



GRUN

*Groundwater Remediation using
Nano/biotechnology with focus on
the Contaminated Resources in Brazil*

ABSTRACT BOOK

Organization



MINISTÉRIO DA
CIÊNCIA, TECNOLOGIA,
INOVAÇÕES E COMUNICAÇÕES



Foreword

We are pleased to announce the Groundwater Remediation using Nano/biotechnology with focus on the Contaminated Resources in Brazil (GRUN) workshop which will be jointly organized by Teesside University (UK) and the Brazilian Synchrotron Light Laboratory (LNLS/CNPEM). This two-day event will take place at the Brazilian Center for Research in Energy and Materials (CNPEM) in Campinas, SP by the date June 24th and 25th, 2019. Also, on June 26th an extra hands-on course will be offered exclusively to 20 participants based on selection by the Organizing Committee.

There will be keynote talks from leading scholars from around the world to discuss the state-of-the-art in groundwater remediation technologies. We will also have speakers from Brazil who will discuss the current state of Brazilian groundwater resources. Novel technologies, such as nan/bioremediation, have shown to be a promising method for in-situ remediation of groundwater resources. This workshop will be the first event in Brazil focusing on the use of metal nanoparticles for in-situ degradation of groundwater contaminants. There will also be discussions on bioremediation processes that use microorganisms to degrade contaminants, again on-situ.

The conference will bring together an interdisciplinary group of researchers and engineers to collectively explore how these technological advances can be applied to Brazilian groundwater systems. We expect a wide range of participants including scientists/engineers, academics, industry representatives, and governmental agents.

Nathaly Lopes Archilha (LNLS)

Chairperson of the GRUN Workshop.

Day 1 – 24/06/2019

Time	Activity
08:00 – 09:15	Conference registration
09:15 – 09:30	Welcome and Introduction to Sirius - the new Brazilian synchrotron light source. <u>Dr. Antônio José Roque da Silva (LNLS/CNPEM)</u> .
Session 1 – Groundwater in Brazil	
9:30 – 10:30	Opening lecture: Perspectives on the investigation and remediation of contaminated sites in Brazil – <u>Dr. Reginaldo Antonio Bertolo</u> (Diretor CEPAS/USP)
10:30 – 11:00	<i>Coffee Break</i>
11:00 – 11:30	In-situ remediation in Brazilian soils: Unexpected findings, challenges and opportunities – <u>Dr. Juliana Gardenalli de Freitas</u> (UNIFESP)
11:30 – 12:00	Oral Presentation: Assessing discrete contaminant mass distribution and storage capacity in weathered bedrock aquifers in tropical regions – <u>Daphne Silva Pino</u> (USP)
12:00 – 13:00	Simultaneous tour visit at the Brazilian Biosciences National Laboratory (LNBio) and Brazilian Nanotechnology National Laboratory (LNNano).
13:00 – 14:00	<i>Lunch</i>
Session 2 – Use of Nanotechnology for Groundwater Remediation (Nanoremediation)	
14:00 – 15:00	Nanoremediation technology with focus on pore-scale physics - <u>Dr. Tannaz Pak</u> (Teesside University)
15:00 – 16:00	Electro-kinetically enhanced zero-valent iron nanoparticles (nZVI): Experiences from France and Switzerland – <u>Prof. Petr Kvapil</u> (Photon Water Technology Company)
16:00 – 16:30	Oral Presentation: Hierarchical mesoporous cobalt ferrite/bio-silica composite for the adsorption of an antibiotic (doxycycline hydrochloride) from waste water. – <u>Sunday Joseph Olusegun</u> (UFMG)
16:30 – 17:00	Oral Presentation: Reusable organo-mineral nanostructured materials with immobilized chelating ligands for selective water purification from toxic and radioactive metals. – <u>Volodymyr Zaitsev</u> (PUC-Rio)
17:00 – 19:00	Poster Session - Drinks and networking

Day 2 – 25/06/2019

Time	Activity
Session 3 – Challenges of Groundwater Nano/BioRemediation	
8:30 – 9:30	Nanoparticles for groundwater remediation: integrating laboratory tests and large-scale modelling to support field applications – <u>Dr. Carlo Bianco (Polytechnic of Turin)</u>
9:30 – 10:15	Nanoecotoxicity: environmental, health and safety – <u>Gabriela Helena da Silva (LNNano/CNPEM)</u>
10:15 – 10:45	Coffee Break
10:45 – 11:15	Oral Presentation: Modifications of nanoscale zero-valent iron (nZVI) including experience from recent application of the novel sulfidated iron nanoparticles (S-nZVI) on a site heavily polluted by trichloroethene (TCE) – <u>Jan Slunsky</u>
Session 4 – Synchrotron Techniques for Groundwater Remediation	
11:15 – 12:00	Introducing the X-ray micro and nanotomography beamline at Sirius – <u>Dr. Nathaly Lopes Archilha (LNLS/CNPEM)</u>
12:00 – 13:00	Simultaneous tour visit at the Brazilian Biosciences National Laboratory (LNBio) and Brazilian Nanotechnology National Laboratory (LNNano).
13:00 – 14:00	Lunch
14:00 – 14:45	Coherent X-ray nanoprobe beamline at Sirius – <u>Dr. Carlos Alberto Perez (LNLS/CNPEM)</u>
Session 5 – Use of Biotechnology for Groundwater Remediation - Bioremediation	
14:45 – 15:15	Oral Presentation: Use of biomolecular tools to enhance understanding about natural attenuation in areas impacted by waste deposits. – <u>Alice Kimie Martins Morita (USP)</u>
15:15 – 15:45	Oral Presentation: Bioremediation of arsenic enriched mining tailings using bioproducts – a strategy to minimize surface and groundwater contamination. – <u>Monica Cristina Teixeira (UFOP)</u>
15:45 – 16:15	Closing Remarks
16:15 – 16:45	Coffee Break
16:45 – 17:45	Visiting the new Brazilian synchrotron light source (SIRIUS)

Day 3 – 26/06/2019

Time	Activity
09:00 – 16:00	MNMs: a modelling tool for nanoparticle transport in porous media – <u>Dr. Carlo Bianco (Polytechnic of Turin)</u>

Summary

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APPLICATION OF Ni/SrTiO₃ NANOPARTICLES FOR THE METHYLENE BLUE PHOTODEGRADATION

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Methylene blue is a widely used dye that gives serious environmental issues, especially concerning the water's quality. There are methods to transfer dyes from solid to liquid phase but side pollution is produced [1]. An efficient method to degradate this dye should be studied. An interesting idea is to use the Sun's energy that arrives at Earth's surface with a power density of 200 W/m² [2] to induce the photodegradation of methylene blue by using catalysts [1]. Brazil has a great potential for the capture of this energy. However, due to the typical band gap of these catalysts only photons of the UV region can be absorbed, which represents only 5% of the intensity of the solar spectrum at the Earth surface. Ni/SrTiO₃ nanoparticles (NPs) are able to extend the absorption of the ultraviolet radiation to the visible region of the spectrum [3], then increasing the photocatalytic activity. In this work, Ni NPs were synthesized according to previous work [4] and exposed to thermal treatments at 100°C, 300°C and 500°C during 1h in atmosphere aiming to tune the Ni size and oxidation state. After, these Ni NPs were supported on commercial SrTiO₃ and applied to the methylene blue photodegradation using a homemade photoreactor, which is equipped with two 15 W lamps that simulate the solar spectrum. After the reaction, UV-Vis measurements showed a photocatalytic activity increase of up to 38% in comparison to the NPs without thermal treatment. The NPs were characterized by XRD, SAXS and XPS techniques before and after the reaction. The XRD patterns showed the presence of the SrTiO₃, SrCO₃ and TiO₂ crystalline phases for the support and Ni and NiCl₂ for the NPs. Rietveld refinement results showed a mean size of the SrTiO₃ and Ni NPs of 40 nm and 2 nm, respectively. SAXS curve fitting suggests SrTiO₃ NPs with mean size in accordance to the XRD results and show that Ni NPs present two distinct NPs population: a spherical one and a core-shell like structure.

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ASSESSING DISCRETE CONTAMINANT MASS DISTRIBUTION AND STORAGE CAPACITY IN WEATHERED BEDROCK AQUIFERS IN TROPICAL REGIONS

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Traditional field-characterization methods, usually applied for developing conceptual models and remediating contaminant source zones in porous and shallow aquifers, are not normally applicable in the context of fractured weathered bedrock. Therefore, this research aimed to apply the DFN method [1] to establish a conceptual model regarding contaminant migration and interaction with the bedrock matrix with a weathering profile [2]. The study was conducted at a site contaminated by chlorinated solvents in Sao Paulo, Brazil. The high-resolution rock sampling and analysis indicated the existence of residual PCE in discrete zones along the profile, mainly related to (i) lithological contacts and (ii) the interface weathered soil/soft weathered bedrock (SWB). The latter comprises 99% of the total mass of chlorinated ethenes, conceptually designating remedial target zones. In the transition zone of SWB and hard weathered bedrock (HWB), the contaminant concentration profile is continuous, indicating that rock weathering effects favour the interaction between contaminant and rock matrix, enhancing contaminant storage capacity. A natural attenuation capacity related to biological degradation of the dissolved PCE was also observed along the HWB profile. Although the contaminant mass in this horizon represents only 1% of the total mass along the profile, contaminant back-diffusion can sustain dissolved concentrations over time and maintain the continuous vertical mass flux into deeper parts of the aquifer. Brief, the microscale variation of contaminant distribution (two to three orders in a centimetric scale) suggests the effect of microscale lithological or hydraulic conductivity variability. Nevertheless, some questions remain open: how is the contaminant retention regarding matrix and fracture porosity at the different geologic materials? Do microfractures play a role in this scenario? And can fractures with no indication of water flow be significant retaining contaminants?

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BIOREMEDIATION OF ARSENIC ENRICHED MINING TAILINGS USING BIOPRODUCTS - A STRATEGY TO MINIMIZE SURFACE AND GROUNDWATER CONTAMINATION

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Arsenic is naturally found in association with gold minerals widely exploited in Minas Gerais, Brazil for centuries, mainly at the region named Iron Quadrangle. As a consequence of this economic activity, large amounts of As containing mine tailings were, and still are, produced and discharged. Soil washing technique using bioproducts/biosurfactants was tested to promote As mobilization from As contaminated soil samples collected at an abandoned gold mine. Two biosurfactant-producing mixed bacterial cultures were selected after being adapted to As (As III, 8 mg.L⁻¹). Biosurfactant extracts stability was tested under different experimental conditions. Soil flushing and soil washing tests were conducted in flasks and columns (10 cycles), bench scale. Biosurfactants efficiency was compared against SDS, Saponin and Soy lecithin 1% solutions. Biological extracts were stable over wide pH (3-11) temperature (28-50 °C) and salinity (1-5% NaCl - p.v⁻¹) ranges. The pH and the solid:liquid ratio influence on the results were markable. The best results were obtained at pH 11.0 and a solid liquid ratio of 1:40 (g.mL⁻¹). Biosurfactants efficiency was higher than those observed for SDS (0.87%), saponin (0.57%) and soy lecithin (2.63%). During column removal tests running at room temperature, pH 11.0, and 1% NaCl (p.v⁻¹) the cumulative arsenic removals (after 10 cycles) were of 25%, approximately. The As removal values achieved using biological extracts represent a significant amount of As fraction which could be easily mobilized causing environmental and human health risks, eventually. The attenuation of As toxicity after this bioremediation process is under investigation through ecotoxicology tests [1]. This is an innovative proposal to avoid water contamination but, As removing mechanisms were not totally explained. Some more accurate approach is needed, thus justifying the use of the Synchrotron radiation facilities.

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COMPREHENSIVE ANALYSIS OF DIFFERENT IRON NANOPARTICLES SYNTHESIS TECHNIQUES USED FOR REMEDIATION OF CONTAMINATED AREAS

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Even though the world's available water may seem abundant, only 1% of it is on the surface, while 69% is in the frozen form and the other 30% stored in aquifers [1], which some part of it is already being used. In 2010, worldwide, 70% of the water withdrawals were used for irrigation, 21% for domestic use, and 9% for industrial use [2]. Even though the groundwater may be of extremely important use, a considerable part of it contains contaminants, which can turn this aquifer unusable for years. Some of the major sources of contamination in groundwater are farming chemicals, septic waste, landfills, uncontrolled hazardous waste, and atmospheric pollutants [3]. As these contaminants should be removed for the safe use of groundwater resource, many remediation techniques are being tested, including biological, physical, chemical and thermal processes. From these possible techniques, chemical oxidation and reduction technologies have proven to be of particular interest. There are two main reductants in this class the polysulphides and nanosized zero valent iron (nZVI). The advantages of the chemical process are the fast and possible complete degradation, applicability for a wide range of organic contaminants, and the use of lower cost and easily delivered to the surface reagents [4]. Some examples of developing researches and tests for groundwater remediation using nZVI are in the Czech Republic and Spain [5]. In the first case, it was achieved a non-aqueous phase liquid contaminant (NAPL) reduction of 85% to 95%. For the second case, a high formation of ferric iron, which increased from a concentration of 8.6 to 83 mg/L indicates that nZVI particles have effectively reduced the arsenic present into its metalloid form, much less toxic than its oxidized form [6]. In this study, technologies used for the production of nZVI are discussed, pointing out the advantages and disadvantages of each production process conditions, and the remediation main results and applicability.

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DETERMINATION OF REMOVAL MECHANISM OF Cr (VI) USING Fe-Cu BIMETALLIC NANOPARTICLES

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The use of FeO nanoparticles (Fe NPs) has presented a great interest as adsorbent material. It has been extensively used for the decontamination of aqueous matrices. However, this material has some limitations when used in aqueous matrices and porous media. To resolve these problems, the use of bimetallic nanoparticles (BMNPs), specifically, FeCu BMNPs had been reported, because this material has a higher reactivity, colloidal stability and removal rate compared with Fe NPs [1,2,3]. The aim of this work was to synthesize and characterize Fe NPs and FeCu BMNPs and evaluated its removal capacity to determine the removal mechanism of Cr(VI). The synthesis of these nanoparticles was realized employing the chemical reduction method with NaBH₄ [4, 5] and the sorption studies were realized using 40 mg L⁻¹ of Cr, NaCl 0.1 (mol L⁻¹), pH 8,5 and 100 mg of nanomaterials. The characterization pre and post sorption of nanoparticles by Scanning Electron Microscopy (SEM) showed that the nanoparticles exhibit transformation respect to pre-sorption case, associated to removal processes with Cr. By X-ray Diffraction (XRD), a new signal in post-sorption diffractogram associate to FeCr₂O₄ was identified. Beside by X-ray photoelectron spectroscopy (XPS), we can observe that the Cu present in the nanostructure is rusty to Cu (I) or Cu(II) and the Fe to (II) and (III). In the case of the analyte, it can be sorbed in the surface of the nanoparticle like Cr (VI) or (III), precipitate or co-precipitate (FeCr₂O₄) and reduced to Cr (0). Therefore, FeCu BNPs can remove Cr present in water by adsorption, precipitation, co-precipitación and redox mechanism, where the electronic transference between Fe, Cu and Cr is the most important process in this case.

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DEVELOPMENT OF LANGMUIR-BLODGETT FILMS OF LUMINESCENT AMPHIPHILIC 1,3,4-OXADIAZOLE DERIVATIVES

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The study of molecular interactions that arise in processes of self-organization is a very interesting field, once self-organized materials have many applications and can suit specific properties. The Langmuir and the Langmuir-Blodgett (LB) techniques allow the study and deposition of ultra thin films, constituted by few molecular layers. The LB films shows high molecular organization and can be employed as chemical and biological sensors, membranes, non-linear optical devices, diodes, conducting films and thermochromic devices [1]. Some 1,3,4-oxadiazole heterocycle derivatives show intense fluorescence, liquid crystalline behavior, chemical and thermal stabilities and has been explored in LB films [2]. In this study, two amphiphilic compounds were synthesized and characterized, the 2-(4-dodecyloxy-naftyl)-5-(4-pyridyl)-1,3,4-oxadiazole (NFT1) and the 2-(4-dodecyloxy-naftyl)-5-(2-pyridyl)-1,3,4-oxadiazole (NFT2). ¹H NMR, UV-Vis, FTIR, Raman, ESI-MS, fluorescence spectroscopy, MQLP and DSC were employed in the study. Only NFT1 exhibited the liquid crystal behavior, showing an organized structure in a smectic A mesophase. Both compounds form stable monolayers at liquid-air interface. NFT1 exhibits a typical pressure-area isotherm, whilst NFT2 exhibit a plateau at $P = 8 \text{ mN m}^{-1}$, that is probably related to a change of the molecular orientation in the interface. LB films were deposited on quartz and gold substrates and characterized by UV-Vis and FT-IRRAS spectroscopies. The results revealed the formation of molecular aggregates [3], consistent with our self-assembly model.

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The studies and characterizations of the LB films confirmed the choice of the ideal parameters of deposition. The molecular interactions present in the films can be useful in the development of molecular dispositives. The studies of luminescent aren't complet yet.

ECOTOXICOLOGY EVALUATION OF THE HYBRID NANOPARTICLES OF TITANIUM DIOXIDE COATED WITH CARBON NANOTUBES (TiO₂/CNT) IN *Danio rerio* (ZEBRAFISH) EMBRYOS

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Titanium dioxide NP and carbon nanotubes (CNT) are amongst of the most popular nanoparticles studied these days, due to their properties and applications. Their hybrid (CNT/TiO₂) can have an even enhanced performance, as enhanced photocatalytic activity [1] and micro pollutants sorption [2], but there are few studies on its effects in living organisms. There is a potential risk to the presence of these NPs in environment due to the lack of knowledge about how they behave in natural ecosystems, since their properties cannot be predicted by the study of the parent material. As literature shows, nanoparticles can induce inflammation and stimulate or suppress the immune system in vivo [3]. Embryo assays were based on the OECD protocol Fish Embryo Toxicity test - FET - Test No. 236 [4]. The exposures were performed in 24-well microplates with 2 ml of each test solution (0, 6.25, 12.5, 25, 50 and 100 mg/L), triplicate, 60 organisms per concentration (20 per microplate), conditioned in a climatic chamber (SL-24 Solab Scientific) (27°C ± 1 12h light). The hybrid was synthesized by the CVD method as in the reference [5]. Titanium dioxide coated with carbon nanotubes were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and RAMAN microscopy. The LC50 is above the highest concentration tested (100 mg/L). Beyond that, the only effect observed during the test was behavior alteration (35% of organisms) exposed to the last concentration. During 96 hours of exposure to CNT/TiO₂, mortality was not observed. **Conclusions:** The hybrid nanoparticle CNT/TiO₂ presents low acute toxicity to zebrafish embryos, although future tests must be done to a better elucidation of the potential ecological risk of nanostructure (CNT/TiO₂), such as biochemistry and chronic toxicity tests. **Key words:** Titanium dioxide, carbon nanotubes, ecotoxicology.

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EMISSIONS OF BIOGENIC METHANE AS INDICATED BY $\delta^{13}\text{C}$ - CH_4 AND $\delta^2\text{H}$ - CH_4 AND N_2O FLUXES ALONG THE RHIZOSPHERE PROFILES OF FORAGE SPECIES

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Pasture management may influence the soil organic carbon content and moisture, improving the conditions for the establishment of soil microbiome in the pastureland. It is known that the microbes play a key role in soil processes and can act as a source or sink of nitrous oxide (N_2O) and methane (CH_4), components of greenhouse gases (GHG) with larger radioactive force than carbon dioxide (CO_2). In a similar way, it is known that the application of synthetic fertilizers (N) (such as urea) results in biogenic CH_4 and N_2O emissions to atmosphere. Despite this, the understanding of the microbial processes associated with N_2O and CH_4 emissions in pasture areas is still limited. In this way, the present propose attempts to seek information on the biogenic emissions of CH_4 e N_2O , gathering a multidisciplinary team in the conduction of experiments that shall integrate knowledge in the area of mineral nutrition, environmental biogeochemistry and soil microbiology. The experiment will be conducted in Botucatu-SP with three forage grasses (i) *Urochloa ruziziensis*, (ii) *Panicum maximum* and (iii) *Brachiaria* var. *Ipyporã*, where the microbial population will be examined as to its role in N_2O and CH_4 fluxes, acting as source or sink in soil pastures. In addition, plots containing ^{15}N -urea will be installed for monitoring ^{15}N in the soil-plant system. Air sampling will be done in static chambers and the N_2O and CH_4 emissions will be determined by gas chromatography and the biogenic isotopic composition of $\delta^{13}\text{C}$ - CH_4 , $\delta^2\text{H}$ - CH_4 . At the same time, soil will be sampled at depths of 0-10, 10-20, 20-30, 30-40 cm for molecular, chemical and physical analyzes. The aim of this study is to evaluate the microbial genes associated to biogenic processes to produce N_2O (ammonia oxidizing) and CH_4 (methanogenic and methanotrophic) gases as indicators by different pasture species. Additionally, analysis of the isotopic signature of the biogenic CH_4 along the profiles of the forage species.

Fe SPECIATION IN SEAWATER FROM GUARATUBA BAY, BRAZIL

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Low Fe availability in combination with relatively large cellular demands among phytoplankton cause Fe to be a central determinant of world ocean productivity. The chemistry of Fe in oceans is characterized by its very low solubility, from nano to picomol levels, although complexation of Fe by organic ligands increases its solubility [1]. Thus, many studies have been developed and related to the speciation of this element to better understand its behavior in seawater. The voltammetric method used is based on the adsorptive properties of the Fe(III)-2,3-dihydroxynaphthalene (DHN) complexes on the hanging mercury drop electrode with catalytic enhancement by bromate ions. Voltammetric titration was used to evaluate Fe speciation. The different forms of the metal investigated are then computed via mass-balance equations, according to the van den Berg–Ruzic model [2]. Compromise conditions were defined and optimized. LOD and LOQ are 40.0 pmol L⁻¹ and 135 pmol L⁻¹, respectively. Guaratuba Bay is a subtropical estuary on the Southern Brazilian coast. In the summer its population can increase six-fold as a result of the intensive tourism activities in its surroundings. Besides, domestic sewage is still considered problematic due to poor collection and treatment [3]. The determination of the total Fe content was consistent with sampling conditions, with 252.4, 3.40 and 8.63 nmol L⁻¹ for samples 1, 2 and 3, respectively, which demonstrates the effect of high population density, especially on site 1, which has the highest contribution of Fe and organic matter. Results from voltammetric titration and the van den Berg–Ruzic model for sample 1 show that most of Fe is complexed (248.7 nmol L⁻¹) and only 3.7 pmol L⁻¹ corresponds to the labile fraction, which is justified by the high concentration of natural ligands (332.5 nmol L⁻¹) as well as by its high conditional stability constant (7.94 x 10¹²).

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HIERARCHICAL MESOPOROUS COBALT FERRITE/BIO-SILICA COMPOSITE FOR THE ADSORPTION OF AN ANTIBIOTIC (DOXYCYCLINE HYDROCHLORIDE) FROM WASTE WATER

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Inadequate treatment of pharmaceutical wastewater from point source led to possible leaching of antibiotics into groundwater, such as doxycycline (DOX), which is among the group of antibiotics that are classified under tetracycline [1]. Just like every antibiotic, its presence in surface water, ground water and sediments is hazardous to the environment hence the need to remove them and make the environment pollutant-free [2]. Cobalt ferrite/bio-silica was synthesized, calcined, characterized and applied as an adsorbent for the treatment of DOX. Characterization of the adsorbent showed that calcination did not affect the morphology of the composite, although the specific surface area, magnetization and diffractogram of the composite were significantly affected at calcination temperature of 700°C. The as-prepared composite has the highest surface area (283 m²g⁻¹), while the composite calcined at 700 °C has the lowest (148 m²g⁻¹), but highest magnetic saturation (20 emu g⁻¹). Adsorption capacity was influenced by many factors such as specific surface area, surface charge, solution temperature and presence of ions, while the mechanism entails electrostatic interaction and hydrogen bond. Adsorption data fitted well with Langmuir isotherm, having the monolayer adsorption capacity of 920.77 and 674.83 mg.g⁻¹ for the as-prepared and sample calcined at 700°C, respectively. The adsorption is endothermically favored and spontaneous.

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IN SITU STUDY OF NON-AQUEOUS PHASE LIQUID (NAPL) REMOVAL BY NANOFLUID INJECTION

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Inadequate operations of anthropogenic activities such as agricultural practices, oil exploration, mining and incorrect management of industrialized wastewaters are impacting the quality of groundwater [1]. These water reservoirs are important drinking water resources since they represent 99% of the fresh liquid water in Earth [2] and besides the difficult to access it has become vulnerable to pollution. Once contaminated with non-aqueous phase liquids (NAPL), groundwater remediation is a challenge because of their persistence against degradation agents and resistance to mobility [3], requiring new technologies. In this study, the action of silica nanoparticles (NP) was evaluated as a remediation technique, using the X-ray microtomography (μ CT) to evaluate the oil/aqueous phases arrangement in the pore scale. Nanoparticles of 30, 60 and 100 nm of diameter were synthesized by the modified Stöber method and characterized by Dynamic light scattering (DLS), Zeta potential, Scanning Electron Microscopy (SEM) e Fourier transform Infrared spectroscopy (FTIR) analyzes. 3D images generated from this technique were automatically segmented with the aid of a “deep learning” based network, semi-automatically using threshold and watershed tools and, when necessary, manual corrections were applied. From the image analysis obtained from the μ CT images, it was observed that the NP-30 and NP-60 had a slight effect on the NAPL removal in comparison to NP-100 which presented a substantial action in the mobilization and removal of oil, even at low concentrations, increasing the recovery from 44 to 56% of the initial volume of oil.

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IRON PARTICLE SIZE INFLUENCY ON REMEDIATION OF CHLORINATED SOLVENTS IN GROUNDWATER

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This work evaluated the influence of iron particle size on the degradation process of tetrachloroethene contamination in water samples. The study was performed in column tests containing a porous media and zero valent iron (ZVI), and may or may not contain other elements that could aid in the degradation process. This paper is the first step in phd in nanotechnology.

MODIFICATIONS OF NANOSCALE ZERO-VALENT IRON (nZVI) INCLUDING EXPERIENCE FROM RECENT APPLICATION OF THE NOVEL SULFIDATED IRON NANOPARTICLES (S-nZVI) ON A SITE HEAVILY POLLUTED BY TRICHLOROETHENE (TCE)

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Last fifteen years the zero-valent iron nanoparticles have been often delivered in form of water slurry and used for in-situ groundwater remediation contaminated primarily with chlorinated hydrocarbons, hexavalent chromium, other organic substances and heavy metals. Many researchers are focusing on modification of nanoparticles in aqueous suspension in order to enhance product properties and prolong shelf life. Surface stabilization of nanoparticles can optimize reactivity and migration properties of nanoparticles in order to meet specific requirements of every remediation project, but it is unable to completely prevent the aging of the product caused by high reactivity of nanoparticles in water environment. Far more appropriate solution, especially when nZVI shall be applied in large quantities, is the preparation of fresh water slurry from a dry powder on-site just before an application. This solution enables the application of highly reactive product containing lowest ratio of agglomerated nanoparticles. Both approaches (stabilization of aqueous suspension and using of dry nano-powder) are discussed in the first part of the presentation. Second part of the presentation is dedicated to inorganic modification of nZVI by sulphur structures. As research of sulfidated nanoparticles has shown, S-nZVI has earned a reputation as a promising material due to its high reactivity towards some pollutants, its increased mobility, and its longevity caused due to suppressed corrosion. This new product has been therefore deployed on a pilot site to verify laboratory findings in the real environment. The site contaminated by TCE (reaching up to 400 000 µg/L) was remediated using 150 kg of S-nZVI (NANOFER 25DS from NANO IRON) which was applied in August 2018. Application of S-nZVI resulted in increasing pH, decreasing redox potential and evolution of gaseous products of CHCs degradation (ethane, ethene, acetylene).

REUSABLE ORGANO-MINERAL NANOSTRUCTURED MATERIALS WITH IMMOBILIZED CHELATING LIGANDS FOR SELECTIVE WATER PURIFICATION FROM TOXIC AND RADIOACTIVE METALS

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Here we report the results of application of nanostructured hybrid organo-mineral adsorbents with covalently immobilized strong complexing agents for water purification from toxic and radioactive metals. We developed procedures for preparation of the adsorbents having layer of chelating agents. These agents react with certain groups of metal ions and extract them from contaminated water. Then the adsorbed metals can be re-extracted and concentrate for further utilization and the material can be reused. Selectivity of immobilized ligands towards certain metal ions ensures the assure adsorption selectivity. Covalent immobilization ensures stability of the adsorbents. Currently we developed procedure of immobilization and studied a wide range of strong chelation ligands. Some of them have selectivity to most of heavy metals (for example 2,6-pyridinedicarboxylic acid (PdCA), and ethylenediaminetriacetic acid (EDTA)), others have selectivity to rare earth elements (REEs) and trans-uranium elements (for example hydroxamic acid (BPHA) and aminomethylphosphonic acid (ADPA)). Several nanomaterials were studied as prospective supports for ligand immobilization. Mainly these are nanostructured materials such as silica gel (SiO₂) and natural diatomites layered materials, such as clay (bentonites): and magnetic nanomaterials (Fe₃O₄/SiO₂). Metal adsorption selectivity, capacity and kinetics were studied in dynamic (solid-phase extraction, SPE) and static (dispersive solid phase extraction, DSPE) conditions for different type of surface water (natural and industrial). Also, some adsorbents were studied for REEs pre-concentration and separation as prospective substitution for solvent extraction of REEs form recyclable sources such as e-waste.

STUDY OF COBALT FERRITE PRODUCED BY SOL-GEL: PERFORMANCE AS LUBRICATING OIL ADSORBERS

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Cobalt ferrite samples were produced from nitrates using an orange albedo extract as precursor. The initial mixtures were subjected to isothermal treatments at 1073 and 1173 K for 4, 6, 8, 12, 16, 36 and 48 h. The composition of the resulting powders was studied using Fourier Transform Infrared Spectroscopy and X-ray scattering. Ferrites were used in magnetically assisted separation for oil adsorption in effluents. We observed that the oil absorption is dependent on the time and temperature of the isothermal treatment used in the preparation of the ferrites. Particles with oil adsorption efficiency of 4 gg^{-1} were produced at 1073 K at 12 h.

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USE OF BIOMOLECULAR TOOLS TO ENHANCE UNDERSTANDING ABOUT NATURAL ATTENUATION IN AREAS IMPACTED BY WASTE DEPOSITS

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The inadequate waste disposal may represent an important source of water pollution, even after the ending of disposal activities. The knowledge of the physicochemical and microbiological conditions of these areas is essential for the understanding of the attenuation processes, contributing to the prediction of the necessity of intervention actions. This study performed an integrated evaluation of the physicochemical and microbiological conditions of an area impacted by an irregular waste deposit, situated in São Carlos city, Brazil, in a Guarani Aquifer recharge zone. The objective was to characterize the impacted area and evaluate the potential of natural remediation. Groundwater and surface water samples were collected, as well as solid waste samples from the deposit, and physicochemical (COD, N-NO₃⁻, N-NH₄, SO₄²⁻, Cl⁻, F⁻, TKN, major ions and heavy metals) and microbiological (PCR-DGGE) analysis were performed. The initial diagnosis permitted to observe high concentrations of contaminants inside the waste deposit, but considerable reduction downstream it. The microbiological results allowed to observe important similarities of Archaea populations in the wells with higher levels of contamination, but the same behavior was not observed for Bacteria populations. Richer and more diverse ecosystems were noticed in the sites with higher concentrations of organic matter, dissolved ions and other contaminants. Our results showed that the contaminated site was not toxic for the majority of microbiological populations, and that currently, the most active populations in contaminants degradation might be the Archaea ones, due to the deposit's age. In samples of solid waste, higher diversities of Bacteria and Archaea were found at 1m deep, but a reduction occurred at 2m deep. This behavior was attributed to the existence of the water table at about 2m deep, which could have affected microbiological processes due to the lower availability of oxygen.

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