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Magnetic particles in algae biotechnology: recent updates

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Abstract
Magnetic nano- and microparticles have been successfully used in many areas of algae biotechnology, especially for harvesting of algal biomass, separation of algal biologically active compounds, immobilization of algal cells, removal of important xenobiotics using magnetically modified algae, or for the preparation of magnetic catalysts; alternatively, algae have been employed for the production of magnetic iron oxide nanoparticles. In this short review paper, the relevant data published in the period 2016–2019 are summarized.

Keywords Algal biotechnology · Magnetic particles · Flocculation · Xenobiotics · Macroalgae extracts

Introduction

Magnetically responsive materials are typical examples of smart materials exhibiting several types of interaction with external magnetic field (Safarik et al. 2012). Such materials have found many important applications in almost any area of biosciences, biotechnology, and environmental technology, including also algae research and (bio)technology.

Magnetic nano- and microparticles have been successfully used for harvesting of microalgal biomass from cultivation media, magnetic labeling of microalgal cells, magnetic separation of microalgal biologically active compounds, magnetic detection of algae toxins, and preparation of magnetically responsive catalysts applicable in microalgal biotechnology. Magnetically modified microalgal cells have been employed as efficient biosorbents of important pollutants or part of whole-cell biosensors. Despite the fact that there is a real boom of studies employing magnetic particles for microalgae separation from large volumes, other areas of algal research and (bio)technology have not fully employed the potential offered by magnetically responsive materials.

This topic has been reviewed recently in detail by the authors of this paper (Safarik et al. 2016b, 2017). Currently, new scientific studies focusing on magnetic particles in combination with micro- and macroalgae have been performed in this interdisciplinary research. In this short review, new data published mainly in the period 2016–2019 (not presented in above mentioned review papers) are summarized. We hope that this paper will stimulate the microalgae and macroalgae research community in finding further progressive applications of magnetically responsive materials.

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Magnetic harvesting (flocculation) of microalgae

Recovery and harvesting of microalgal biomass represent a critical bottleneck of any large-scale algal biotechnology process. There are various harvesting techniques available (e.g., centrifugation, sedimentation, filtration, ultrafiltration, and flotation; Milledge and Heaven 2013), but the flocculation-based processes have acquired much attention due to their promising efficiency and scalability (Matter et al. 2019). Flocculation with the aid of magnetic particles is of high interest; magnetic particles are highly attractive harvesting agents due to their biocompatibility, efficiency, non-destructive nature of the magnetic field, easy manipulation, and potential regeneration. Ideal magnetic particles should be of low cost, easy to prepare, stable, and reusable. Several parameters are usually studied to optimize the flocculation process, including pH, magnetic (nano)particle dosage, temperature, composition of culture media, and conditions for the release of cell bound particles (Seo et al. 2017; Matter et al. 2019). The examples of recently published approaches are shown in Table 1.

Naked magnetic (nano)particles have often been used for microalgae cell flocculation, including commercially available magnetite nanoparticles (NPs) for *Chlorella vulgaris* (Zhu et al. 2019), microwave-synthesized magnetite microparticles for *Nannochloropsis oceanica* (Boli et al. 2017), or magnetite NPs prepared by coprecipitation of Fe^{2+} and Fe^{3+} at high pH for *Scenedesmus ovalternus* and *Chlorella vulgaris* (Fraga-Garcia et al. 2018). In specific cases also rather exotic magnetic flocculants, e.g., commercially available yttrium iron oxide ($Y_3Fe_5O_{12}$) NPs have been successfully used for *C. vulgaris* (Zhu et al. 2019). Surface-modified magnetite particles also have been prepared and efficiently employed for algae flocculation; positively charged polyethylenimine–magnetite particles were used for magnetic harvesting of negatively charged *Chlorella zofingiensis*, *C. vulgaris*, *Chlorella sorokiniana*, *Chlorella ellipsoidea* and *Botryococcus braunii* (Gerulová et al. 2018). Also, flocculation of different types of *Microcystis aeruginosa* was studied using polyethylenimine-coated magnetic nanoparticles (Yang et al. 2018a). However, it was observed that for *Scenedesmus* sp., coated magnetite NPs did not show better harvesting efficiency compared to uncoated nanoparticles, which is why cheap naked magnetite NPs can be used with advantage (Abo Markeb et al. 2019).

Magnetic flocculation of microalgal cells can be successfully combined with other procedures leading to target algal products; conversion of the *Scenedesmus obliquus* cells/particle slurry to biocrude oil using hydrothermal liquefaction process has been described. Zn-ferrite NPs enabled higher production of biocrude oil than naked magnetic iron oxide NPs (Egesa et al. 2018).

Regeneration of bound magnetic particles from the separated algal biomass is necessary to lower the cost of magnetic flocculants and the whole algae separation process. The regeneration process depends both on the magnetic flocculants and microalgae species. In many cases, ultrasonication in water or in organic solvents, treatment at high pH, or the combination of both procedures can be used successfully (Egesa et al. 2018; Xu et al. 2017, 2019; Abo Markeb et al. 2019). Alternatively, the bound iron oxide particles can be dissolved by strong acid and the released iron ions used for new magnetic particles synthesis (Duman et al. 2019).

A review of patented innovative harvesting processes for microalgal biomass production including magnetic flocculation techniques has been published recently (Deconinck et al. 2018). Despite the fact that a large number of studies have been published in this area, the application of magnetic particles needs to consider the complex impacts on the downstream processing of products production. Currently, such issues have not been addressed and need further investigation (Yin et al. 2020).

Magnetic separation and determination of algal biologically active compounds

Isolation and purification of biologically active compounds, including proteins, peptides, (poly)saccharides, oligonucleotides, nucleic acids, lipids, as well as of other specific molecules, are used in almost all branches of biosciences and biotechnologies. Isolation procedures, applicable also for work in complex solutions and suspensions, have become available for both small- and large-scale processes. Specific group of isolation techniques is based on the use of magnetically responsive materials, which can be applied for magnetic adsorption, affinity, ion exchange or hydrophobic batch separation, and applications of magnetically stabilized fluidized beds or magnetically modified two-phase systems (Safarik and Safarikova 2004; Franzreb et al. 2006).

Algae are very well known source of various valuable biologically active compounds (Hayes et al. 2019); on the contrary, selected algae can also produce important toxic compounds. There are many procedures describing isolation and separation of bioactive compounds from algae (Sosa-Hernández et al. 2018). Surprisingly, separations based on the use of magnetically responsive materials (Safarik and Safarikova 2004; Franzreb et al. 2006) have not found many applications in algae research and (bio)technology. Magnetic solid-phase extraction (MSPE), developed in 1999 by Safarikova and Safarik, has become a very useful tool for the preconcentration and separation of large amount of biologically active compounds, pollutants, heavy metal ions, etc. present in low concentrations (Safarikova and Safarik 1999; Jiang et al. 2019); this procedure has been efficiently used for the analysis of algal toxins (Li et al. 2017).

Fucoidan and laminarin, selected as typical brown algae water-soluble polysaccharides with interesting pharmaceutical properties, were separated from brown algae extract using magnetically responsive graphene oxide modified by four imidazole-based ionic liquids. Single-factor experiments showed that the extraction efficiency of polysaccharides was affected by the amount of ionic liquids for modification, solid–liquid ratio of brown alga and extraction agent (ethanol), the stirring time of brown alga and ionic liquid-modified magnetic graphene oxide materials, and amount of ionic liquid modified magnetic graphene oxide materials added to the brown alga sample solution. The results indicated that 1-(3-aminopropyl)imidazole chloride modified magnetic graphene oxide exhibited better extraction ability than graphene oxide, magnetic graphene oxide, and other three ionic liquid–modified magnetic graphene oxide materials. The highest extraction recoveries of fucoidan and laminarin extracted by 1-(3-aminopropyl)imidazole chloride modified magnetic graphene oxide were 93.3 and 87.2%, respectively; the adsorbent capacities were 100.2 mg g^{-1} for fucoidan and 38.6 mg g^{-1} for laminarin. In addition, solid materials could

Table 1 Examples of magnetic flocculants for algae separation

Diamagnetic material	Magnetic flocculant (label)	Treated algae	Reaction conditions	Other details	Reference
–	Microwave-synthesized magnetite microparticles	*Nannochloropsis oceanica*	High separation efficiency at wide range of pH and particle dosage	Adsorption of iron oxide particles on algal cells described by Freundlich model	Boli et al. (2017)
–	Microwave-synthesized magnetite microparticles	*Scenedesmus rubescens*, *Dunaliella tertiolecta*	The removal efficiency was between 75 and 91% for 6.2 and 62 mg L^{-1} magnetic particles	Strong electrostatic attraction between algal cells and magnetite particles observed	Vergini et al. (2016)
–	Magnetite NPs (50–100 nm; Sigma-Aldrich)	*Chlorella vulgaris*	pH 6.2 optimal for biomass harvesting	62.9% of Fe_3O_4 NPs released at pH 12.3	Zhu et al. (2019)
–	Magnetite NPs (Fe^{2+} and Fe^{3+} precipitation; 10–12 nm)	*Scenedesmus obliquus*	Efficient flocculation at pH 4–6	Combination of magnetic flocculation and algal/particle slurry conversion to biocrude oil using hydrothermal liquefaction	Egesa et al. (2018)
–	Magnetite NPs (Fe^{2+} and Fe^{3+} precipitation; 11.15 ± 1.57 nm)	*Scenedesmus*	Harvesting efficiency ca 90%	adsorption of NPs described by Langmuir model; maximum adsorption capacity 3.49 g dry cell weight g^{-1} Fe_3O_4 NPs	Abo Markeb et al. (2019)
–	Magnetic NPs (Fe^{2+} and Fe^{3+} precipitation)	*Synechocystis*, *Stigeoclonium*, *Nannochloropsis*, *Microcystis*	Harvesting efficiency higher than 94,78% for all strains	Regeneration of bound magnetic particles studied	Xu et al. (2017)
–	Magnetic NPs (Fe^{2+} and Fe^{3+} precipitation)	*Chlorella*	Harvesting efficiency >94%	ζ-Potential of the particles 11.9 mV	Ferraro et al. (2018)
–	Magnetic NPs (Fe^{2+} and Fe^{3+} precipitation)	*Scenedesmus ovalternus*, *Chlorella vulgaris*	Harvesting efficiencies greater than 95%	Separation primarily depended on the NPs-to-microalgae mass ratio, the effects of pH and ionic strength were less significant	Fraga-Garcia et al. (2018)
–	Maghemite (Fe^{3+} and pomegranate peel extract)	Blooming microalgae (mainly *M. aeruginosa*)	Harvesting efficiency 82.4%	Particle regeneration by strong acid treatment	Duman et al. (2019)
–	Fe-based nanomaterials ($NaBH_4$ and Fe^{3+})	*Chlorella*	High harvesting efficiency in a broad pH and temperature range	Recycled medium maintained normal cell growth with early stage stimulation, followed by growth inhibition	Liu et al. (2018)
–	Mg or Zn ferrite (coprecipitation method; 16–18 nm)	*Scenedesmus obliquus*	Separation efficiency of 99% was reached at pH 4	Combination of magnetic flocculation and algal/particle slurry conversion to biocrude oil using hydrothermal liquefaction	Egesa et al. (2018)
–	NH_2-terminated $ZnFe_2O_4$ NPs (octahedrally shaped)	*Chlorella*	$ZnFe_2O_4$ octahedrons used as magnetic flocculants and cell-disruption agents	$ZnFe_2O_4$ was both magnetic and had photocatalytic ability	Seo et al. (2018)
–	Sphalerite (natural; particle size < 38 μm)	*Chattonella marina*	100% alga removal in 180 min at pH 5.5		Wang et al. (2017a)

Table 1 (continued)

Diamagnetic material	Magnetic flocculant (label)	Treated algae	Reaction conditions	Other details	Reference
				Cell membrane was damaged and the intracellular content was released out after flocculation	
–	Yttrium iron oxide ($Y_3Fe_5O_{12}$) NPs (< 100 nm; Sigma-Aldrich)	*Chlorella vulgaris*	pH 7.3 optimal for biomass harvesting	More efficient flocculant than magnetite NPs	Zhu et al. (2019)
–	Natural magnetic clay particles	*Chlorella*	Harvesting efficiency > 94%	Flocculated cells enabled good adsorption of zinc ions	Ferraro et al. (2018)
Nanosilicate platelet from montmorillonite	Magnetite NPs (Fe^{2+} and Fe^{3+} precipitation)	*Microcystis aeruginosa*	Algal cells turbidity reduced by 67%	High removal of microcystin-LR observed	Chang et al. (2017)
Poly-arginine	Porous Fe_3O_4 microspheres	*Chlorella*	Harvesting efficiency > 95%	Best results with poly-arginine with molecular weight 15,000–70,000 D	Liu et al. (2017)
Polyacrylamide	Commercial magnetite nanoparticles	*Chlamydomonas* sp.	More than 97% of chlorophyll *a* and 87% of turbidity removed	Magnetic flocculation of algae-laden raw water	Ma et al. (2020)
Polyethylenimine	Magnetite NPs (Fe^{2+} and Fe^{3+} precipitation)	*Chlorella zofingiensis*, *Chlorella vulgaris*, *Chlorella sorokiniana*, *Chlorella ellipsoidea*, *Botryococcus braunii*	Harvesting efficiencies of 68–97% achieved at pH 4	The maximum adsorption capacities of algae were 0.823–6.047 g per g of flocculant	Gerulová et al. (2018)
Polyethyleneimine	Magnetite NPs (Fe^{2+} and Fe^{3+} precipitation)	*Chlorella pyrenoidosa*, *Scenedesmus obliquus*	Harvesting efficiency of *C. pyrenoidosa* was 98.92% while that of *S. obliquus* was 98.45%	The process did not reduce the lipid content of microalgae and quality of biodiesel	Liu et al. (2019)
Polyethylenimine	Magnetic iron-oxide NPs (Sigma-Aldrich)	*Microcystis aeruginosa*	Harvesting efficiency depended on cell and surface types	Extracellular polymeric substances affected the flocculation process significantly	Yang et al. (2018a)
Polyethylenimine (branched)	Natural magnetic clay particles	*Chlorella*	Harvesting efficiency > 94%	Clay-based flocculant increased the amount of removed Zn^{2+}	Ferraro et al. (2018)
Polymer brushes	Silica-coated iron oxide nanoparticles	*Chlamydomonas reinhardtii*, *Nannochloropsis gaditana*	Proof-of-concept design of supercoagulants	Rapid and irreversible microalgae coagulation achieved	Kuang et al. (2019)
Polyphenols from *Larix gmelinii*	Ferrocene used for magnetic composite preparation	*Chlorella vulgaris*	93.0% harvesting efficiency at pH 9.03	Flocculant detachment at pH 9.8 and with ultrasonication (95.6% of recovery efficiency)	Wang et al. (2018)
Polypyrrole (polymerization of pyrrole the presence of $FeCl_3$	Commercial magnetite particles	*Botryococcus braunii*, *Chlorella protothecoides*, *Chlorella vulgaris*	Recovery higher than 90%	The highest harvesting efficiency was at pH 10.0	Hena et al. (2016)
Silica	Magnetic NPs (Fe^{2+} and Fe^{3+} precipitation)	*Chlorella pyrenoidosa*	Flocculation efficiency 83.7%	Conversion of microalgae lipid to fatty acid methyl esters by direct transesterification	Vashist et al. (2019)

be separated and reused easily owing to their magnetic properties (Wang et al. 2017b).

Algal toxins are unique types of toxins generated with harmful algal blooms in water bodies. Algal toxins are hard to separate after they enter the water treatment processes, so an efficient procedure is required to remove the toxin from the water. A novel nanohybrid material, namely magnetic nanosilicate platelet (MNSP), was prepared and used for the removal of microcystin toxins. MNSP was fabricated by a special treatment of a clay mineral, montmorillonite, and then its surface was decorated with magnetite nanoparticles by in situ synthesis. The nanohybrid enabled efficient removal of microcystin-LR (99.39% at a concentration of 100 ppm), while pristine nanosilicate platelet could remove only 36.84% at the same dosage (Chang et al. 2017).

Magnetic separation of algal toxins can be negatively influenced by natural organic matter (NOM). During the study of adsorption of microcystin-LR on iron oxide NPs, it was observed that various types of NOM, namely extracellular polymeric substances from cyanobacteria and sodium salt of alginic acid from brown algae, efficiently stabilized the nanoparticles, but substantially decreased the toxin adsorption. The results indicated that NOM and toxin compete for limited adsorption sites (Yang et al. 2018b).

Microcystins produced by freshwater cyanobacteria can be efficiently determined in environmental water, using magnetic solid-phase extraction and high-performance liquid chromatography with UV detection. The magnetic composite material, which was combined with cetylpyridinium chloride, was prepared by hydrothermal synthesis. Under the optimal conditions, the limit of detection of microcystin-LR was 0.001 μg L^{-1} and the limit of quantification was 0.0028 μg L^{-1}, while the limit of detection of microcystin-RR was 0.001 μg L^{-1} and the limit of quantification was 0.003 μg L^{-1}. The magnetic solid-phase extraction adsorbent used in this method has the advantages of simple preparation, low price, and easy solid–liquid separation, and it can be used for the rapid and sensitive monitoring of trace microcystins in environmental water samples (Li et al. 2017).

Direct competitive enzyme-linked immunomagnetic colorimetric assays (ELIMC) have been developed for the determination of domoic acid, okadaic acid and saxitoxin in seawater. Magnetic beads with immobilized anti-rabbit IgG enabled immobilization of the specific rabbit IgG. Competition of the analyzed toxin with the toxin-horseradish peroxidase conjugate towards the bound specific antibody took place in a single and short step procedure, carried out into a microtube. The non-bound reagents were then discarded by capturing the immunomagnetic beads with a magnet, and after washing, the beads were suspended in peroxidase substrate solution. After a short incubation time, a stop solution was added and the activity of the captured enzyme was measured spectrophotometrically. In the presence of toxin, competition occurs and consequently, the rate of color production decreases proportionally to the concentration of the toxin (Petropoulos et al. 2019).

A similar approach was used for the determination of okadaic acid using epoxy group activated carbon shell magnetic beads with immobilized goat against mouse antibody. Mouse monoclonal antibody against okadaic acid, okadaic acid-horseradish peroxidase conjugate, and okadaic acid containing sample were simultaneously mixed with magnetic beads in a 96-well microtitration plate. After incubation, washing, and peroxidase substrate addition, the absorbance of the reaction mixture was measured (Pang et al. 2019).

Magnetic beads (NucleoMag Plant kit) were used for efficient, reliable, and fast DNA extraction of several macroalgae species. DNA extracted from macroalgae (*Ulva* spp.) using this method is of high quality and purity, allowing successful library preparation for next generation sequencing (Fort et al. 2018).

Algae-based production of magnetic iron oxide nanoparticles

Various procedures have been used to synthesize magnetic nano- and microparticles, such as classical coprecipitation, reactions in constrained environments (e.g., microemulsions), sol-gel syntheses, hydrolysis and thermolysis of precursors, sonochemical and microwave reactions, hydrothermal reactions, flow injection syntheses, electrospray syntheses, and mechanochemical processes (Laurent et al. 2008; Wu et al. 2015).

Biosynthesis of metal and metal oxide NPs using biological materials is currently of high interest. The nanobiotechnology synthesis of nanoparticles can be included into the group of clean manufacturing technologies. Clean technologies can significantly reduce environmental contamination and decrease the use of currently employed toxic chemicals and solvents, thus reducing the hazards to human health (Schröfel et al. 2014; Fawcett et al. 2017). The synthesis of nanoparticles can usually utilize plant tissues, plant extracts, exudates, and other parts of living and dead plants (Mahdavi et al. 2013).

Green biosynthesis of iron oxide nanoparticles employs the bottom-up approach where the iron atoms assemble to form clusters and then eventually the nanoparticles. The biological compounds present in green materials may act as both reducing and capping agents that can stabilize the nanoparticles during the synthesis process. Using this approach, it is possible to control the size and shape of the nanoparticles which can be used in various applications. Concentration of both metal salt and biological compounds, reaction time, as well as temperature and pH of the solution can be modified to obtain specific nanoparticles (Yew et al. 2020).

Recently, also marine macroalgae extracts have been successfully employed for the biosynthesis of magnetic iron oxide nanoparticles (Fawcett et al. 2017; Yew et al. 2020). Different types of brown, red, and green seaweed belonging to genera *Sargassum*, *Colpomenia*, *Kappaphycus*, *Padina*, *Pterocladiella* (*Pterocladia*), and *Ulva* have been used for this purpose (see Table 2 for more information). Usually, magnetite nanoparticles were synthesized by reduction of ferric chloride solution with seaweed water extract containing sulfated polysaccharides acting as both reducing agent and efficient stabilizer. In several papers, magnetite nanoparticles were biosynthesized using the mixture of Fe^{3+} and Fe^{2+} ions with a 2:1 molar ratio. The nanoparticles exhibited usually spherical or cubic shape with diameters ranging from 10 to 33 nm.

Biosynthesized iron oxide magnetic NPs have been applied for specific applications. Magnetite NPs prepared by the extracts of seaweeds *Padina pavonica* and *Sargassum acinarium* were entrapped in calcium alginates beads and used as magnetically responsive adsorbent for Pb^{2+} ion adsorption. Higher adsorption capacity was observed for alginate beads containing *P. pavonica*–synthesized magnetite (El-Kassas et al. 2016).

Ulva flexuosa–derived Fe_3O_4 NPs exhibited strong antibacterial action in in vitro tests against human pathogenic bacteria including *Staphylococcus epidermidis*, *Bacillus subtilis* and *Bacillus pumilus*, and moderate antifungal activity against *Saccharomyces cerevisiae*. The same NPs exhibited low acute toxicity against the rotifer *Brachionus rotundiformis* (Mashjoor et al. 2018). Similar results were obtained with magnetite NPs prepared with *Ulva prolifera* extract (Mashjoor et al. 2019).

Magnetite (Fe_3O_4) and cobalt ferrite ($CoFe_2O_4$) NPs were prepared by the coprecipitation method in aqueous solutions of a well-characterized agar obtained from the red marine alga *Gelidium robustum*. Highly crystalline-coated magnetite NPs were obtained; on the contrary, lowly crystalline cobalt ferrite NPs were formed. The NPs formed exhibited high degree of biocompatibility and can be considered as promising candidates for biomedical applications such as magnetic hyperthermia treatment for cancer therapy (Diaz-Blels et al. 2018).

Also, *Chlorella vulgaris* aqueous extract has been employed for algae-assisted auto-combustion method to prepare cobalt ferrite $CoFe_2O_4$ nanoparticles. After mixing *Chlorella* extract with cobalt nitrate and ferric nitrate solutions, urea solution was added to the mixture under mixing. After water evaporation by heating, the temperature was raised to 160 °C to achieve self-ignition; at this point, the dried gel was burnt in a self-propagating manner producing huge volume of gases and leaving behind dry and loose ferrite powder. The average particle size was 21.0 nm (Satheeshkumar et al. 2020).

Immobilized and modified algae cells

An absolute majority of prokaryotic and eukaryotic cells is diamagnetic. To add a response to external magnetic field,

Table 2 Examples of marine alga used for the biosynthesis of magnetic iron oxides

Marine alga	Precursors	Diameter (nm)	Shape	Other details	Reference
Colpomenia sinuosa	$FeCl_3$	11.24–33.71	Nanospheres	Antibacterial property	Salem et al. (2019)
Kappaphycus alvarezii	$FeCl_2 + FeCl_3$	14.7 ± 1.8	Spherical	Estimated crystallite size was 16.79 nm by XRD	Yew et al. (2016)
Padina pavonica	$FeCl_3$	10–19.5	Spherical	Entrapment in calcium alginate	El-Kassas et al. (2016)
Pterocladiella capillacea	$FeCl_3$	37.6 ± 4.8	Cubic	Methotrexate immobilized on chitosan-modified NPs	Ali et al. (2018)
Pterocladia capillacea	$FeCl_3$	16.85–22.47	Nanospheres	Antibacterial property	Salem et al. (2019)
Sargassum acinarium	$FeCl_3$	21.6–27.4	Spherical	Entrapment in calcium alginate	El-Kassas et al. (2016)
Sargassum boveanum	$FeCl_2 + FeCl_3$	116 ± 21.2			Mashjoor et al. (2019)
Sargassum crassifolium	$FeSO_4 + FeCl_3$	4.94–35.4	Spherical	Thermogravimetric analysis performed	Budlayan et al. (2019)
Sargassum muticum	$FeCl_3$	18 ± 4	Cubic	Saturation magnetization 22.1 (emu g^{-1})	Mahdavi et al. (2013)
Ulva clathrata	$FeCl_2 + FeCl_3$	144 ± 19.2			Mashjoor et al. (2019)
Ulva flexuosa	$FeCl_2 + FeCl_3$	12.3 ± 1.7	Cubo-spherical	Saturation magnetization 31.05 (emu g^{-1})	Mashjoor et al. (2018)
Ulva flexuosa	$FeCl_2 + FeCl_3$	13.80 ± 2.3			Mashjoor et al. (2019)
Ulva intestinalis	$FeCl_2 + FeCl_3$	167 ± 24.3			Mashjoor et al. (2019)
Ulva linza	$FeCl_2 + FeCl_3$	193 ± 23.2			Mashjoor et al. (2019)
Ulva prolifera	$FeCl_2 + FeCl_3$	10.05 ± 1.2	Cubo-spherical	Saturation magnetization 38.18 (emu g^{-1}); specific surface area 16.31 m^2 g^{-1}	Mashjoor et al. (2019)

several modification procedures can be used such as the non-specific attachment of magnetic nanoparticles (e.g., by the magnetic fluid treatment), binding of maghemite or magnetite particles on the cell surface, covalent immobilization of magnetic particles on cell surface, immobilization of cells to magnetically responsive carriers, specific interactions with immunomagnetic nano- and microparticles, magnetic quantum dots or magnetoliposomes, biologically driven precipitation of paramagnetic compounds on the cell surface, and crosslinking of the cells or isolated cell walls with a bifunctional reagent in the presence of magnetic particles or entrapment (together with magnetic particles) into biocompatible polymers (Safarik et al. 2014).

Recently, *C. vulgaris* cells were modified with magnetite nanoparticles. The impact of various concentrations of magnetic nanoparticles on the microalgal cells growth and their metabolic status was investigated over 12 days. It was observed that high concentration of magnetic particles caused toxicity in microalgal cells damaging their organelles, mitochondria, and chloroplasts. After more than 6 days of exposure to stress generating concentrations of magnetic nanoparticles, it was found that microalgae could overcome the resulted damages. Therefore, in the aspect of the biotechnological process and environmental concerns caused by long-term exposure to magnetic nanoparticles, potential harmful toxic effects should only be expected during the initial days and at high concentrations (Taghizadeh et al. 2020).

A scalable and rapid method to prepare magnetically responsive agarose microbeads containing *C. pyrenoidosa* or other microbial cells was developed, using low-temperature melting agarose and food-grade sunflower oil as the main components for the emulsification process. The microscopic algae cells were immobilized in ~ 100-μm-sized beads. Magnetically responsive microbeads were prepared by the immobilization of magnetically modified cells (using poly(allylamine)-stabilized magnetic nanoparticles) or by incorporation of magnetic calcium carbonate microcrystals. It was observed that the cells encapsulated in magnetically responsive microbeads were viable (Konnova and Fakhrullin 2017).

Magnetic algae–derived biosorbents for xenobiotics removal

Various types of organic and inorganic xenobiotics can be found in water systems all over the world. Several techniques for their removal have been developed; in many cases, biosorbents prepared from appropriate biological wastes have been used successfully. Magnetically responsive biosorbents enable their selective separation from the system using external magnetic field (Safarik et al. 2018).

Biomass from unicellular algae and marine macroalgae represents a typical example of low-cost, renewable natural material which can be obtained in large quantities. In many cases, huge amounts of marine algae can be found in beaches, thus causing problems to the tourist industry; the obtained biomass can be efficiently used as adsorbents for the removal of specific pollutants or for biochar production. In addition to native algae biomass, also waste biomass obtained after selected industrial processes (e.g., solvent extraction of oil or colorants) can be used for the preparation of efficient adsorbents. Special types of magnetic biosorbents have been prepared from microalgae and marine macroalgae; a review chapter summarizing this topic has been published recently (Safarik et al. 2020).

Magnetically modified algal biomass has been efficiently used for metal ion removal. Iron oxide particles and natural magnetic clay coated with polyethylenimine were successfully applied in the harvesting of *Chlorella* sp. Zinc ion removal efficiency of *Chlorella* cells was analyzed both before and after magnetic harvesting in order to determine the effect of magnetic particles on remediation efficiency. Native *Chlorella* cells exhibited quite high remediation efficiency; in addition, zinc-loaded *Chlorella* cells were perfectly harvested by both magnetic materials. Native *Chlorella* cells flocculated with polyethylenimine-coated magnetic clay exhibited high efficiency of zinc ion removal (Ferraro et al. 2018).

Chlorella vulgaris cells coated with magnetic iron oxide NPs were successfully employed in the removal of Cd(II) and Pb(II) from aqueous solutions. High percentage uptakes of these two toxic ions were observed in a wide range of pH and initial adsorbent concentrations. The material was found to be efficient in the rapid uptake of Cd(II)/Pb(II) from aqueous solutions. Simultaneous sorption experiments have shown that Cd(II) and Pb(II) were adsorbed at the different binding sites of the magnetic biosorbent; Cd(II) ions were bound with weak electrostatic forces to the dissociated carboxyl or hydroxyl groups, whereas Pb(II) ions were chemically bound with the amino groups (Lalhmunsiama et al. 2017).

Spirulina (*Arthrospira*) *platensis* modified with magnetite NPs and potassium nickel hexacyanoferrate was used as a biosorbent for uptake of Cs^+; maximal adsorption capacity of 149 mg g^{-1} was reached. The cesium uptake was selective in the presence of Na^+ and K^+ ions. The used sorbent was easily separated by magnetic field and regenerated, keeping 85% of its initial capacity after five regeneration cycles (Azizkhani and Faghihian 2019).

Magnetically responsive algae-based biosorbents have also been applied for dye removal. The brown alga *Sargassum horneri* magnetically modified with microwave-synthesized iron oxide nano- and microparticles was used for adsorption of five water-soluble dyes of different chemical structures from aqueous solutions. The biosorption was studied in a batch system under different conditions. The adsorption equilibrium data were analyzed by the Langmuir and Freundlich isotherm models. The highest maximum adsorption capacity was observed for Acridine Orange (193.8 mg g^{-1}) and the lowest one for Malachite Green (110.4 mg g^{-1}). The sorption kinetics could be described by the pseudo-second-order model, and the thermodynamic studies indicated exothermic nature of biosorption process in the temperature range studied (Angelova et al. 2016).

Magnetic derivative of tropical marine green calcareous alga *Cymopolia barbata* was used as a biosorbent for the efficient Safranin O removal from aqueous solutions. *Cymopolia barbata* biomass was magnetically modified using microwave-synthesized magnetic iron oxide nano- and microparticles; this modification was simple and inexpensive, without the need of drying step. The Safranin biosorption was studied in a batch system under various conditions. Time necessary to reach equilibrium was 90 min. The adsorption isotherm data exhibited best correlation to the Freundlich and Langmuir adsorption models. The maximum adsorption capacity reached the value 192.2 mg g^{-1} (dry mass). Kinetic data were best fitted to the pseudo-second-order model. The adsorption process was exothermic and spontaneous (Mullerova et al. 2019).

Sargassum swartzii biomass modified with nanoscale zerovalent iron particles was employed for Crystal Violet adsorption from water solutions. Maximum biosorption capacity was observed at pH of 8. The Langmuir isotherm model enabled to calculate maximum adsorption capacity (200 mg g^{-1}). Dye desorption was carried out with 0.1 M HCl (Jerold et al. 2017).

The brown alga *Cystoseira barbata* coated with magnetite particles was used for the removal of Methylene Blue from aqueous solution. The equilibrium data was analyzed with the Langmuir and Freundlich isotherms. The results showed that the maximum adsorption capacities were achieved at pH 2 and reached to 5.74 and 1.08 mg g^{-1} at 25 and 45 °C, respectively (Ozudogru et al. 2016).

The red unicell *Porphyridium* sp. has been modified by coating with Fe_3O_4 and silica NPs and utilized as a biosorbent for the removal of Methylene Blue. The adsorption followed the pseudo-second-order kinetic model and Freundlich adsorption isotherm. Maximum adsorption capacity was 96.93 mg g^{-1} at pH 6; this adsorbent can be used repeatedly (Buhani et al. 2019).

Biochar is a carbon-based material produced by pyrolysis of biomass in the absence of oxygen. In specific cases, algal biomass can be applied as biochar precursor. *Laminaria* (*Saccharina*) *japonica*–derived activated carbon/iron oxide magnetic composites were prepared by heating powdered biomass in nitrogen atmosphere; after cooling, the carbonized material was impregnated with ferric chloride and activated at 600–800 °C in nitrogen atmosphere. This biosorbent was used for adsorption of acetylsalicylic acid; the maximum adsorption capacity was ca 127 mg g^{-1} at 10 °C. The adsorption process followed the pseudo-second-order kinetic model and was controlled by physisorption and exothermic mechanisms (Jung et al. 2019).

Acid Orange 7 was separated by a magnetically modified brown marine macroalga biochar prepared by an electromagnetization technique. Magnetite-modified biochar exhibited high porosity which enabled high adsorption performance and easy magnetic separation from aqueous media. Maximum adsorption capacities were 190, 297, and 382 mg g^{-1} at 10, 20, and 30 °C, respectively (Jung et al. 2016).

Waste kelp and hijikia (a common seaweed found in South Korea that causes waste problems) were used to prepare magnetically modified biochar. Algae biomass was impregnated with $FeCl_3$ solution and after drying this material was pyrolyzed at 500 °C under nitrogen. The prepared biochars demonstrated a high selectivity for copper (69.37 mg g^{-1} for kelp magnetic biochar and 63.52 mg g^{-1} for hijikia magnetic biochar), showing twofold greater removal efficiency than for zinc and cadmium (Son et al. 2018a).

Chitosan-modified magnetic kelp (brown algae) biochar was successfully synthesized for efficient removal of copper ions from wastewater. This chitosan containing composite exhibited 6 times higher surface area (6.17 m^2 g^{-1}) than the pristine magnetic kelp biochar (0.97 m^2 g^{-1}). The presence of new functional groups in chitosan-modified biochar improved the Cu^{2+} adsorption capacity. It was shown that the optimum pH value for the adsorption process was 6.9 (Son et al. 2018b).

The magnetite-modified activated carbon from *Sargassum oligocystum* was employed as a recyclable and efficient adsorbent for the removal of Methylene Blue and Methyl Violet from aqueous solutions. The adsorption process data matched well with the pseudo-second-order and Freundlich isotherm models. The maximum adsorption capacities were around 60 mg g^{-1} for both dyes (Foroutan et al. 2019).

The marine green alga *Enteromorpha* (*Ulva*) modified with $Co(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ and subsequently carbonized at 700 °C was used as an efficient adsorbent for Methyl Blue removal. This carbon-based adsorbent contained highly dispersed CoO_x/MoO_y NPs on its surface and exhibited magnetic properties. High maximum adsorption capacity for Methyl Blue (1587.3 m^2 g^{-1}) was observed (Yang et al. 2019).

Harmful algal bloom biomass (blue–green algae) and ferric ammonium citrate or ferric nitrate were employed as precursors for preparing magnetic algal-based biochar. This material efficiently removed Cr(VI); the adsorption values were 165 m^2 g^{-1} at pH 2 and 73 m^2 g^{-1} at pH 6, with rapid kinetics. The composites maintained 73–82% of their removal capacity after five removal/recovery cycles (Cui et al. 2019).

Magnetic catalysts in algae biotechnology

Utilization of magnetically responsive materials and particles can bring a considerable simplification into algal-based biorefinery technologies, based on their fast, simple, and selective separation even from various difficult-to-handle environments and conditions. Magnetically responsive (bio)catalysts can be reused after their simple magnetic recovery, thus avoiding the filtration or centrifugation separation processes. Additionally, application of magnetic (bio)catalysts can significantly improve the productivity, economic feasibility, sustainability, and product quality during the algal-based biorefinery processes (Safarik et al. 2016a).

Magnetic catalyst based on Fe_2O_3 “core” particles was prepared by precipitation; subsequently, it was coated by porous silica and combined with clinoptilolite. This magnetic catalyst showed good performance for *Chlorella* hydrothermal liquefaction and derived biocrude upgrading. In 320–350 °C regime and under subcritical water, palmitic acid conversion was improved by 14–29% with the catalyst. Methyl palmitate conversion was 56% and decarboxylation selectivity to pentadecane was improved to 62% on the developed catalyst (Bian et al. 2017).

Magnetic NPs formed by Zn- and Mg-doped ferrite, used for *Scenedesmus obliquus* magnetic flocculation, were applied to convert the algal/particle slurry to biocrude oil using hydrothermal liquefaction. Liquefaction of algal/magnetic NPs slurry gave a biocrude oil yield of 37.1% while algae yielded only 23.2%. Hydrocarbon production in Zn-ferrite catalyzed and uncatalyzed biocrude oil formation were 46.5 and 19.9%, respectively, while the formations of heptadecane from Zn-ferrite catalyzed and uncatalyzed biocrude oil productions were 37.8 and 10%, respectively (Egesa et al. 2018).

Some reviews summarizing latest developments in microalgae-biofuel production with nanoadditives as catalysts, including magnetic ones, have been published recently (Hossain et al. 2019; Nematian and Barati 2019).

Conclusions

Magnetically responsive nano- and microparticles or their composites with diamagnetic materials have increasing potential for applications in many fields of biosciences, biotechnology, and environmental technology. These materials have also found interesting applications in algae biotechnology. Although such materials have been mainly used in small-scale (laboratory) applications, their ability to interact with external magnetic field predetermines their future applications also in large-scale biotechnology processes. Low cost, biocompatibility, high availability, and variability of magnetic materials and composites will enable their wide application in the near future.

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