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TITLE:	**SUPERPARAMAGNETIC COMPOSITE PARTICLES WITH SPECIFIC SURFACE MODIFICATIONS FOR THE CONTINUOUS SEPARATION OF HEAVY METAL IONS FROM WATER (PARAMAGSEP)**	
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Summary

Superparamagnetic composite particles (SPMC) are particles in a µm- or sub µm-range with embedded iron oxide nanoparticles. These composite particles are magnetised under the influence of a magnetic field, but lose their magnetisation when the magnetic field is switched off.

The objective of the PARAMAGSEP-project was to develop a new continuous flow magnetic separation technology for the cleaning of waste water using surface modified SPMC in order to remove hazardous heavy metal ions from waste water.

The general approach for the material and process development was the use of wet chemical routes for the synthesis and processing of nm-scaled particles and stabilised suspensions of iron oxide particles. These magnetic particles could then be transferred into composite particles by enclosure in a silica matrix. The following surface modification with metal ion-complexing agents led to a re-suspendable material which was able to act as a magnetic separation material with a variable selectivity and capacity for hazardous heavy metal ions in waste water. The selectivity and capacity of the obtained superparamagnetic composite particles still have potential for further development.

After complexation and separation of the ion-loaded SPMC, the complex could be loosened by a change in pH or in ionic environment. By this route, a separation of heavy metal ions from waste water could be shown. The separated heavy metal ions could be either disposed in a highly concentrated form or they ccould be recovered by different state-of-the-art-techniques (e.g. electrodeposition).

The project ended up in a bench-scale demonstrator unit with complexation, separation, decomplexation and recovering or recycling of raw materials.

The results of the project will be used by HIMTECH, IET, ARCON MINES Limited and Carlow Radiators Ltd. to improve the effectiveness of their own waste treatment procedure and to improve the environmental aspects of this technology by recycling or recovering of raw materials.

The Consortium

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Profiles of the individual partners

Coordinator: INM – Institut für Neue Materialien gem. GmbH (GERMANY)

INM is a research centre founded in 1987, employing about 200 people. Its head, Prof. Dr. H. Schmidt, has more than 25 years experience in inorganic and inorganic-organic composite science and technology, especially with regard to application. In the past 13 years, new synthesis and processing routes for nanoparticles in powders and suspensions have been developed, comprising functional coatings on particles. One of INM's main focuses is the technological development downstream to the industrial user community. As a result, over 100 industrial projects are carried out at present. Special emphasis is put on efficient wet chemical preparation and processing techniques. The research centre provides chemical synthesis of sol-gel materials including scaling up in a pilot plant, as well as characterisation (mechanical, optical, structure, reactions), clean room techniques, coating and separating techniques, and basic characterisation of fine particle morphology and properties. The institute carries out fundamental developments and contract research with industry up to the development of key-turn technologies. INM is involved in several EU projects as well as various major national BMBF industrial projects.

C-Tech Ltd (Great Britain)

In spring 2001 the former Process Innovation Division of EA Technology (which was involved in PARAMAGSEP from the beginning) became Capenhurst.tech Ltd., first as a wholly owned subsidary of EA Technology, later as a completely independent company. Shortly after the termination of the project, the company changed its name into C-Tech Ltd.

The parent company was established in 1966 and named EA Technology in 1991. It is a privately owned industrial company designated as an SME.

EA Technology has established world recognition in providing extensive RTD services to Energy Utilities, and developing products and processes for the industrial, commercial and domestic markets. The company now provides industrial services, computer and manufacturing facilities. EA Technology licenses products and processes both in the UK and overseas. Joint venture companies have also been established to exploit particular technologies and products.

Over 1500 patents have been taken out since 1966, and currently over 350 of these are active, covering a broad spectrum of technologies. A wide range of industrial developments have been demonstrated to show higher productivity, increased competitiveness, improved product quality and better environmental performance. The company employs 240 staff of whom 90 are senior scientists, it has extensive well equiped laboratories and other industrial facilities for work in developing new products and processes for industry, commerce and the home.

HIMTECH - Hessische Industriemüll Technologie GmbH (Germany)

HIMTECH as an environmental engineering services company supports authorities, investor groups and operating companies with the up-to-date know-how and experience in the field of industrial and hazardous waste, especially in minimisation, waste management, plant engineering and operation, site remediation, depositories and personnel training. More than 35 employees, comprising all engineering disciplines, are available to meet the customers' requirements.

HIMTECH's services are based on 25 years of waste management experience of its mother company, the HIM Hessische Industriemüll GmbH. Since 1978 HIM is exclusively responsible on behalf of the State of Hesse for management, treatment and disposal of hazardous waste. HIM's operating experience includes chemical-physical treatment of liquid waste (e. g. separation of heavy metals from waste water), hazardous waste incineration and emulsion separation as well as laboratories, collection stations, intermediate storage sites and landfills.

All chemical–physical treatment facilities, which include thermal and chemical emulsion separation of organic waste and chemical treatment of inorganic waste (e. g. separation of heavy metals) are designed, built and operated by HIM itself. Since its foundation HIMTECH is responsible for the complete engineering work at these treatment facilities. Additionally HIMTECH has performed projects regarding chemical-physical treatment technology in different countries, e.g. Austria, Spain and Turkey. Due to these projects and its own and HIM's experience HIMTECH has the necessary technical and market knowledge available regarding heavy metal-containing waste water.

Inter Euro Technology (Ireland)

IET was founded in 1989 to provide a technical and scientific engineering and planning in the areas of electrochemistry, electroplating, chemical and oil processing. To date, it has concentrated on providing a service to Irish Industry in the areas of waste treatment and metals recovery, including commercial and industrial applications of electrochemistry. It also has a major role in the introduction of new marker systems in Ireland for rebated gasoil in 1989 and for kerosene. It is currently assisting in an EC study on marker systems for Europe.

Carlow Radiators Ltd (Ireland)

Carlow Radiators Ltd is a light engineering company established in 1979. It is situated on a large well-serviced site with extensive workshop facilities and with experienced and well-qualified metalworking and engineering staff.

They manufacture heat exchange units and specialise in the repair and supply of tanks and radiators for motor vehicles and in the repair of industrial heat exchange units. They have carried out development work on production of metal fluxes and metal recovery systems and have developed and integrated process for metal recovery by cementation using scrap materials.

They are now expanding into chrome plating by taking over a plating plant where the owner is retiring. This will be relocated in Carlow. This will be very useful as a working plant where innovative or improved water treatment systems can be introduced on a trial basis.

Arcon Mines Ltd. (Ireland)

Arcon Mines is a mining company mainly active in Ireland. Since 1981, Arcon Mines had been carrying out exploration activities on Prospecting Licence Area 586. In 1989, Arcon

Mines started to prepare the Galmoy Mine for the production of zinc. In February 1995, the final licence required by Arcon Mines was issued by the Department of Transport, Energy and Communications and construction started on site in June 1995. The underground mine was brought into production in December 1996 and development completed in March 1997. The surface facilities were gradually brought on-line 1995 and 1996, culminating in the commissioning period in Jan. and Feb. 1997 and the commencement of concentrate production in March 1997.

The planning application included a comprehensive Environmental Impact Statement. The development of environmental protection thinking and legislation in recent years is evident in Arcon Mines ´s planning conditions. Because Galmoy Mine is equiped with state of the art waste treatment technologies, it is the most modern and environmentally friendly in Europe as a result.

Nevertheless Arcon Mines is interested in new developments for waste treatment with respect to effectivity and costs. Mainly an integration of waste treatment into production with a recycling of metals and water would be a big progress.

Scientific and Technical Performance

Objectives

Various toxic metal ions occur in many industrial processes. The different established separation techniques have several disadvantages: They produce large quantities of metal-containing sludge, have a low selectivity and a simple integration of the separation step into the process is not possible with respect to recycling. There is further need for an integrated closed-loop process for the recycling of water with reduced final waste. Such an advanced separation technique should allow the recycling and reuse of water and valuable metals.
The objective of the PARAMAGSEP-project was the separation of heavy metal ions such as Hg, Pb, Zn, Cd, Cr, Ni and Cu from waste water samples in order to reach national and European drinking water standards. Priorities were the development of an integrated closed-loop technology for the cleaning of metal-containing waste water, allowing recycling and reuse of the water in the industrial process. The project involved the development of a advanced separation technology with superparamagnetic composite particles. The magnetic separation developed also allows the recovery and reuse of metals of sufficient value. Final waste can be reduced to an absolute minimum, as there is no sludge resulting from usual sedimentation process.

Technical Approach

In order to form stable suspensions of the particles in the polluted water, small particles in the micrometer range have to be used. But magnetic particles in the micrometer range exhibit magnetic remanence, i.e. after a first exposure to an external magnetic field they remain magnetised. This results in agglomeration of the small particles to much bigger agglomerates which have a smaller surface area for adsorption and a much stronger trend for settlement, and can therefore not be resuspended in a solution in order to be reused.
So for this application particles had to be used, which can be magnetised by an external field, but loose their magnetisation once the field is switched off. Such particles can be created using a phenomenon called superparamagnetism (SP). SP occurs in ferro- or ferri-magnetic particles of a size so small that the magnetisation of the (typically single magnetic domain) particle can be changed by thermal fluctuations. Maghemite particles with diameters below 30 nm show superparamagnetic behaviour.
On the other hand, single superparamagnetic iron oxide particles (< 30 nm) were not suitable for the use in magnetic separation methods. They require very high magnetic field strengths and gradients in order to be separated from the solutions, because the magnetic forces acting upon them are very small due to the small particle size. Therefore it was nescessary

to incorporate a large amount of superparamagnetic nanoparticles (magnetic cores) into one composite particle by embedding them in a non magnetic matrix material. Such composite particles can be separated in magnetic fields of lower strength, and they do not aggregate irreversibly as the individual magnetic moments of the different cores can not couple to form an resulting remanent magnetic field. Finally, the surface of the superparamagnetic composite particles was modified with suitable complexing agents for binding the different heavy metalions in the waste water.

Synthesis of composite particles

A first step in the preparation of the composite particles was the synthesis of the superparamagnetic cores. This was done using a controlled precipitation method from aequeous solutions of iron salt precursors, and resulted in stable suspensions of iron oxide (maghemite) nanoparticles in water. The superparamagnetic nanoparticles were between 10 and 20 nm in diameter and had specific saturation magnetisations of typically more than 60 EMU / g.

In a second step, such suspensions of nanoparticles were then used as an ingredient for sols that were spray-dried to produce small particles in the size range around 2 µm. The particles consisted of the nanoparticles dispersed in a silicate based xerogel matrix. By a thermal treatment the xerogel could be densified to form a glass-like matrix showing not only good stability against chemical attack itself, but also protecting the embedded nanoparticles. The resulting iron oxide – glass composite particles had typical saturation magnetisations around 20 EMU / g.

The final particles were obtained in a third step consisting of a surface modification with ligands able to form stable complexes with some or all of the ions of interest. The ligands were usual chelating compounds such as diketones, amidoximes, thioamines, quinoline, organic poly acids or malonesters, modified with silane groups in order to allow for covalent bonding to silicate surfaces. Most of these compounds had to be synthesized during the project.

Lab-scale extraction experiments

The selection of the industrial effluent streams was executed based on the experiences of the project partners. Mine waters were obtained from ARCON MINES with significant concentrations of Zn and Pb. Also selected were waste water streams from the galvanic, the printing and the chemical industry, containing as other relevant ions Ag, Cu, Cd, Cr^{III}, Ni, Pd, Hg, Fe and Co.

Lab scale screening experiments were performed to determine the complexing capacity of the particles with various ligands against those ions. This was done by measuring the decrease of the concentration of the ion of interest, when a solution containing initially

50 ppm of that ion was treated with a small amount of particles. The separated particles were then treated with nitric acid in order to release the ions collected before.

In these screening experiments capacities (expressed as milligrams of heavy metal ions per gram of particles) ranging from 7 mg/g (Co, Ni) up to over 93 mg/g (Pb) could be found for optimized ligands. Recovery ratios were above 80 % for all ions and could be optimized in some cases by using different eluents.

In further lab scale experiments it was shown that a high recovery rate can be achieved even if the quantity of eluent is much less than that of the original solution. This leads to a significant increase of the metal ion concentration. A factor of 25 was demonstrated using a 15.6 ppm Zn solution.

Experiments on recycling capability were also performed. It could be shown that several cycles of complexation, magnetic separation and decomplexation could be executed, although with every cycle the capacity of the particles was reduced by a few percent.

Bench-scale separation setup

After the development of the particles, the next step was to demonstrate the magnetic separation concept on bench scale. For this a rig was set up allowing for the treatment of batches of 10 litres of water at a time. For a continuous separation process, at least two such units would have to be operated in parallel.

The central components of the rig were a holding vessel, where the complexation and decomplexation reactions could take place, and, connected to this, an electromagnetic separator, through which the contents of the holding vessel could be circulated. Additional tanks were for the raw and the treated waste, as well as for the acid used for the decomplexation. The rig was mounted on wheels, with overall dimensions of 2200 mm (length) x 700 mm (width) x 1700 mm (heigth), such that it would fit trough a standard doorway.

Bench-scale operation

The bench scale rig was tested by the partners Arcon Mines, Carlow Radiators and HIMTECH with their respective waste streams. Mixed results were obtained.

As far as the complexation step was concerned, rather satisfactory results were obtained by Arcon Mines and Carlow Radiators, as laboratory results could be confirmed in principle. In the experiments performed by Arcon Mines, it could be shown that even very low concentrations of Zn in the range of 100 ppb could be significantly reduced with removal ratios over 60 %. However, the regeneration of the particles was only partly successful, as the removal ratios with regenerated particles were much lower.

HIMTECH performed tests with a waste stream from galvanic industry containing several different transition metal ions. The results were rather disappointing, showing that there was hardly any removal of metal ions. Instead, the particles seemed to be attacked by some ingredient of that waste stream. This result, which was not analysed in detail, indicates that the PARAMAGSEP process, requires a well-defined waste stream rather than being suitable for general waste treatment.

During the operation of the rig, some difficulties were found, mainly associated with particles sticking to some parts of the pipes and with incomplete release of the particles from the separator. It was also found that not all the particles could be separated from the fluid in a single pass. However, such problems can solved by further development.

Economic aspects

Based on the data obtained by the lab-scale experiments an economic assessment was executed. The costs for existing ways of disposal recovery in public facilities based on chemical-physical treatment (neutralisation, oxidation/reduction, precipitation, filtration) were investigated. The costs were ranging from 50 to 250 €, depending on the heavy metal content and the general composition of the waste. Efforts for transportation of the waste to the facilities were not included in these costs. The typical annual throughput of a public chemical - physical treatment facility amounts to 3.000 - 50.000 tons. Other treatment techniques for more special case are electrochemical treatment, removal of metals by ionexchange or solid state extraction or the recovery of metal by the metal industry (i.e. mainly the addition of wastes with high metal content to ores for melting).

The costs for the treatment of heavy metal containing waste water with the PARAMAGSEP-technology will have to compete with these existing state-of-the-art technologies.

The main advantages for PARAMAGSEP were found in the following areas:

- the potential for the metal recovery leading to a economical benefit by the recovered metals,
- the selectivity towards a certain metal in a well defined mixture of metal ions,
- the possibility to treat waste streams with only very small concentration of metal ions.

Based on these considerations the furture end user partners in the project came to the conclusion that PARAMAGSEP is a technology with an exciting potential for the recovery of very rare or very toxic metals in low to medium concentrations from special waste streams.

Based on reasonable assumptions for parameters influencing the cost of using the PARAMAGSEP-technology, such as

- cost for the particles
- recovery rate of the particles within the process

- number of cycles to be processed with the particles
- capacity of the system ⇒ size of the reactors
- beside general aspects like:
- investment costs
- operational costs (personal energy, media etc.)
- operation time
- infrastructural aspects
- licensing aspects

we estimate the cost to be in the range of 100 - 250 € per ton. Thus the PARAMAGSEP-technology does indeed have the potential of competing with other techniques in some cases.

Conclusions

The work done in the course of the PARAMAGSEP project demonstrated the principle that metal ions could be taken out of dilute solutions by complexes on magnetic particles and then released into a more concentrated solutions by changing the acidity or ionic environment. Whereas lab scale trials produced very promising results, the bench scale trials revealed that some more development is required before the PARAMAGSEP process is ready for practical application. Some of the trials were cut short as the magnetic particles failed to regenerate properly after repeated cycles.

Specifically the work with the bench scale unit showed that it is relatively easy to collect most of the superparamagnetic particles in a magnetic separator. More work is required to ensure effective release.

Exploitation and follow-up actions

The members of the PARAMAGSEP consortium agreed that the PARAMAGSEP process proved many of the high expectations which were set into it by the start of the project.
Regarding its very innovative nature, the results obtained were more than satisfactory. Not too surprisingly, some problems became apparent during the projects term, but solutions to all of them seem feasible. Thus, although the PARAMAGSEP process is at this moment not in a state which would permit to install a industrial size treatment plant, the results obtained clearly justify further efforts to reach this state.
All consortium members confirmed their willingness to collaborate further in order to achieve this goal.
The most suitable strategy seems to be an effort concentrating on applications where the PARAMAGSEP process offers clear economic advantages over existing technologies. This seems to be the case especially where metal ions have to be removed from very dilute solutions, which is interesting either for either very valuable or highly toxic metals.
Once the process could be established for such applications, an adaptation to more general waste water treatment would seem much easier.

A possible next step would thus be a follow-up project based on the results of PARAMAGSEP with the general direction of the optimization and industrial application of the technology developed especially for the separation of very precious or very toxic metal ions from dilute waste water streams.