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Account / Revue

Magnetic nano- and microparticles for metal removal and environmental applications: a review

Audrey-Flore Ngomsik^a, Agnès Bee^b, Micheline Draye^a, Gérard Cote^a,
Valérie Cabuil^{b,*}

^a *Laboratoire d'électrochimie et de chimie analytique (LECA), Équipe procédé de séparation et radiochimie, École nationale supérieure de chimie de Paris (université Paris-6), 11, rue Pierre-et-Marie-Curie, 75005 Paris, France*
^b *Laboratoire « Liquides ioniques et Interfaces chargées » (LI2C), université Pierre-et-Marie-Curie (Paris-6), 4, place Jussieu, 75005 Paris, France*

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Abstract

Besides the numerous applications of magnetic particles in the fields of medicine, diagnostics, molecular biology and bio-inorganic chemistry, a high potential exists for these particles in environmental sciences. Several methods have been proposed these last years for the separation of metals from wastewater using either micro- or nano-magnetic particles. We describe here the synthesis of such particles, compare their magnetic properties, and discuss the possibility of selectivity for metals ions, namely radionuclides. **To cite this article:** *A.-F. Ngomsik et al., C.R. Chimie 8 (2005).*

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Résumé

Aux côtés des nombreuses applications des particules magnétiques dans les domaines de la médecine, du diagnostic, de la biologie moléculaire et de la chimie bio-inorganique, un potentiel élevé existe dans le domaine de l'environnement. Plusieurs méthodes ont été proposées ces dernières années pour la séparation des métaux dans les déchets aqueux, utilisant, soit des micro-, soit des nanoparticules magnétiques. La synthèse et les propriétés magnétiques de ces particules sont décrites, ainsi que les possibilités d'optimisation de ces particules, notamment en vue de leur sélectivité vis-à-vis radionucléides. **Pour citer cet article :** *A.-F. Ngomsik et al., C.R. Chimie 8 (2005).*

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* Corresponding author.

E-mail addresses: ngomsik@ccr.jussieu.fr (A. Bee), draye@enscp.jussieu.fr (M. Draye), cote@ext.jussieu.fr (G. Cote), cabuil@ccr.jussieu.fr (V. Cabuil).

1. Introduction

Separations using magnetic gradients, as the so-called High Magnetic Gradient Separation (HGMS), are now widely used in the fields of medicine, diagnostics, molecular biology, bioinorganic chemistry and catalysis [1,2]. They are also well known in the field of mining and ore beneficiation [3]. In HGMS, a liquid phase containing magnetic particles is passed through a matrix of wires magnetized by an applied magnetic field. The particles are held onto the wires, but can be released if the magnetic field is cut off. If these particles are tailored in order to fix specific metal species or molecules, the latter can be isolated from water, waste or slurries.

Indeed magnetic particles are widely used in the framework of the reprocessing of waste, for example for the remediation of heavy metals. For such an application, it is necessary to use a method of purification that does not generate secondary waste, and involves materials that can be recycled and easily used on an industrial scale. The integrated process which couples magnetic separation (not always 'high-gradient' one) together with surface complexation adsorption, ionic exchange and solvent extraction is sometimes called magnetically assisted chemical separation (MACS), and is considered as promising in order to reduce the aqueous stream volume of high activity waste [4,5].

In MACS processes, particles are usually micrometric ones. They are made of magnetite nanoparticles embedded into a polymer microsphere with a diameter ranging between 0.1 and 25 μm . These microspheres are of the same type as the so-called Solvent Impregnated Resins (SIRs), except that they contain magnetic material [6]. The MACS process implies several important steps: (i) the impregnation of the magnetic microspheres with an extractant of a hazardous metal; (ii) the introduction of the functionalized particles into a matrix of waste containing this metal; (iii) the separation of the particles and metal from the whole, thanks to a magnetic gradient. The use of nanoparticles, having a diameter ranging between 4 and 15 nm, either dispersed in an extracting solvent [7], or (and) specifically coated by complexing species [8] has also been described for MACS.

An efficient system of particles for MACS process is a system for which the sorption capacity of the particles is important and the magnetic field gradient as

small as possible. The particles have to become magnetized at low field, but not to stay magnetized if the field is cut off. Low price is of course an advantage, but more difficult to achieve when specificity is needed. The efficiency of the process is usually evaluated only as a whole through the measurement of the partition coefficient K_d ¹. Experimental adsorption isotherms can also be plotted and compared to the Langmuir and Freundlich model or to the extended Langmuir model of Brunauer, Emmet, and Teller (BET) in order to have idea of the adsorption mechanism [9].

Here we compare the advantages of nano- and microparticles according to the recent publications in the field.

2. Description and synthesis of nano and microparticles for MACS processes

The magnetic component of the micro and nanoparticles used for MACS process, is usually magnetite Fe_3O_4 (or its products of oxidation $\gamma\text{-Fe}_2\text{O}_3$). Indeed, magnetite is a suitable material on the magnetic point of view, and is moreover easy to synthesize and rather cheaper than other materials that would involve metals (Fe, Co) or other oxides (of the type MFe_2O_4).

These nanoparticles can be used directly for MACS processes, without or with a specific coating by complexing species, or entrapped in a polymer matrix to produce microparticles.

2.1. Synthesis of nanoparticles

Chemical synthesis of colloidal magnetite is known for a long time: aqueous mixtures of ferric and ferrous salts are mixed at room temperature with an alkali in order to induce the immediate precipitation of a black magnetic product constituted of rocklike magnetite particles, which are negatively charged and associated to the counter-ions of the alkali [10]. During this step, the average diameter of particles can be monitored between 5 and 100 nm through the nature of the alkali, its concentration, the concentration of the ferric and ferrous

¹ K_d (ml/g) is usually defined by $K_d = \frac{V}{m} \frac{(c_i - c_f)}{c_f}$, where V is the volume of the aqueous phase and m the mass of particles, c_i , the concentration of the metal to remove before the contact with particles and c_f , the concentrations of metal after the contact.

salt, the ratio Fe(II)/Fe(III), the ionic strength, the temperature, the way of admixing the reactants and the efficiency of the stirring. The system is always polydisperse in size, but at once all these parameters are fixed, the result of the synthesis is reproducible [11–13]. Colloidal magnetite gets easily oxidized if it is kept under usual atmosphere; indeed the product often called magnetite is in fact bertholide, i.e. a ferric oxide which composition is between the one of magnetite (Fe_3O_4) and the one of maghemite ($\gamma\text{-Fe}_2\text{O}_3$).

It can dissolve in acidic medium: this dissolution is faster as the particles size is smaller, and as the concentration of acid is higher [14]. In order to avoid this dissolution magnetite can be deliberately oxidized to maghemite, dispersing the magnetic particles in acidic medium and stirring them with ferric nitrate [15]. The maghemite particles obtained are then chemically stable in alkaline and acidic medium. The saturation magnetization of maghemite is slightly lower than the one of magnetite but the difference of magnetization is largely counterbalanced by the gain of chemical stability.

It is often reported that magnetite has a high capacity of retention of cations, and the ferric oxide nanoparticles can thus be used without any further surface modification [14,16]. pH is in this case a key parameter as it controls the surface charge density and thus the adsorption phenomenon and the surface complexation [14]. For magnetite, the pH of the point of zero charge may vary according to the synthesis process or (and) the purity of the oxide. It is nevertheless found always around pH 7 [14,17].

Nevertheless to provide to these nanoparticles a good specificity, some special surface modifications can be made. For example, the retention of americium (III), europium (III) and uranium (IV) on alumina α , in presence of simple organic complexants like acetate, oxalate and carbonate has been studied [18].

Nanoparticles coated by a bifunctional polymer layer have been recently used as extractants for organic compounds [19]. The Fe_3O_4 particles are synthesized into an aqueous solution of a copolymer constituted by a PAA backbone grafted by PEO and PAA side chains. PEO ensures the hydrophilicity and the colloidal stability although PPO ensures hydrophobicity and the solubilization of organic compounds. The total thickness of the polymer layer is about 9 nm and the diameter of magnetic particles around 10 nm. Particles coated with a simple hydrophobic surfactant, and dis-

persed in an organic solvent extractant can also be used [18]. The surfactant can be for example sodium oleate. Another alternative is to coat the nanoparticles by a bifunctional molecule complexing by one end the metallic surface, and by the other end the heavy ion (for example) to separate from a waste. The idea is to choose the complexing end of the molecule in order that is specific of the ion or molecule to extract. Calixarenes are good examples of such systems [20]. Nevertheless, synthesis of calixarenes themselves is not very easy.

2.2. Synthesis of microparticles

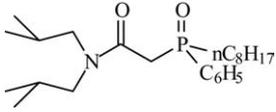
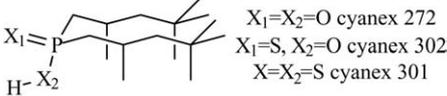
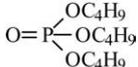
The microparticles are often commercial carriers made of magnetite particles dispersed in a cross-linked polymer matrix. For biological separation, the commercial particles are polystyrene latex and many improvements have been made in order to increase the amount of magnetic material in the latex and reduce the polydispersity. Specific molecules are chemically grafted on the latex and many commercial tests are available and can be purchased from several firms [21].

For heavy metal separation, the microspheres are of the same nature as the so-called SIRs, except that they contain magnetic material. SIRs are porous polymer beads within which a liquid extractant is dispersed. The preparation of SIRs implies: (i) the choice of the extractant with a specific affinity toward the targeted species; (ii) the choice of the polymeric substrate that has to allow correct impregnability of the extractant; (iii) the choice of the process for impregnation.

Usual extractants are organic organophosphorus species, neutral one as octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) [22,23] or organic acids as the so-called Cyanex species (Table 1). But other molecules could be used. Many ‘Cyanex-type’ extractant are available (for example, bis(2,4,4-trimethylpentyl)phosphonic acid, or bis(2,4,4-trimethylpentyl)dithiophosphonic acid), according to the nature of the groups linked to phosphorous as depicted on Table 1 [24–26].

These extracting solvent have to be adsorbed on the particles and this obligation drives the choice of the polymer. Typical polymers used are polyacrylamide, polymethylmethacrylate, polyvinylalcohol, polyethylenglycol [27]. Polyacrylamide based polymers seems to give the better results for extractants adsorption [23].

Table 1
Selective extractants used in remediation

CMPO	Octylphenyl- <i>N,N</i> -diisobutylcarbamoyl-methyl phosphine oxide	
Cyanex	Bis(2,4,4-trimethylpentyl) phosphinic acids	
TBP	Tributylphosphate	

Commercial polyacrylamide based magnetite particles are available, with diameters between 0.1 and 25 μm .

Three main synthesis processes of the magnetic microspheres can be used: (i) absorption of a magnetite dispersion into polymer microspheres, using a solvent evaporation technique [23], (ii) absorption of a ferrous ferric solution into the polymer microspheres and synthesis of magnetite inside these microspheres, (iii) synthesis of the polymer microspheres into a dispersion of magnetic particles in order to entrap them during the polymerization process, as it is usual for the synthesis of magnetic polystyrene latex [28].

Inpregnation of the polymeric particles by the extractant is a solvent evaporation process: the microspheres are dispersed in a volatile solvent, and the extractant, usually dispersed in TBP (tributyl phosphate) is added; the organic solvent is evaporated and the particles are then ready to be used. In the case of polyacrylamide particles, it has been proved that the efficiency of the extractants is enhanced by such a polymeric environment, perhaps because of the presence of the amide groups that can act as donors [29].

One can imagine that a 'two-component' material could be sufficient, if the polymer constituting the particles has itself functional groups, able to complex metal ions. But in this case the slow intraparticle diffusion of the species to complex is a limitation as the price, if synthesis of specific polymers has to be made as it was the case for arsenic removal [5]. Nevertheless following the same kind of idea, biopolymers as alginic acids based polymers could be serious candidates for extraction of heavy metals [30].

3. Effect of a magnetic force on magnetic nano and microparticles used for extraction

Suitable particles for magnetically assisted separation are superparamagnetic particles: the application of a magnetic field of low intensity induces the magnetization of the material and thus makes the use of a magnetic force possible, but when the magnetic field is cut off, the magnetization immediately decreases to zero [31]. This last point is important for the release of particles after adsorption of the waste.

Magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are ferromagnetic materials. Their specific magnetization M_s is around 450 kA/m (that means about four times lower than the one of Iron $\text{Fe}(\alpha)$, but metallic nanoparticles are highly oxidizable). But at once particles are small enough in order to be magnetic monodomains (diameter lower than 10 nm) and to have a small energy of anisotropy, they become superparamagnetic and can be used for MACS process by themselves, or once entrapped into a polymer matrix.

The shape of the magnetization curve of an assembly of superparamagnetic grains is well described by the Langevin formalism and the magnetic susceptibility can be related to the volume fraction of particle Φ and to the particles volume through:

$$\chi = \frac{\Phi M_s^2 \langle V^2 \rangle}{3 \langle V \rangle k_B T} \quad (1)$$

where M_s is the saturation magnetization of the materials, and V their volume.

The intensity of the magnetic moment of a particle μ , that is proportional to the specific magnetization of the material constituting the grain (M_s), and to the volume of this grain (V) ($\mu = M_s V$) is of the order of $\mu = 5.4 \times 10^{-20}$ A m² (which corresponds to about 6000 μ_B) for 7-nm diameter maghemite particles [32].

Properties of microparticles are in fact the properties of an assembly of nanoparticles. If these nanoparticles are superparamagnetic, application of a magnetic field will align their moments according to the Langevin formalism and the microparticles will get magnetized, with a resulting moment that is proportional to the number of encapsulated particles. The susceptibility of the material constituting the microparticles can be related to the volume fraction of particles through (Eq. 1).

The application of a magnetic field only orientates the magnetic moment of the particles. The application of a magnetic gradient is needed to apply a force. The magnetic F_m on a particle of volume V_p and susceptibility χ_p dispersed in a medium of susceptibility χ_m is given by $F_m = V_p \mu_0 M^* \nabla H$, where μ_0 is the permeability of air and M^* is the relative magnetization between the magnetic particles dispersed and the dispersion medium:

$$M^* = H_0 \frac{9(\chi_p - \chi_m)}{(3 + \chi_p)(3 + \chi_m)}$$

where H_0 is the applied magnetic field [33].

When the dispersion medium is a non-magnetic one, $M^* = H_0(\chi_p - \chi_m)$, and [34]:

$$F_m = V_p \mu_0 H_0 (\chi_p - \chi_m) \frac{dH}{dz}$$

Thus, effective ways of enhancing the magnetic force are: (i) increasing the susceptibility of the particles, (ii) increasing the gradient, (iii) using a high magnetic field. Particles size is also an important parameter, as the magnetic force is proportional to the particles volume.

The motion of particles is the result of the competition between the viscous force F_v , the magnetic force F_m , and the gravity F_g . Effective separation requires $F_m > F_g + F_v$. In the case of nanoscopic particles, that means particles submitted to Brownian motion, writing the continuity equation

$\frac{\partial c}{\partial t} + \nabla(\vec{J}_D + \vec{J}_m) = 0$, one arrives to:

$$\frac{\partial c}{\partial t} = \frac{1}{6\pi\eta r} [kT(\nabla^2 c) - \nabla(V_p \mu_0 (\chi_p - \chi_m) \nabla H c)]$$

It means that the difference between the susceptibility of particles and the one of the dispersing medium is again the driving parameter. This plays in the favor of microscopic particles but aggregated nanoscopic particles can also be good candidates for a quick separation.

4. Compared efficiency of nano and microparticles

As told in the introduction, the efficiency of the process is usually evaluated only as a whole through the measurement of the partition coefficient K_d , but this efficiency can be discussed in terms of four parameters.

4.1. The magnetic field gradient

The results reminded on part 2, indicating that the difference between the susceptibility of particles and the one of the dispersing medium is an important parameter, play in the favor of microscopic particles.

Indeed, nanoparticles have been poorly studied, even for HGMS processes. Nevertheless, as soon as they are agglomerated, low gradients are sufficient to separate them from a waste mixture [30]. It may be necessary to add agglomerating agents, especially in model solutions, but the magnetic field itself can enhance the aggregation of nanoparticles, especially in real waste mixtures that content many species that can act as flocculating agents. The ideal situation is the one for which the extraction of the metal species by itself induces precipitation, but it is difficult to quantify the gradient that is necessary for an efficient separation, because it is difficult to estimate the aggregates dimensions. Anyway, maghemite nanoparticles coated by dimercaptosuccinic acid, or by aminosilanes have been described as challengers of magnetic latex for cells sorting and immunoassays [35,36].

It is of course easier to separate microparticles, and it is as easier as the particles are more magnetic. Improvement of the process would be to increase the volume fraction of magnetic oxide in the microparticles, but this can lead to a decrease of the sorption capacity, as the latter is related to the non-magnetic material.

4.2. The sorption capacity and the particles size

The sorption capacity is first related to the specific surface of particles, which can be determined by nitrogen adsorption. This surface is directly related to the particle size for ‘hard’ particles, namely the nanometric particles. If a ligand is fixed on the particles surface to complex the metal, the efficiency will be related to the number of such ligands per particle.

In the case of polymeric particles, the relation to the size is less direct because the porosity of the coating becomes the key parameter. Indeed, the efficiency is related to the extractant absorption capacity, which is function of the particles volume and porosity, but also to the chemical nature of the polymer and its interaction with the extractant.

4.3. The partition coefficient

4.3.1. Case of the ferric oxide nanoparticles

It is established that magnetite particles, without any surface coating, have a high capacity of retention for Ba^{2+} and Eu^{3+} , and that a surface complexation theory, coupled to the diffuse-layer model, allows to fit the sorption experimental results [17]. Uranium(IV) adsorption can also be modeled by the same way [14]. So-called Hydrated Ferric Oxides (HFO) are also known to sorb heavy metals or arsenic oxyacids or oxyanions but it seems that it was difficult to use them in fixed-bed columns [37]. In such a separation process, specificity is only related to the difference of the sorption constant K . For example, in the case of Ba^{2+} and Eu^{3+} , the pK differ from 1.5 unit, indicating that selective separation of these cations will not be perfect. The pH is of course the key parameter, on one hand because it controls the surface charge density of particles, on the other hand, because the chemical nature of metallic cations also depends on the pH.

4.3.2. Case of the polymer microparticles

Even without extractant, magnetite particles dispersed in polymer microparticles can keep their own affinity for heavy metals [6].

The use of extractant in MACS involving CMPO/TBP system has proved a much better efficiency to remove transuranic elements (TRU) from nitric, hydrochloric acid solutions and various simulant waste solutions than the traditional separation pro-

cesses. Values of K_d , may range (for 0.88 μm particles) between 3000 and 5000 ml/g for Am and 50000–100000 ml/g for Pu according to the acidic medium [38].

The use of CYANEX 272 coated microparticles showed also good efficiency for Zn(II) over pH 4 and Cd(II) over pH 6. CYANEX 301 appeared to be less selective between transition metals at low pH, but very selective for heavy metals and alkaline earth [24].

Another important parameter, specific of these microparticles, is the location of the nanometric magnetic grains inside the microscopic ones. A better efficiency is obtained when nanoparticles are located in the core of the polymer core. Indeed, when they are located at the surface, they can obstruct the access of the extractant to the polymer core [8]. This cannot be controlled if microparticles are commercial products, and depends on the nature of the polymer, and on the size of the magnetite particles.

4.4. Durability of the magnetic carrier and reusability

An important parameter in the choice of a magnetic carrier for MACS process is the chemical stability of the carrier. Indeed, the medium from which metals have to be separated is often a strong acidic environment.

That is an important limitation in the case of the nanometric magnetite particles; indeed magnetite dissolves in strong acidic media, and the smaller are the particles, the faster is the dissolution. The particles surface has thus to be protected and it is not sure that a single layer of surfactant or of tri-block copolymer can be sufficient. Moreover, this decomposition accelerates when the temperature increases. In less concentrated acidic media, decomposition of magnetite leads to maghemite, that is also a magnetic oxide, but Fe(II) is released in the medium [15].

This decomposition of the magnetic particles can also occur in microscopic particles, especially if they are not confined in the polymer core. But strong alkaline or acidic media can also alter the later or alter the interaction between the magnetic particles and the matrix.

In the case of the extraction of radionuclides, the resistance of the coatings and magnetic cores to radiolytic damage has also to be considered. The radiolytic stability of the microparticles particle was checked by

using ^{60}Co gamma irradiation, and evaluating their effectiveness in removing TRU elements from 2 M HNO_3 solutions. It appeared that hydrolysis played a larger role than radiolysis in the degradation of the extraction capacity of the particles [4,39].

Another important point is the possibility to reuse the magnetic particles for new cycles of separation. The use of magnetite particles without any coating allows this using pH modification if the latter modifies the values of the adsorption constants. When the particles are coated by ligands able to complex the metal ions, the ligands have to be designed in order to allow reversibility of the complexation. Concerning impregnated microparticles, as soon as it is established that the magnetic content stays encapsulated, the reuse of particles can be achieved by desorption of the extractant. A good knowledge of the interaction polymer-extractant and of the way to modify it can improve the process.

5. Conclusion

Although microparticles have been extensively studied for metal extraction, little experiments have been carried out using nanoparticles. Even if the latter seem to have a higher specific surface because of their small diameter, the latter has to be compared to the porosity of polymer microparticles.

Microscopic particles evidently possess many advantages related to their easy separation. Many improvements can be imagined, parallel, of course, to the increase of the magnetic oxide volume fraction, especially in order to propose specific extraction of a given metal from a mixture. The regeneration of the magnetic carrier is poorly described and is a relevant problem.

Nanoparticles have the advantage to avoid a ‘dilution’ of the magnetism, but the separation is possible only if particles aggregate during extraction. An advantage of nanoparticles is their possibility to stay dispersed as individual grains in a process; but it needs to ensure at the same time complexation and colloidal stability in the medium of extraction. This possibility is a defect for separation, but we have seen that this defect can be turned adding a flocculating agent, and that particles can spontaneously precipitate in the magnetic field gradient if they are poorly stabilized [40]. Phase behavior of dispersions of magnetic nanoparticles is now well

known and allows to predict the conditions for agglomeration of particles in aqueous or organic medium [41], but such a prediction needs a good knowledge of the waste mixture. This possibility to stay dispersed can be an advantage if the process needs fluids circulation because such dispersions of nanoparticles behave almost as Newtonian solutions contrary to dispersions. Some ways of improving the process could be found in this direction.

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