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Short Communication

Reusable superparamagnetic nanocomposite particles for magnetic separation of iron hydroxide precipitates to remove and recover heavy metal ions from aqueous solutions

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ABSTRACT

Superparamagnetic nanocomposite microparticles act as seeds for iron hydroxide precipitates. Flocculation of iron hydroxide is applied to adsorb and entrap heavy metal ions dissolved in water. The flocculation product gets deposited on the surface of the nanocomposite microparticles. Due to the nanoproperty superparamagnetism the particles are switchable magnets and can be separated together with their load from water by an external magnetic field gradient. In an acidic solution, particles are cleaned by dissolution of the iron hydroxide precipitate. A silica surface protects the superparamagnetic microparticles from dissolution rendering their reuse as seeds and magnetic carriers possible. Repetition of the separation and recovery process leads to a significant increase of concentration of heavy metals in the acid cleaning solution, which paves the way for further recycling procedures of these elements.

1. Introduction

Heavy metal ions e.g. from Cd, Cr, Cu, Pb, Zn, As or Hg, originating from natural geological or industrial sources are hazardous pollutions in water [1]. The water has to be purified from these contaminants before being used as drinking water or further being discharged. But, heavy metals may also be valuable elements for industrial applications. It is therefore highly desirable to find processes that not just remove, but also recover dissolved heavy metals. Ideally, polluted water is cleaned from highly diluted heavy metal ions and these ions are regained in a concentrated form, allowing their recycling for instance via electrowinning [2].

A well known process to remove heavy metals ions is the addition of Fe or Al salts. Flocculation and precipitation of Fe or Al hydroxide colloids leads to adsorption and coprecipitation of other dissolved ions [3,4]. Unfortunately, the flocs are voluminous and mechanically unstable [4]. Therefore they have to be separated by a slow sedimentation generating a still very voluminous sludge which has to be dried or filtered and eventually deposed as toxic waste [5]. Incineration of the sludge at elevated temperatures might be harmful due to potential formation of heavy metal chloride gases. A much more preferable way of recycling heavy metals was recently demonstrated. A filtered and concentrated heavy metal hydroxide sludge was redissolved through acid treatment and the recycling of the heavy metals was achieved by electrowinning [2]. However, separation by filtration is still a tedious and impractical process step. Magnetic separation could be a fast and easily performable alternative.

Some magnetic separation techniques for heavy metal ion removal have been published before [5–13]. A sophisticated and energy intensive method is the in-situ crystallisation of magnetic particles in waste water, the so-called ferrite process [6–8]. Typically, Fe(II) salt is added and the water temperature risen to about 60 °C. Subsequently, Fe(II) is oxidised by air bubbling and consequently magnetite (Fe_3O_4) is precipitated together with incorporated heavy metal ions. The magnetite (ferrite) crystals can be magnetically separated. Eventually, a waste product has to be deposited.

Another way is the use of magnetic ion-exchange particles, e.g. in the *Sirofloc* [5] or *Miex* [9] process. The complex interactions of the ion-exchanger with the aqueous environment afford a precise adjustment of the process to the specific conditions of the respective targeted purpose.

A direct magnetic separation of precipitated hydroxide flocs seems to be more preferable. As iron hydroxide flocs are only weakly magnetic, precipitation is performed in presence of (usually micron sized) magnetite seed particles [6,10–14]. Seed-grown

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flocs can be separated magnetically. Magnetite microparticles typically possess a remanent magnetisation, i.e. once separated, they might hardly detach from the separator and remain magnetically agglomerated [5]. Redissolution of the hydroxide precipitate in an acid, without dissolving the magnetite particles, might also be difficult to perform, so that the separated product would be rather deposited with the magnetite added to the amount of waste. A recovery of the heavy metals and a reuse of magnetic seed particles would therefore be much more beneficial.

In this work, superparamagnetic nanocomposites, i.e. micron-sized silica particles containing nano-magnetite, were used as magnetic seeds. The nano-property superparamagnetism equips the particles with a magnetic switchability. They are magnetically responding to an external magnetic field and can be extracted via magnetic separation from water, but as soon as the external field is removed, the particles magnetisation is switched off and they behave like any other suspended matter. Exploiting the acid stability of the particles, a process was developed to enrich heavy metals, originally highly diluted in water, via magnetic seeding-flocculation and recovery in an acid solution. Following this strategy, a reusability of the magnetic particles is achievable. Water cleaning is possible and the concentration of heavy metals in acid might pave the way to apply a recently published method to electrowinning and thus recycle the metals from this acid solution for further use [2].

2. Experimental procedures

2.1. Chemicals

H_3AsO_4, $Cd(NO_3)_2{\cdot}4H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Hg(NO_3)_2{\cdot}H_2O$, $Pb(NO_3)_2$, $CrCl_3{\cdot}6H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$, $FeCl_3{\cdot}6H_2O$, sodium hydroxide (NaOH, 1 M) and hydrochloric acid (HCl, 1 M) were purchased from Sigma-Aldrich in high purity grade.

2.2. Synthesis of superparamagnetic nanocomposite microparticles

The synthesis and characterisation of superparamagnetic nanocomposite microparticles was recently published [15]. The composite particles consist of superparamagnetic magnetite nanoparticles (8–10 nm) in a silica matrix. Composite particle sizes are several tens of μm.

2.3. Removal and recovery of metal ions

Heavy metals and Mg(II) and Ca(II) ions were dissolved in 1 l deionised water to yield concentrations of approximately 1 mg/l, respectively 100 mg/l for each element. To avoid premature precipitations, the pH was adjusted to 4 by hydrochloric acid. Exact concentrations were analysed by inductive coupled plasma optical emission spectroscopy (ICP-OES).

The flocculation solution was prepared by dissolving 500 mg $FeCl_3{\cdot}6H_2O$ and 200 mg $CaCl_2$ in 100 ml deionised water. The addition of Ca was necessary to promote flocculation.

One milliliter of the flocculation solution and 100 mg of superparamagnetic nanocomposite microparticles were added to 100 ml of the heavy metal ion solution under stirring. The pH was raised to 7.5–8 by addition of NaOH (e.g. 0.2 ml 1 M NaOH). After stirring the solution at 300 rpm for 1–5 min, the precipitate was separated with a handheld magnet (Supermagnet Q404020N, energy product: 42 kJ/m^3, supermagnete.de). Concentrations of ions in the remaining solution were analysed by ICP-OES. It should be pointed out, that it was deliberately avoided to carry out any filtering operations (e.g. with a membrane filter as it is often done in a standard ICP-OES analysis routine) of the solutions before analysis, to guarantee that the purification of the water is only achieved due the magnetic separation process. The separated particles were suspended in 10 ml 0.1 M HCl and stirred for 10 min. The acid-treated particles were magnetically separated again, washed once with deionised water and used as seeds for the following precipitation. All experiments were performed at room temperature (20 °C).

2.4. Analyses

Scanning electron microscopy (SEM) was carried out with a Zeiss Supra25 SEM at 3 keV. Energy dispersive X-ray analyses (EDX) were done at 15 keV (Supra 25) at a working distance of 8 mm. Zeta potentials were measured on a Malvern Instruments Zeta Sizer Nano. Concentrations of metal ions were analysed via inductive coupled plasma optical emission spectroscopy (ICP-OES) using a Varian Vista-Pro CCD.

3. Results and discussion

Superparamagnetic magnetite nanoparticles [16,17], enclosed in a silica matrix (amorphous SiO_2) to form micron-sized composite particles [15], are used as seed particles and magnetic carriers for iron hydroxide flocs. Due to their superparamagnetic properties, the microparticles are switchable magnets. At first, they can easily be dispersed like any non-magnetic particulate matter in water. However, they turn into magnetic particles if exposed to an external magnetic field. Due to their size (1–50 μm) easy magnetic separation is possible even without high magnetic gradients [15].

The composite microparticles are negatively charged due to their silica surface over a wide range of pH. Precipitated iron hydroxide flocs possess a positive zeta potential from pH 2 to around 7.5. Thus, electrostatic attraction may contribute to hydroxide precipitation on the silica surface (Fig. 1).

Flocculation of added (dissolved) iron salt in a heavy metal containing solution (mixture of Cd, Cr, Cu, Pb, Zn, As, Hg) in presence of suspended superparamagnetic composite particles, by raising the pH of the solution from 4 to approximately 8, yields a completely magnetically separable product after 1–5 min (Fig. 2). A visibly clear aqueous solution remains (Fig. 2). Without the magnetic particles the flocculated precipitate cannot be separated magnetically.

The magnetically separated product is treated in a small volume of hydrochloric acid to dissolve iron hydroxide and coprecipitated heavy metal ions. Cleaned magnetic composite particles are again magnetically separated and then reused in the next precipitation step (Fig. 3).

It should be mentioned that before reusing the particles as seeds again, an additional washing step (with a very small amount of deionised water) is applied to avoid any carryover of the acidic heavy metal solution into the water that shall be purified. This

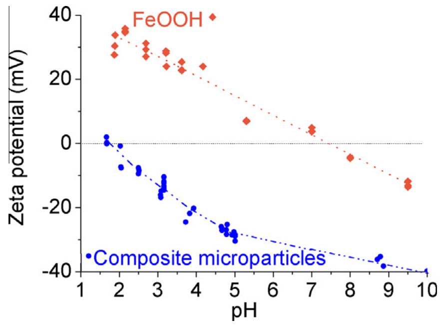

Fig. 1. pH dependence of zeta potentials of magnetic seed particles (composite microparticles) and precipitated iron hydroxide.

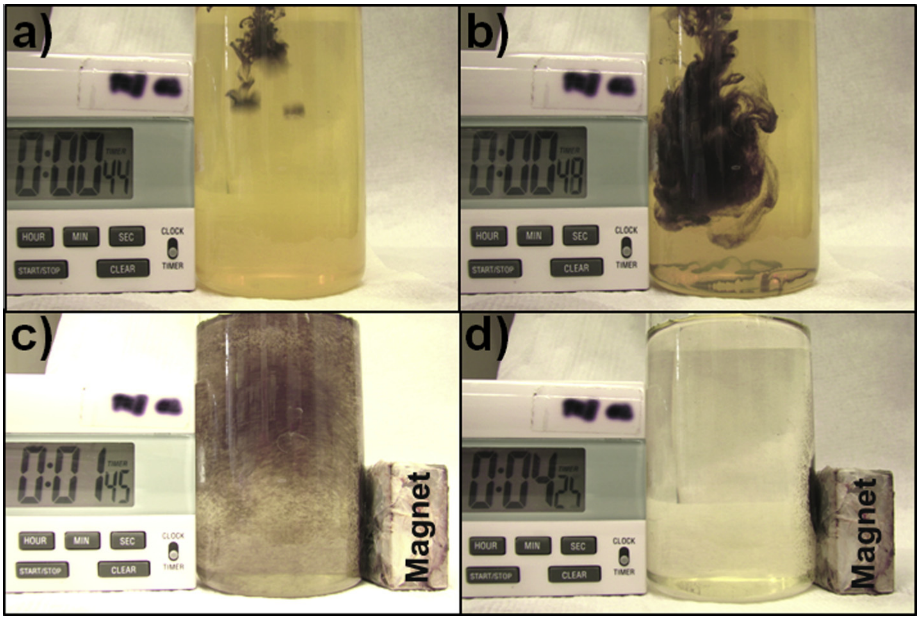

Fig. 2. (a and b): Addition of Fe(III) salt solution and magnetic composite particles to a heavy metal ion solution, (c and d): magnetic separation of precipitate after pH increase to 8.

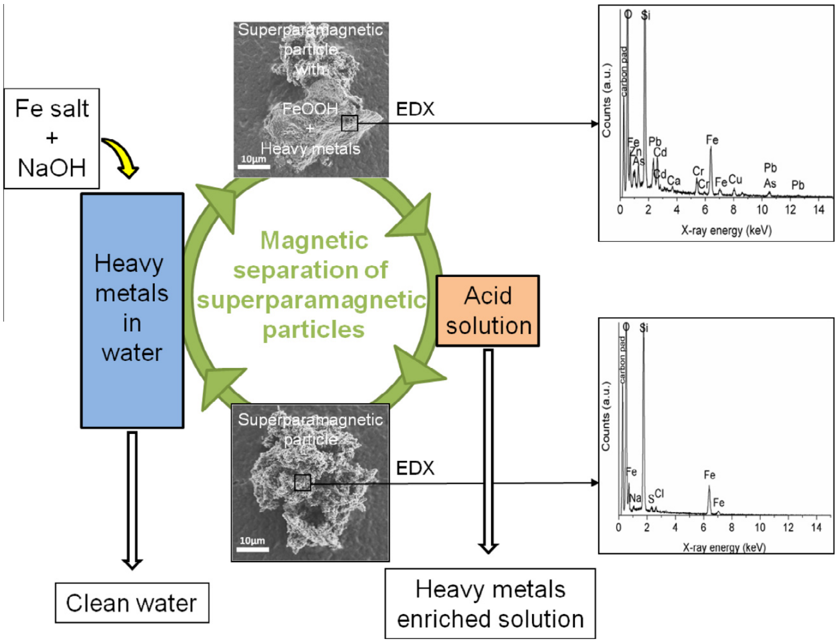

Fig. 3. Scheme for removal and recovery of heavy metal ions from an aqueous solution (SEM images and EDX analyses show the precipitate of iron hydroxide and heavy metal ions on a magnetic composite particle and their absence after acid treatment).

might be critical in a technical (large scale) process: Adding the acidic heavy metal containing wash water to the recovery solution will lead to dilution; discharging it into the water, that is meant to be purified, will lead to acidification of this water and a circulation of metal ions. The latter also holds if the washing step is completely skipped. However, process solutions might be found to minimise this problem.

Fig. 3 also shows two scanning electron microscopy (SEM) images of individual superparamagnetic nanocomposite microparticles. In the top image the particle is covered with the flocculated iron hydroxide containing heavy metals. Energy dispersive X-ray analyses (EDX) of the flocculated product on the particle confirms its heavy metal load (inset Fig. 3). The bottom SEM image depicts a magnetic particle after acid treatment where the heavy metals were successfully removed (EDX inset).

Remaining concentrations (given in percent of starting concentrations, equal to approximately 1 mg/l for each ion) of heavy metal ions after precipitation and magnetic separation are shown in Fig. 4a for three water cleaning cycles with the same magnetic particles. With the exception of Hg, more than 95% (often more than 99%) of the heavy metals could be removed. Remaining concentrations are below 10 ppb.

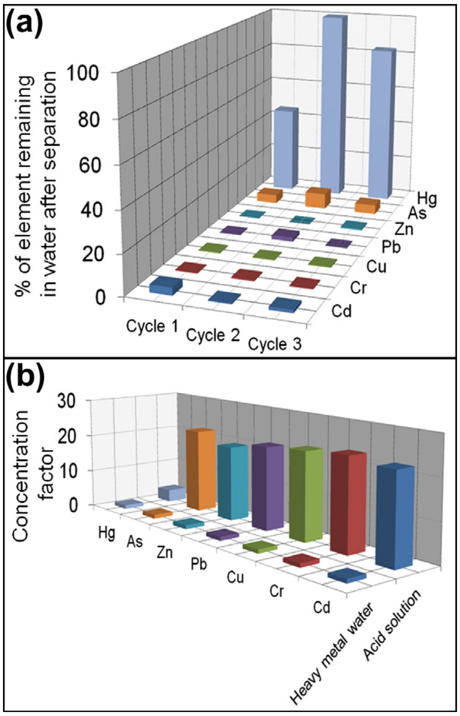

Fig. 4. (a) Percentage of remaining ion concentrations after three precipitation/separation cycles with the same magnetic composite particles. (b) Factors of concentration-increase in the cleaning acid after three recovery steps.

The difficulties to remove Hg might be related to a prevailing polyhydroxy complex for this element. Such complexes are known to hardly precipitate with the ferric floc [18].

Very similar results were observed for starting concentrations of 100 mg/l for each kind of ion and with the same dosed amount of Fe(III) salt solution and magnetic composite particles, indicating the good precipitation and separation capacity. The remaining concentration of Fe ions in water after magnetic separation was typically 0.04 mg/l in all cases.

It is worth noting that when magnetic particles are modified with precipitated iron hydroxide *before* being added to the heavy metal solution, the removal of the heavy metal ions (after 10 min) was considerably less effective. The same holds for adsorption on the nanocomposite particles (without any iron hydroxide) [15]. Furthermore, only less than 20% of heavy metal ions could be removed by the nanocomposite particles, if the pH of the water, after addition of the iron salt solution, was too low for the setting in of flocculation of iron hydroxides. Therefore, it seems that it is the *incorporation/coprecipitation* of heavy metals during the in-situ flocculation of iron hydroxide that leads to scavenging of heavy metals rather than any surface adsorption processes.

After each of the three precipitation/separation steps, the magnetic composite particles were recovered in a small volume (10 ml) of hydrochloric acid. The acid dissolved the precipitates from the surface of the composite particles, but not the particles themselves due to their acid resistant silica surface [15]. Using the same acid solution over and over again, it was possible to concentrate the heavy metals in this small amount of solution. Ion concentrations in the acid were determined exemplarily after the third cleaning step. The factors of concentration increase for each kind of metal ion are given in Fig. 4b (for comparison, the heavy metal concentration in water, set to 1, is also shown). Concentrations increase typically by factors of 20 to 23 after only three cycles, indicating the impressive potential of the process to concentrate formerly highly diluted heavy metals. Unavoidably, Fe ions are enriched in the cleaning solution up to 250 mg/l as well. A separation of the different heavy metals from the iron content in the cleaning solution might be possible by electrowinning, as recently published [2]. After such treatment, a reuse of the iron enriched, and heavy metal depleted, recovery solution as flocculant could be considered.

4. Conclusion

Superparamagnetic nanocomposite microparticles with a silica surface act as seed particles and carriers for iron hydroxide precipitation in aqueous solution, e.g. in heavy metal contaminated water. The precipitate is separable in a magnetic field gradient. Microparticles can be cleaned in acid and redispersed in new contaminated water to again act as seeds for the next precipitation step. Due to the superparamagnetic properties, dispersion is easily possible without facing the problem of magnetic agglomeration. In the acid used to recover the particles, iron ions and co-precipitated heavy metal ions are enriched through the repeated recovery steps, which paves the way for achieving concentrations that allow a recovery for instance by electrowinning.

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