume fraction in a fluid, as well as the magnetic diameter of the nanoparticles, as reported in various studies on magnetic fluids [14–16].

From Fig. 1, a, one can observe the typical magnetization behavior at room temperature and at 2 K for a magnetic fluid based on a mineral oil and iron oxide nanoparticles. It is evident that the magnetization is well saturated at higher magnetic fields, reaching the value of 3.56 kA/m at 6 T and room temperature. Furthermore, at room temperature, the magnetization exhibits zero hysteresis, indicating the superparamagnetic behavior of magnetic nanoparticles. The blocking regime is reflected in the remarkable coercivity detected at 2 K [15].

Figure 1, b shows the well-known temperature-dependent behavior of the magnetization measured on a magnetic nanofluid with iron oxide nanoparticles in ZFC and FC regimes. Clearly, the ZFC maximum around 230 K is ascribed to the phase transition (solidification) of the carrier oil. On the other hand, the low-temperature maximum around 30 K represents the area of blocking temperatures, and, therefore, a transition from the superparamagnetic to the blocked state of magnetic nanoparticles.

Dynamic magnetic properties of magnetic fluids are investigated in AC magnetic fields. When exposed to an external AC magnetic field, the nanoparticles may undergo the magnetization reversal and follow

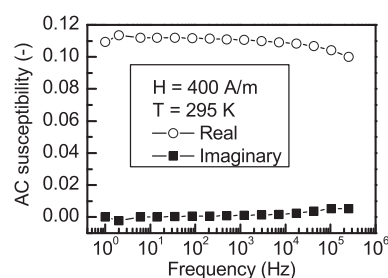


Fig. 2. An example spectrum of the real and imaginary parts of the complex magnetic susceptibility usually measured on a magnetic fluid containing magnetic nanoparticles with a mean diameter around 10 nm. Reproduced, with modification, from [15]

the field changes via two possible mechanisms. Depending on the characteristic relaxation time, the small single-domain nanoparticles prefer the internal magnetization reversal (Néel relaxation), while the greater particles with thermally blocked magnetic moments relax via a physical rotation (Brownian relaxation). To reveal the characteristic relaxation times, the method of AC magnetic susceptometry may be employed, by means of which one measures the frequency-dependent real and imaginary parts of a complex magnetic susceptibility [17].

A typical spectrum of the complex magnetic susceptibility of a magnetic fluid based on iron oxide nanoparticles with a mean diameter of 10 nm is presented in Fig. 2. The spectra were obtained at room temperature, when the nanoparticles are free to respond the excitation AC magnetic field via both relaxation mechanisms. The ability of nanoparticles to follow the field changes is reflected in the negligible magnetic loss (imaginary susceptibility) and the qua-

sic constant behavior of the real magnetic susceptibility without any remarkable dispersion in the frequency range up to 250 kHz. The characteristic relaxation times of the majority of the present nanoparticles are supposed to appear at higher frequencies [15].

3. Modification of Diamagnetic Biological Materials Using Magnetic Fluids

Several procedures have been already developed for the conversion of diamagnetic biomaterials into their magnetic derivatives using magnetic fluids. Such a modification can significantly simplify the separation of magnetic materials from complex systems, such as various suspensions, waste water, cultivation media, biological fluids, tissue homogenates, etc., using permanent magnets or magnetic separators. In this review, we will focus only on postmagnetization procedures. Magnetic modification of selected groups of biomaterials will be discussed in detail.

3.1. Plant-derived biomaterials

Extremely simple procedure employs a perchloric acid-stabilized magnetic fluid which was mixed with a methanol suspension of the diamagnetic material to be modified. During the mixing, magnetic iron oxide nanoparticles from the magnetic fluid firmly precipitated on the surface of particles. This procedure was used for a magnetic modification of plant-derived materials including sawdust [18, 19] (see Fig. 4 in [18]³), peanut husks [20–22], spent tea leaves [23], spent grain [24, 25] (see Fig. 1 in reference [24]⁴) or spent coffee grounds [26]. These magnetic materials were used as adsorbents for the removal of water-soluble organic dyes or heavy metal ions or as carriers for the immobilization of selected enzymes. Similar procedure, but employing tetramethylammonium hydroxide-stabilized magnetic fluid, was used for a modification of defective green coffee, coffee silverskin, and spent coffee grounds; magnetized materials were employed as potential low-cost adsorbents for environmental technology applications [27]. During several experiments, it was observed that the properly performed magnetic modification has not caused a

substantial decrease of the adsorption capacities of modified adsorbents.

Some diamagnetic materials could not be modified using the above-mentioned methanol/acid FF system. An alternative procedure was developed, which is based on the direct mixing of the material to be modified with a water-based ionic magnetic fluid stabilized with perchloric acid. After the drying, aggregates of magnetic iron oxide nanoparticles were deposited on the treated material, enabling its magnetic separation (see Figs. 1 A, B in [28]⁵). Spent tea leaves modified with this procedure efficiently adsorbed water-soluble organic dyes [28]. Also, sea-grass *Posidonia oceanica* was magnetically modified using the same approach [29].

In Table 1, the comparison of maximum adsorption capacities of selected ferrofluid-modified plant materials for organic dyes is summarized.

3.2. Microbial and microalgal cells

Living microbial cells can be efficiently magnetically modified using magnetic fluids [30]. Baker's yeast cells were modified with three magnetic fluids under different conditions (ferrofluid stabilized with tetramethylammonium hydroxide in 0.1 M glycine–NaOH buffer, pH 10.6; perchloric acid-stabilized ferrofluid in 0.1 M acetate buffer, pH 4.6; citrate ferrofluid in 0.1 M glycine–HCl buffer, pH 2.2). All procedures enabled to form magnetically responsive yeast cells in a short time due to the precipitation of magnetic iron oxide nanoparticles on the yeast cell surface (see Figs. 1 and 2 in [31]⁶). Using citrate FF-modified cells, the complete magnetic separation took a long time. The substantially shorter separation time was achieved by magnetically responsive yeast cells modified with perchloric acid-stabilized FF and with tetramethylammonium hydroxide-stabilized FF. The latter magnetic yeast cells provided significantly better results for the activities of tested intracellular enzymes. Therefore, this type of whole-cell biocatalyst was used for the hydrogen peroxide decomposition and the sucrose conversion into glucose and fructose, due to the presence of active intracellular catalase and invertase [31]. The different physiological states of

³ <https://www.degruyter.com/view/j/hfsg.2007.61.issue-3/hf.2007.060/hf.2007.060.xml>

⁴ <https://onlinelibrary.wiley.com/doi/abs/10.1002/jsfa.5930>

⁵ <https://www.sciencedirect.com/science/article/abs/pii/S0032591012003932>

⁶ <https://www.sciencedirect.com/science/article/abs/pii/S0963996909000052>

Table 1. Comparison of maximum adsorption capacities Q_{\max} (mg/g) of ferrofluid-modified plant-derived materials for tested dyes

Dyes	Colour index number	Maximum adsorption capacities of ferrofluid modified plant derived materials (mg/g)						
		Spruce sawdust [18]	Spruce sawdust [17]	Peanut husks [19]	Spent coffee grounds [25]	Spent grain [24]	Spent tea leaves [27]	<i>Posidonia oceanica</i> [28]
Acridine orange	46 005	24.1		71.4	49.3		98.8	
Aniline blue	42 755					44.7		
Bismarck brown	21 000	52.1		95.3	97.8	72.4	71.7	
Crystal violet	42 555	52.4	51.1	80.9	36.7	40.2	100.1	
Malachite green	42 000				62.9		66.2	
Methyl green	42 585						30.8	
Methylene blue	52 015							133.3
Nile blue A	51 180					64.1	87.1	
Safranin O	50 240	25.0		86.1	34.3		84.7	

yeast cells can lead to various magnetic modifications; using dormant yeast cells, only surface-modified cells were obtained, while the magnetic modification of actively growing yeast cells led to the accumulation of a magnetic modifier in the periplasmic space [32].

In order to prepare stable magnetic adsorbents for the removal of selected organic and inorganic xenobiotics, the magnetically modified cells can be heated in a boiling water bath to kill the cells [33]. A magnetic modification of dried *Kluyveromyces marxianus* (fodder yeast) and *Chlorella vulgaris* cells required a thorough washing with 0.1 M acetic acid to remove a substantial portion of soluble macromolecules that, otherwise, caused the spontaneous precipitation of a magnetic fluid; after washing and suspending the cells in an acetic acid solution, the addition of perchloric acid-stabilized magnetic fluid resulted in the formation of magnetically modified yeast (see Figs. 1 and 2 in [34]⁷) and microalgae cells [30, 34, 35].

Naturally occurring micrometer-sized, with high aspect ratio, native and autoclaved *Leptothrix sp.* sheaths were efficiently modified with a perchloric acid-stabilized magnetic fluid (see Figs. 1, *d*, *e* in reference [36]⁸). The prepared magnetically responsive sheaths were tested as an inexpensive adsorbent for the crystal violet removal from aqueous solutions [36]. The same adsorbent exhibited also the efficient adsorption of Amido black 10B [37].

⁷ <https://www.sciencedirect.com/science/article/pii/S0141022906005424>

⁸ <https://www.sciencedirect.com/science/article/abs/pii/S0928493116308013>

Examples of ferrofluid-modified microbial and microalgae cells and their applications are presented in Table 2.

3.3. Animal eukaryotic cells

Ferrofluid-modified animal eukaryotic cells have also found interesting applications. During the transplantation of cells, it is necessary to track and monitor the grafted cells in the transplant recipient. To screen cells both *in vitro* and *in vivo*, biocompatible magnetic fluids (usually used as negative contrast agents during the magnetic resonance imaging) have been used to label the stem cells; nanoparticles can often be taken up by cells during the cultivation by endocytosis. The magnetically labeled cells enable either the *in vitro* detection by staining for iron to produce ferric ferrocyanide (Prussian blue) or the *in vivo* detection using the MRI visualization, due to the selective shortening of the T2-relaxation time, leading to a hypointense (dark) signal. MRI can be used to evaluate the engraftment of cells, the time course of cell migration, and their survival in the targeted tissue [48–50]. In order to simplify the preparation of magnetically labeled cells, a device for the magnetosonoporation of target cells has been developed that employs the ultrasound treatment [51].

3.4. Biopolymers

In addition, (bio)polymer gels can be efficiently magnetically modified with the use of magnetic fluids. Bacterial cellulose produced by *Komagataeibacter sucrofermentans* was magnetically modified using

Table 2. Examples of ferrofluid-modified microbial and microalgae cells and their applications

Modified cells	Ferrofluid used for magnetic modification	Application	Other details	Ref.
<i>Bacillus circulans</i>	Citrate-stabilized ferrofluid	Cyclodextrin glucanotransferase synthesis by semicontinuous cultivation	Magnetic nanoparticles bound on the cell walls were partially released during the cultivation	[38]
<i>Chlorella vulgaris</i>	Water-based magnetic fluid stabilized with perchloric acid	Adsorption of aniline blue, Bismarck brown Y, Congo red, crystal violet, safranin O and Saturn blue LBRR 200	Adsorption equilibrium data fit Langmuir isotherm equation; q_m were in the range 24.2 and 257.9 mg/g	[35]
<i>Chlorella vulgaris</i>	Same	Characterization by means of electron spin resonance spectroscopy and conventional magnetic methods	Magnetic behavior of the modified cells is mainly dominated by the superparamagnetic relaxation of isolated single domain magnetic iron oxide nanoparticles	[39]
<i>Escherichia coli</i>	Water-based magnetic fluid stabilized with oxidized oleic acid	Facile recycling of <i>Escherichia coli</i> cells from suspensions	Mechanism of magnetic nanoparticles binding to the cell surface was studied	[40]
<i>Kluyveromyces marxianus</i>	Water-based magnetic fluid stabilized with perchloric acid	Adsorption of Sr(II) ions	Adsorption equilibrium data fit Langmuir isotherm equation; $q_m = 140.8$ mg/g	[41]
<i>Kluyveromyces marxianus</i>	Same	Adsorption of acridine orange, amido black 10B, Bismarck brown Y, safranin O, crystal violet, Saturn blue LBRR 200 and Congo red	Adsorption equilibrium data fit Langmuir isotherm equation; q_m were in the range 29.9 and 138.2 mg/g	[34]
<i>Kluyveromyces marxianus</i>	"	Characterization by means of electron spin resonance spectroscopy and conventional magnetic methods	Magnetic behavior of the modified cells is mainly dominated by the superparamagnetic relaxation of isolated single domain magnetic iron oxide nanoparticles	[39]
<i>Leptothrix</i> sp.	"	Adsorption of crystal violet or amido black 10B	Adsorption equilibrium data fit Langmuir isotherm equation; $q_m = 166.6$ or 339.2 mg/g, resp.	[36, 37]
<i>Rhodotorula glutinis</i>	"	Adsorption of uranium ions	Adsorption equilibrium data fit Langmuir isotherm equation; $q_m = ca$ 190 mg/g	[42]
<i>Saccharomyces cerevisiae</i>	"	Adsorption of acridine orange, aniline blue, crystal violet and safranin O	Adsorption equilibrium data fit Langmuir isotherm equation; q_m were in the range 19.6 and 430.2 mg/g	[33]
<i>Saccharomyces cerevisiae</i>	"	Study of interaction of yeast cells with magnetic iron oxide nanoparticles	Magnetic iron oxide nanoparticles found in periplasmic space during active growth	[32]
<i>Saccharomyces cerevisiae</i>	Water-based magnetic fluid stabilized with dimercaptosuccinic acid	Magnetic resonance and transmission electron microscopy characterization	Magnetic resonance data confirmed strong binding of magnetic nanoparticles to the cells	[43]
<i>Saccharomyces cerevisiae</i>	Water-based magnetic fluid stabilized with tetramethylammonium hydroxide	Study of hydrogen peroxide decomposition and sucrose conversion	The biocatalyst was stable; the same catalytic activity was observed after one-month storage at 4 °C	[31]
<i>Saccharomyces cerevisiae</i>	Water-based magnetic fluid	Adsorption of direct scarlet dye	The adsorbed dye could be eluted in 70% alcohol	[44]

Continuation of Table 2

Modified cells	Ferrofluid used for magnetic modification	Application	Other details	Ref.
<i>Saccharomyces cerevisiae</i>	Water-based magnetic fluid stabilized with oxidized oleic acid	Facile recycling of <i>Saccharomyces cerevisiae</i> cells from suspensions	Mechanism of magnetic nanoparticles to the cell surface was studied	[40]
<i>Saccharomyces cerevisiae</i> subsp. <i>warum</i>	Water-based magnetic fluid stabilized with perchloric acid	Adsorption of Cu(II) ions	Adsorption equilibrium data fit Langmuir isotherm equation; $q_m = 1.2$ mmol/g	[45]
<i>Saccharomyces cerevisiae</i> subsp. <i>warum</i>	Same	Adsorption of Hg(II) ions	Adsorption equilibrium data fit Langmuir isotherm equation; $q_m = 114.6$ mg/g	[46]
<i>Saccharomyces cerevisiae</i> subsp. <i>warum</i>	"	Adsorption of aniline blue, Congo red, crystal violet, safranin O and naphthol blue black	Adsorption equilibrium data fit Langmuir isotherm equation; q_m were in the range 11.6 and 228.0 mg/g	[47]

perchloric acid-stabilized magnetic fluid (see Figs. 1 and 2 in [52]⁹). Magnetic bacterial cellulose was used as a carrier for the immobilization of the affinity ligands, enzymes, and cells [52]. Magnetic chitosan gels can be simply prepared by dissolving chitosan in acetic acid solution and the subsequent slow addition of a magnetic fluid; glutaraldehyde and ethylenediamine were used to form the gel [53].

4. Modification of Diamagnetic Inorganic and Organic Materials Using Magnetic Fluids

Postmagnetization procedures have been also successfully used for the magnetic modification of non-biological materials. Direct mixing of water-based acid ferrofluid with the treated material enabled one to prepare magnetically modified montmorillonite (see Figs. 1, *c*, *d* in [28]¹⁰) which was used as a carrier for the immobilization of lipase and β -galactosidase; immobilized enzymes showed the long-term stability without leaching of an enzyme from the support and enabled their repeated use without significant loss of their activity [28].

The natural saponite clay was magnetically modified by contact with a citric acid-stabilized magnetic fluid. The prepared adsorbent was employed for the adsorption of malachite green, Congo red,

and indigo carmine from water solutions [54]. Magnetic nanocomposite sorbents for the disposal of synthetic detergents from wastewater were prepared from clay minerals (saponite, palygorskite, and spondyle clay) after their magnetic modification with oleic acid-stabilized magnetic fluid. Comparison of sorption properties showed that magnetic composite sorbents had efficiency of the adsorption removal of anionic surfactants and polyphosphates from aqueous solutions 2–8 times higher compared to native clay minerals [55]. Similar magnetic adsorbents were used for the removal of malachite green and Congo red [56].

Direct mixing of water-based acid ferrofluid with the treated material was used for a modification of commercially available SEPABEADSB[®] EC-HA which were subsequently employed for the immobilization of diamine oxidase from *Pisum sativum*; this complex was part of a fiber optic biosensor for the determination of biogenic amines [57].

Magnetic modifications of four different electrospun nanofibrous textiles, based on polyamide, polyvinyl alcohol, polycaprolactone, and polyurethane was performed using a simple spray modification procedure employing a magnetic fluid stabilized with perchloric acid and a chloroform-based magnetic fluid. The magnetic modification led to the deposition of magnetic iron oxide nanoparticles on the surface of textile nanofibers (see Figs. 4, 5, and 6 in [58]¹¹). Magnetically modified nanotextile exhibited

⁹ <https://www.sciencedirect.com/science/article/abs/pii/S092849311631654X?via3Dihub>

¹⁰ <https://www.sciencedirect.com/science/article/abs/pii/S0032591012003932>

¹¹ <https://www.sciencedirect.com/science/article/abs/pii/S0304885318319528>

peroxidase-like activity using chromogenic substrate N,N-diethyl-p-phenylenediamine (DPD); after the assay purple-colored reaction product was formed (see Fig. 8 in [58] and the link above). Ferrofluid-modified nanotextile thus represents a promising composite nanozyme applicable in various biochemical, biomedical, and biotechnology applications [58].

5. Conclusions

Various progressive materials, including magnetically responsive ones, have already found many important applications in biosciences, biotechnology, and environmental technology. As shown in this review, magnetic fluids can be successfully used for the magnetic modification of wide variety of both biological and non-biological diamagnetic materials, ranging from particles up to high aspect ratio materials, (bio)polymer gels, and (nano)textiles. Ferrofluid derivatization leads to the localization of magnetic iron oxide nanoparticles within the pores of treated materials, on the surface of materials or within the (bio)polymer gels. Magnetic materials can be selectively separated from difficult-to-handle environments by means of a magnetic separator. That's why the ferrofluid-modified materials have been used as adsorbents, carriers, or whole-cell biocatalysts. In addition of having several types of responses to external magnetic fields, the peroxidase-like activity of bound magnetic iron oxide nanoparticles is of interest.

Comment

Because the printed version of the Ukrainian Journal of Physics does not enable to publish grayscale figures, readers are requested to use the attached links to check the original papers for the photo documentation.

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1. I. Safarik, K. Pospiskova, E. Baldikova, M. Safarikova. Magnetically responsive biological materials and their applications. *Adv. Mater. Lett.* **7**, 254 (2016).
2. I. Safarik, K. Pospiskova, K. Horska, M. Safarikova. Potential of magnetically responsive (nano)biocomposites. *Soft Matter* **8**, 5407 (2012).
3. I. Safarik, K. Pospiskova, K. Horska, Z. Maderova, M. Safarikova. Magnetically responsive (nano)biocomposites. In: *Intracellular Delivery*. Edited by A. Prokop, Y. Iwasaki, A. Harada (Springer, 2014), Vol. 2.
4. T. Kanjilal, C. Bhattacharjee. Green applications of magnetic sorbents for environmental remediation. *Materials Research Foundations (Organic Pollutants in Wastewater I)* **29**, 1 (2018).
5. R.E. Rosensweig. *Ferrohydrodynamics* (Dover, 2014) [ISBN: 9780486678344].
6. S. Odenbach (Ed.) *Colloidal Magnetic Fluids: Basics, Development and Application of Ferrofluids* (Springer, 2009) [ISBN: 978-3-540-85386-2].
7. O.V. Tomchuk, L.A. Bulavin, V.L. Aksenov, M.V. Avdeev. Small-angle scattering in structural research of nanodiamond dispersions. In: *Modern Problems of the Physics of Liquid Systems*. Edited by L.A. Bulavin, L. Xu (Springer, 2019).
8. A. Nagorny, V.I. Petrenko, M. Rajnak, I.V. Gapon, M.V. Avdeev, B. Dolnik, L.A. Bulavin, P. Kopcansky, M. Timko. Particle assembling induced by non-homogeneous magnetic field at transformer oil-based ferrofluid/silicon crystal interface by neutron reflectometry. *Appl. Surface Sci.* **473**, 912 (2019).
9. A.V. Nagorny, M.V. Avdeev, O.V. Yelenich, S.O. Solopan, A.G. Belous, A.V. Shulenina, V.A. Turchenko, D.V. Soloviov, L.A. Bulavin, V.L. Aksenov. Structural aspects of Fe₃O₄/CoFe₂O₄ magnetic nanoparticles according to X-Ray and neutron scattering. *J. Surf. Invest.: X-ray, Synchrotron and Neutron Techniques* **12**, 737 (2018).
10. A. Nagorny, L. Bulavin, V. Petrenko, M. Avdeev, V. Aksenov. Sensitivity of small-angle neutron scattering method at determining the structural parameters in magnetic fluids with low magnetite concentrations. *Ukr. J. Phys.* **58**, 735 (2013).
11. L. Melniková, V.I. Petrenko, M.V. Avdeev, V.M. Garamus, L. Almásy, O.I. Ivankov, L.A. Bulavin, Z. Mitroova, P. Kopcansky. Effect of iron oxide loading on magnetoferritin structure in solution as revealed by SAXS and SANS. *Colloids Surf. B* **123**, 82 (2014).

12. V.I. Petrenko, M.V. Avdeev, V.M. Garamus, L.A. Bulavin, P. Kopcansky. Impact of polyethylene glycol on aqueous micellar solutions of sodium oleate studied by small-angle neutron scattering. *Colloids Surf. A* **480**, 191 (2015).
13. S. Bedanta, W. Kleemann. Supermagnetism. *J. Phys. D* **42**, 013001 (2008).
14. M. Rajnak, Z. Wu, B. Dolnik, K. Paulovicova, J. Tothova, R. Cimbala, J. Kurimsky, P. Kopcansky, B. Sundén, L. Wadsö, M. Timko. Magnetic field effect on thermal, dielectric, and viscous properties of a transformer oil-based magnetic nanofluid. *Energies* **12**, 4532 (2019).
15. M. Rajnak, M. Timko, P. Kopcansky, K. Paulovicova, J. Kuchta, M. Franko, J. Kurimsky, B. Dolnik, R. Cimbala. Transformer oil-based magnetic nanofluid with high dielectric losses tested for cooling of a model transformer. *IEEE T. Dielect. El. In.* **26**, 1343 (2019).
16. M. Rajnak, Z. Spitalsky, B. Dolnik, J. Kurimsky, L. Tomco, R. Cimbala, P. Kopcansky, M. Timko. Toward apparent negative permittivity measurement in a magnetic nanofluid with electrically induced clusters. *Phys. Rev. Applied* **11**, 024032 (2019).
17. K.K. Narayanasamy, M. Cruz-Acuña, C. Rinaldi, J. Everett, J. Dobson, N.D. Telling. Alternating current (AC) susceptibility as a particle-focused probe of coating and clustering behaviour in magnetic nanoparticle suspensions. *J. Colloid Interface Sci.* **532**, 536 (2018).
18. I. Safarik, P. Lunackova, E. Mosiniewicz-Szablewska, F. Weyda, M. Safarikova. Adsorption of water-soluble organic dyes on ferrofluid-modified sawdust. *Holzforschung* **61**, 247 (2007).
19. I. Safarik, M. Safarikova, F. Weyda, E. Mosiniewicz-Szablewska, A. Slawska-Waniewska. Ferrofluid-modified plant-based materials as adsorbents for batch separation of selected biologically active compounds and xenobiotics. *J. Magn. Magn. Mater.* **293**, 371 (2005).
20. I. Safarik, M. Safarikova. Magnetic fluid modified peanut husks as an adsorbent for organic dyes removal. *Phys. Procedia* **9**, 274 (2010).
21. L. Rozumová, O. Životský, J. Seidlerová, O. Motyka, I. Šafařík, M. Šafaříková. Magnetically modified peanut husks as an effective sorbent of heavy metals. *J. Environ. Chem. Eng.* **4**, 549 (2016).
22. L. Rozumova, J. Seidlerova, I. Safarik. Nanomodified low-cost biological material for the removal of heavy metal ions. In: *Advances in Materials Science for Environmental and Energy Technologies V*. Edited by T. Ohji, R. Kanakala, J. Matyas, N.J. Manjooran, G. Pickrell, W. Wong-Ng (Wiley, 2016), p. 147–158.
23. L. Rozumova, J. Seidlerova, I. Safarik, M. Safarikova, M. Cihlarova, R. Gabor. Magnetically modified tea for lead sorption. *Adv. Sci. Eng. Med.* **6**, 473 (2014).
24. K. Pospiskova, I. Safarik. Magnetically modified spent grain as a low-cost, biocompatible and smart carrier for enzyme immobilisation. *J. Sci. Food Agr.* **93**, 598 (2013).
25. I. Safarik, K. Horska, M. Safarikova. Magnetically modified spent grain for dye removal. *J. Cereal Sci.* **53**, 78 (2011).
26. I. Safarik, K. Horska, B. Svobodova, M. Safarikova. Magnetically modified spent coffee grounds for dyes removal. *Eur. Food Res. Technol.* **234**, 345 (2012).
27. A. Zuorro, R. Lavecchia, S. Natali. Magnetically modified agro-industrial wastes as efficient and easily recoverable adsorbents for water treatment. *Chem. Eng. Trans.* **38**, 349 (2014).
28. I. Safarik, K. Horska, K. Pospiskova, M. Safarikova. One-step preparation of magnetically responsive materials from non-magnetic powders. *Powder Technol.* **229**, 285 (2012).
29. I. Safarik, N. Ashoura, Z. Maderova, K. Pospiskova, E. Baldikova, M. Safarikova. Magnetically modified *Posidonia oceanica* biomass as an adsorbent for organic dyes removal. *Medit. Mar. Sci.* **17**, 351 (2016).
30. I. Safarik, K. Pospiskova, E. Baldikova, M. Safarikova. Magnetically responsive microbial cells for metal ions removal and detection. In: *Handbook of Metal-Microbe Interactions and Bioremediation*. Edited by S. Das, H.R. Dash (CRC Press, 2017) [ISBN: 9781498762427], p. 769–778.
31. M. Safarikova, Z. Maderova, I. Safarik. Ferrofluid modified *Saccharomyces cerevisiae* cells for biocatalysis. *Food Res. Int.* **42**, 521 (2009).
32. R.B. Azevedo, L.P. Silva, A.P.C. Lemos, S.N. Bao, Z.G.M. Lacava, I. Safarik, M. Safarikova, P.C. Morais. Morphological study of *Saccharomyces cerevisiae* cells treated with magnetic fluid. *IEEE Trans. Magn.* **39**, 2660 (2003).
33. I. Safarik, L. Ptackova, M. Safarikova. Adsorption of dyes on magnetically labeled baker's yeast cells. *Eur. Cells Mater.* **3** (Suppl. 2), 52 (2002).
34. I. Safarik, L.F.T. Rego, M. Borovska, E. Mosiniewicz-Szablewska, F. Weyda, M. Safarikova. New magnetically responsive yeast-based biosorbent for the efficient removal of water-soluble dyes. *Enzyme Microb. Technol.* **40**, 1551 (2007).
35. M. Safarikova, B.M.R. Pona, E. Mosiniewicz-Szablewska, F. Weyda, I. Safarik. Dye adsorption on magnetically modified *Chlorella vulgaris* cells. *Fresenius Environ. Bull.* **17**, 486 (2008).
36. I. Safarik, R. Angelova, E. Baldikova, K. Pospiskova, M. Safarikova. *Leptothrix* sp. sheaths modified with iron oxide particles: Magnetically responsive, high aspect ratio functional material. *Mater. Sci. Eng. C* **71**, 1342 (2017).
37. R. Angelova, E. Baldikova, K. Pospiskova, M. Safarikova, I. Safarik. Magnetically modified sheaths of *Leptothrix* sp. as an adsorbent for Amido black 10B removal. *J. Magn. Magn. Mater.* **427**, 314 (2017).
38. M. Safarikova, N. Atanasova, V. Ivanova, F. Weyda, A. Tonkova. Cyclodextrin glucanotransferase synthesis by semicontinuous cultivation of magnetic biocatalysts from cells of *Bacillus circulans* ATCC 21783. *Process Biochem.* **42**, 1454 (2007).
39. E. Mosiniewicz-Szablewska, M. Safarikova, I. Safarik. Magnetic studies of ferrofluid-modified microbial cells. *J. Nanosci. Nanotechnol.* **10**, 2531 (2010).

40. J. Zhao, M. Lin, G. Chen. Facile recycling of *Escherichia coli* and *Saccharomyces cerevisiae* cells from suspensions using magnetic modification method and mechanism analysis. *Colloids Surf. B* **169**, 1 (2018).
41. Y.-Q. Ji, Y.-T. Hu, Q. Tian, X.-Z. Shao, J. Li, M. Safarikova, I. Safarik. Biosorption of strontium ions by magnetically modified yeast cells. *Sep. Sci. Technol.* **45**, 1499 (2010).
42. J. Bai, X. Wu, F. Fan, W. Tian, X. Yin, L. Zhao, F. Fan, Z. Li, L. Tian, Z. Qin, J. Guo. Biosorption of uranium by magnetically modified *Rhodotorula glutinis*. *Enzyme Microb. Technol.* **51**, 382 (2012).
43. J.P.M.G. Morais, R.B. Azevedo, L.P. Silva, Z.G.M. Lavaca, S.N. Bao, O. Silva, F. Pelegrini, C. Gansau, N. Buske, I. Safarik, M. Safarikova, P.C. Morais. Magnetic resonance investigation of magnetic-labeled baker's yeast cells. *J. Magn. Magn. Mater.* **272–276**, 2400 (2004).
44. Q. Wu, Z. Shan, M. Shen, S. Li, H. Chen. Biosorption of direct scarlet dye on magnetically modified *Saccharomyces cerevisiae* cells. *Chin. J. Biotech.* **25**, 1477 (2009).
45. L. Uzun, N. Saglam, M. Safarikova, I. Safarik, A. Denizli. Copper biosorption on magnetically modified yeast cells under magnetic field. *Sep. Sci. Technol.* **46**, 1045 (2011).
46. H. Yavuz, A. Denizli, H. Gungunes, M. Safarikova, I. Safarik. Biosorption of mercury on magnetically modified yeast cells. *Sep. Purif. Technol.* **52**, 253 (2006).
47. M. Safarikova, L. Ptackova, I. Kibrikova, I. Safarik. Biosorption of water-soluble dyes on magnetically modified *Saccharomyces cerevisiae* subsp. *uvarum* cells. *Chemosphere* **59**, 831 (2005).
48. I. Safarik, Z. Maderova, K. Pospiskova, K. Horska, M. Safarikova. Magnetic decoration and labeling of prokaryotic and eukaryotic cells. In: *Cell Surface Engineering: Fabrication of Functional Nanoshells*. Edited by R.F. Fakhrellin, I. Choi, Y.M. Lvov (RSC, 2014), pp. 185–215.
49. E. Sykova, P. Jendelova. Magnetic resonance tracking of transplanted stem cells in rat brain and spinal cord. *Neurodegener. Dis.* **3**, 62 (2006).
50. P. Jendelova, V. Herynek, L. Urdzikova, K. Glogarova, J. Kroupova, B. Andersson, V. Bryja, M. Burian, M. Hajek, E. Sykova. Magnetic resonance tracking of transplanted bone marrow and embryonic stem cells labeled by iron oxide nanoparticles in rat brain and spinal cord. *J. Neurosci. Res.* **76**, 232 (2004).
51. B. Qiu, D. Xie, P. Walczak, X. Li, J. Ruiz-Cabello, S. Minoshima, J.W.M. Bulte, X. Yang. Magnetosonoporation: Instant magnetic labeling of stem cells. *Magn. Reson. Med.* **63**, 1437 (2010).
52. E. Baldikova, K. Pospiskova, D. Ladakis, I.K. Kookos, A.A. Koutinas, M. Safarikova, I. Safarik. Magnetically modified bacterial cellulose: A promising carrier for immobilization of affinity ligands, enzymes, and cells. *Mater. Sci. Eng. C* **71**, 214 (2017).
53. X.-J. Hu, J.S. Wang, Y.G. Liu, X. Li, G.M. Zeng, Z.L. Bao, X.X. Zeng, A.W. Chen, F. Long. Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: Isotherms, kinetics and thermodynamics. *J. Hazard. Mater.* **185**, 306 (2011).
54. O.V. Makarchuk, T.A. Dontsova, I.M. Astrelin. Magnetic nanocomposites as efficient sorption materials for removing dyes from aqueous solutions. *Nanoscale Res. Lett.* **11**, 161 (2016).
55. O. Makarchuk, T. Dontsova, A. Perekos, A. Skoblik, Y. Svystunov. Magnetic mineral nanocomposite sorbents for wastewater treatment. *J. Nanomater.* **2017**, Article ID 8579598 (2017).
56. T.A. Dontsova, E.I. Yanushevskaya, S.V. Nahirniak, O.V. Makarchuk, A.I. Ivanets, M.Y. Roshchina, A.S. Kutuzova, L.M. Kulikov. Directional control of the structural adsorption properties of clays by magnetite modification. *J. Nanomater.* **2018**, Article ID 6573016 (2018).
57. K. Pospiskova, I. Safarik, M. Sebel, G. Kuncova. Magnetic particles-based biosensor for biogenic amines using an optical oxygen sensor as a transducer. *Microchim. Acta* **180**, 311 (2013).
58. J. Prochazkova, K. Pospiskova, I. Safarik. Magnetically modified electrospun nanotextile exhibiting peroxidase-like activity. *J. Magn. Magn. Mater.* **473**, 335 (2019).

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МОДИФІКАЦІЯ ДІАМАГНІТНИХ МАТЕРІАЛІВ ЗА ДОПОМОГОЮ МАГНІТНИХ РІДИН

Резюме

Магнітні рідини (ферофлюїди) мають багато важливих застосувань у різних областях біологічних наук, біотехнології, медицині та екологічних технологіях. У цьому огляді ми узагальнили відповідну інформацію, що стосується магнітної модифікації діамагнітних матеріалів з використанням різних видів ферофлюїдів. Особлива увага приділяється магнітній модифікації біоматеріалів рослинного походження, клітин мікробів та міководоростей, еукаріотичних клітин, біополімерів, неорганічних матеріалів та органічних полімерів. Дериватизація, зазвичай, зумовлена наявністю наночастинок магнітного оксиду заліза в порах оброблюваних матеріалів, на поверхні матеріалів або всередині полімерних гелів. Отримані розумні матеріали демонструють кілька типів реакцій на зовнішнє магнітне поле. Серед них – можливість вибіркового магнітного відділення компонентів від важких для обробки середовищ за допомогою магнітного сепаратора. Матеріали, модифіковані ферофлюїдами, часто використовуються як адсорбенти, носії, композитні нанозими або цільноклітинні біокатализатори.