Curriculum Vitae

Melanie John-Stadler

Ludwig-Maximilians-Universität
Department of Earth and Environmental Sciences
Theresienstr. 41, D-80333 Munich
Phone: +49 (0)89 2180 4276
E-Mail: melanie.john@min.uni-muenchen.de

Born June 11, 1987
Married
German citizenship

Current position:

since 07/2014	Post Doc position in the ForCycle project for wastewater treatment at the Department for Earth and Environmental Sciences, LMU München, Germany

Previous positions:

01/2014 – 06/2016	Doctoral Candidate in the ForCycle project for wastewater treatment headed by Prof. Dr. Soraya Heuss-Aßbichler at the Department for Earth and Environmental Sciences, LMU München, Germany
03/2015 – 03/2016	Supervision of the AAS and ICP-OES Lab
01/2013 – 12/2013	Research assistant at the Department for Earth and Environmental Sciences, LMU München, Germany in the R^3-project for the recovery of heavy metals from MVA residues and filter dust
02/2012 – 10/2012	Student assistant at the Mineralogical State Collection, Munich, Germany
11/2008 – 01/2010	Bene Arzneimittel GmbH, Munich, Germany. Regulatory affairs and laboratory work

Education:

03/2014 – 6/2016	Ph.D. Thesis at the LMU München, Germany “Low temperature synthesis of nano crystalline zero-valent phases and (doped) metal oxides as $A_xB_{3-x}O_4$ (ferrite), ABO_2 (delafossite), A_2O and AO. A new process to treat industrial wastewaters?” (Grade: summa cum laude) Supervised by: Prof. Dr. Soraya Heuss-Aßbilchler
10/2012 – 02/2014	Master Geomaterials and Geochemistry (Grade: 1.3) at the LMU München and the Münchner Geozentrum, Germany Master-Thesis: “Hydrothermal solubility of heavy metals from MVA residues” (Grade: 1.0) Supervised by: Prof. Dr. Thomas Fehr (†)
10/2009 – 07/2012	Bachelor Geosciences, focus: Mineralogy (1.9) at the TU and LMU München, Germany Bachelor-Thesis: “Petrological investigations of the ophiolite complex in Hatay” Supervised by: Prof. Dr. Guntram Jordan and Dr. Melanie Kaliwoda
10/2008 – 07/2009	Bachelor Bioprocess technique at the TU München

Laboratory experience and analytic skills:

- Hydrothermal synthesis techniques
- Hydrothermal leaching experiments (e.g. on solid wastes)
- Nanoparticle synthesis via precipitation processes (freely programmable automatic titrator)
- Structure analyses by XRD and TEM
- Spectroscopy: AAS, ICP-OES, FTIR and RAMAN
- Imaging: SEM and TEM
- Bulk and mineral chemistry: XRF and EMPA
- Physical material properties: VFTB (magnetic measurements), Particle Sizer (light scattering)
- Simulation tools: phreeqC and geochemist workbench

Student supervision / teaching experience

since 4/2016

Master-Thesis: Iphigenia Anagnostopoulos about the upscaling of the hydroxide free wastewater treatment processes in the Cu-Mn-Zn-Al system (co-supervised; in collaboration with Clariant AG)

Bachelor-Thesis:

- Michal Silberhorn: "Characterization of precipitates obtained by Lt-delafossite process from Ag-containing solutions" (co-supervised)
- Manuel Huber: "Synthesis of nano-sized, Mn-containing delafossite via Lt-delafossite process and their magnetic properties" (co-supervised)

Co-supervision of Kai Tandon in collaboration with Clariant AG "Recovery of Au from wastewater of catalytic synthesis" (co-supervised)

4/2015 – 12/2015

Master-Thesis: Kai Tandon: "The ferrite process in the Ni–Fe model system: Characterization of nano crystalline residues" (co-supervised)

Bachelor-Thesis:

- Stefan Rudin: "Mineralogical characterization of nano crystalline residues obtained by ferrite process in the Cu-Fe model system at different temperatures" (co-supervised)
- Clemens Scheiblich: "pH dependency of the ferrite process in synthetic Cu containing wastewater and applicability to wastewater from electroplating industry" (co-supervised)
- Patrick Skrobanek: "A case study to recover Zn from wastewater" (co-supervised)

since 3/2015

- AAS course
- Lab trainee supervision

4/2014 – 7/2014

Bachelor-Thesis: Hannah Spielbauer: "A case study to recover Cu from industrial wastewater" (co-supervised)

01/2013 – 12/2013

Student supervision in the StudiForscht@Geo program. Title: "Developing a database for FTIR and XRD measurement"

Grands and awards:

since 10/2015 Acceptance for the LMUMentoring program (LMU excellent)

Research papers:

John, M., Heuss-Aßbichler, S., Park, S., Ullrich, A., Benka, G., Petersen, N., Rettenwander, D. and Horn, S. R. Low-temperature synthesis of $CuFeO_2$ (Delafossite) at 70 °C: A new process solely by precipitation and ageing. Journal of Solid State Chemistry 233 (2016) 390 – 396

John, M., Heuss-Aßbichler, Ullrich, A. Conditions and mechanisms for the formation of nano-sized Delafossite ($CuFeO_2$) at temperatures ≤ 90°C in aqueous solution. Journal of Solid State Chemistry 234 (2016) 55 – 62

Heuss-Aßbichler, S., **John, M.**, Klapper, D., Bläß, U.W., Kochetov, G. Recovery of Cu as zero-valent phase and / or Cu oxide nanoparticles from wastewater by ferritization. Journal of Environmental Management.

John, M., Heuss-Aßbichler, S., Ullrich A and Rettenwander, D. Purification of heavy metal loaded wastewater from electroplating industry under synthesis of delafossite (ABO_2) by "Lt-delafossite process". Water Research.

John, M., Heuss-Aßbichler S. and Ullrich, A. Purification of wastewater form zinc plating industry by precipitation of (doped) ZnO nanoparticles. Environmental Science and Technology

Conference contributions:

Heuss-Aßbichler, S., Klapper, D., **John, M**. (05/2014) Mineralogical investigations of precipitates obtained by treatment of Cu-rich wastewater by ferrite process. Interfaces of Water and Environmental Science (IAP), Leeuwarden, Netherlands (oral)

John, M., and Heuss-Aßbichler, S. (10/2015) Recovery of heavy metals by ferrite process: New results. Goldschmidt Conference, Prague, Czech republic (oral)

John, M., Ullrich, A., Heuss-Aßbichler, S. (3/2016) Mechanism of delafossite ($CuFeO_2$) formation in aqueous solution. DPG conference, Regensburg, Germany (poster)

John, M., Ullrich, A., Heuss-Aßbichler, S. (3/2016) Low temperature synthesis of CuFeO2 between 50 °C and 90 °C: A new process solely by precipitation and ageing. DPG conference, Regensburg, Germany (oral)

John, M., Heuss-Aßbichler, S., Huber, A.L. (3/2016) Niedertemperatursynthese von Ferrit, Delafossit und metallischen Phasen: Ein neuer Prozess zur Abwasserreinigung? 24 h für Rohstoffeffizienz, Nachwuchsforscherkongress (poster)

Tandon, K., **John,** M., Heuss-Aßbichler, S. (3/2016) The Ferrite Process in the Nickel – Iron Model System: Characterization of Nanocrystalline Residues. 24 h für Rohstoffeffizienz, Nachwuchsforscherkongress (poster)

Heuss-Aßbichler, S., **John, M.**, and Huber, A.L. (2016): Können Buntmetalle effektiv aus Industrieabwässern zurückgewonnen werden? In: Rohstoffeffizienz und – innovationen. 4. Symposium Rohstoffeffizienz und Rohstoffinnovationen, Tutzing, Germany

Accepted Abstracts:

John, M., Heuss-Aßbichler, S., Tandon, K. and Ullrich, A. (9/2016) Purification of noble metal (M) containing wastewaters by precipitation of zero-valent metals and M-Fe-oxide composite nanoparticles. ICSW, Meliá Sitges, Spain

John, M., Ullrich, A. and Heuss-Aßbichler, S. (9/2016) Synthesis and characterization of nano-sized Mn-containing delafossite (CuFeO2) obtained by Lt-delafossite process. MSE, Darmstadt, Germany

John, M. and Heuss-Aßbichler, S. (8/2016) Oxidation of green rust to nano crystalline MFeO2 and MxFe3-xO4 in aqueous solution. Nanoparticle synthesis to remove heavy metals (M) from wastewater! ICEENN, Golden, USA

Heuss-Aßbichler, S., **John, M.**, and Huber, A.L. (6/2016) New procedure to recover heavy metals in industrial wastewater. 8th International Conference on Waste Management and the Environment

Huber, A.L., Heuss-Aßbichler, S., **John, M.** (9/2016) Recovery of heavy metals from industrial wastewater – is it worth it? 5th International Conference on Industrial & Hazardous Waste Management, Crete, Greece

John, M., Heuss-Aßbichler, S., Huber, A. (11/2016) A new concept to recover heavy metals from industrial wastewater. Recy & DepoTech 2016, Leoben, Austria (oral)

Huber, A.L., Heuss-Aßbichler, S., **John, M.** (11/2016) Is an effective recovery of heavy metals from industrial effluents feasible? Recy & DepoTech 2016, Leoben, Austria

Invited talks:

John, M. "Synthesis of (doped) ABO2 nanoparticles: Can this work at temperatures ≤ 90 °C without using an additional reducing agent? " (8/2016) International Conference on applied Crystallography 2016, Houston, USA

Scientific network and collaborations

Prof. Dr. Soraya Heuss-Aßbichler and Prof. Dr. Sohyun Park, LMU München, Germany

Dr. Aladin Ullrich and Prof. Dr. Armin Reller, University Augsburg, Germany

Dr. Daniel Rettenwander, University Salzburg, Austria

Prof. Dr. Liane Benning and Dr. Rogier Besselink, GFZ Potsdam, Germany

Research fields and special interests:

Environmental chemistry, nanoparticle synthesis, hydrothermal processes, precipitation reactions, mineral characterization, phase transitions in aqueous solution, solid and liquid waste treatment

Countries I visited for high school, work, excursion or traveling

Austria, Hungary, Spain, Netherlands, Belgium, England, Croatia, Czech, Italy, Turkey, USA (including Alaska), Canada, Chile, Egypt, South Africa, New Zealand, Cuba

Low temperature synthesis of nano crystalline zero-valent phases and (doped) metal oxides as $A_xB_{3-x}O_4$ (ferrite), ABO_2 (delafossite), A_2O and AO.

A new process to treat industrial wastewaters?

ABSTRACT

MELANIE JOHN. LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN, DEPARTMENT FOR EARTH AND ENVIRONMENTAL SCIENCES, THERESIENSTR. 41, 80333 MUNICH, GERMANY

Though there are various techniques to treat wastewater, heavy metal containing industrial wastewater is directly or indirectly discharged into the environment, especially in developing countries. These wastewaters are hazardous to the environment and pose potential health risks for humans. Due to that, heavy metal pollution has become one of the most serious environmental problems today.

Herein, a facile, environmentally friendly and economic method to treat heavy metal loaded wastewaters at low temperatures (40 °C – 90 °C) is presented through simple synthesis of zero-valent phases, oxides with ferrite (AB_2O_4) and delafossite (ABO_2) structures, and doped heavy metal oxides (AO and A_2O) from aqueous solution. The process is tested for wastewater models and industrial wastewater samples loaded with heavy metals (concentration: 1 mg/l up to > 25 g/l) from different industry branches, including the Cu-finishing industry, electroplating and galvanic companies. Preliminary experiments to recover metals from multi-element wastewaters from the electroplating industry, e.g. from a Pd activator bath and from Cu semis production, are also presented. At optimal conditions, the recovery rate of heavy metals from wastewater is between 99.98 % and 100 % for Cu, Zn, Ni, Ag, Pb, Cr, Pd and Mn, and ≥ 97 % for Sn. Trace elements (up to 5 mg/l) additionally present in industrial wastewaters in many cases are mostly removed completely during treatment.

To characterize the nano-sized crystalline powders in detail, different analytical methods, such as AAS, ICP-OES, XRD, FTIR, SEM, TEM, Mößbauer and magnetic measurements (VFTB and PPMS), are combined. The phase assemblage depends strongly on the experimental parameters. In most cases, the precipitated phases can even be directly controlled by an element and matrix-specific adjustment of the process parameters, e.g. Fe-addition, reaction temperature, initial concentration of heavy metals, pH value, alkalization and ageing conditions. All precipitates are exclusively nanoparticle in size. In general, we distinguish between three different precipitation systems: (1) the ferrite – system, (2) the delafossite – system and (3) the binary metal oxide – system. The volume of the residues from all precipitation systems is very low compared to typical wastewater treatment by hydroxide precipitation using lime, for example. Therefore, pollution and further dissipation of partially rare heavy metals can be avoided using one of these simple and economic processes.

<u>Ferrite – system:</u>

The ferrite process was carried out on Cu, Ni and Zn containing solutions. Wastewater purification rates are ≥ 99.98 % for Cu and ≥ 99.90 % for Ni. The recovery rates of Zn are particularly dependent on pH and temperature, and range between 98.5 % and 99.98 %. By using optimal experimental conditions, near-complete recovery of Cu, Ni and Zn can be achieved.

In all cases, green rust (GR), an Fe^{2+}-Fe^{3+} double-layered hydroxy-sulphate, precipitates first. During ageing, GR transforms to ferrite. The progress of the oxidation process of GR is favored by electron transfer reactions in the Cu – Fe – H_2O – SO_4 – system.

Depending on the experimental conditions, the precipitated phases in the Cu – Fe – H_2O – SO_4 – system are $Cu_xFe_{3-x}O_4$ (ferrite) with x = 0.00 – 0.45, CuO (tenorite), Cu_2O (cuprite) and / or zero-valent Cu^0. No co-precipitated hydroxide phases were detected in aged products. In contrast, neither in the Zn – nor in the Ni – Fe – H_2O – SO_4 – system was it possible to gain precipitates completely free of hydroxides. In the Zn – Fe – H_2O – SO_4 – system, all aged samples consist of a mixture of $Zn_xFe_{3-x}O_4$ (franklinite), ZnO (zincite) and $Fe_{10}O_{14}(OH)_2$ (ferrihydrite). Directly affected by the initial Ni concentration in the Ni – Fe – H_2O – SO_4 – system, either $Ni(OH)_2$ (theophrastite) or a solid solution ($Ni_xFe_{3-x}O_4$) of Fe_3O_4 (magnetite) and $Ni_1Fe_2O_4$ (trevorite) were the main phase precipitates.

<u>Delafossite – system:</u>

In the context of this study, a totally new procedure called Lt-delafossite process was developed to (1) purify wastewater and (2) produce ABO_2 structures at low temperatures between 50 °C and 90 °C.

The results show that it is possible to gain pure delafossite ($CuFeO_2$, $CuFe_{0.9}Mn_{0.1}O_2$) solely by a precipitation and ageing process at low temperature. The water purification rate is ≥ 99.98 % for Cu, Fe and Mn under optimal conditions. The Lt-delafossite process was successfully tested on Cu loaded wastewaters from the electroplating industry.

Lt-delafossite (3R and 2H polytype) crystallizes as hexagonal plates with a diameter ≤ 500 nm and a variable thickness of 5 nm up to 300 nm depending on the ageing time and reaction conditions. In all cases, GR and Cu_2O precipitate first. During

further OH^- supply, GR oxidizes and forms $Fe_{10}O_{14}(OH)_2$, Cu_2O and $CuFeO_2$ crystals. Due to the high pH, further $CuFeO_2$ crystals grow at the expense of the unstable intermediate products $Fe_{10}O_{14}(OH)_2$ and Cu_2O. The reaction rate increases with increasing ageing temperature, reaction pH and, in particular, NaOH concentration in the solution. As a result, delafossite can be synthesized at 70 °C within 10 h or at 50 °C within 7 days. The formation of the 2H polytype of delafossite is favored by additional OH^- supply during the pH-stat time and relatively low temperatures.

In the Ag – Fe – H_2O – system, additionally, core-shell structures of zero-valent Ag^0 @ Fe_3O_4, Ag^0 @ $AgFeO_2$ and Ag^0 thin films were produced.

Binary metal oxide – system:

To gain a residue very low in volume and highly concentrated in one specific element, the added Fe^{2+}-content was lowered. Depending on the experimental parameters, the recovery rates are as good as for the ferrite and the Lt-delafossite process using this "low-Fe" precipitation method. At optimal reaction and ageing conditions, the precipitation of (doped) ZnO (zincite), CuO (tenorite) and Cu_2O (cuprite) directly from industrial wastewaters is possible.