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Trace elements and nutrients adsorption onto nano-maghemite in a contaminated-soil solution: A geochemical/statistical approach

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HIGHLIGHTS

- PO_4^{3-} reduced the As and Cd adsorption capacity of NM in the soil solution.
- High P level in the soil solution improved the immobilization of Al by NM.
- CCD was useful to explain the effects of K^+ and NH_4^+ on the adsorption of TEs by NM.
- High KNO_3 and NH_4NO_3 concentrations reduced TEs levels in soil solution with NM.
- K^+ and NH_4^+ could improve the effectiveness of NM during phytoremediation tasks.

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ABSTRACT

Two experiments were carried out to study the competition for adsorption between trace elements (TEs) and nutrients following the application of nano-maghemite (NM) (iron nano-oxide; Fe_2O_3) to a soil solution (the 0.01 mol L^{-1} $CaCl_2$ extract of a TEs-contaminated soil). In the first, the nutrients K, N, and P were added to create a set of combinations: potential availability of TEs during their interaction with NM and nutrients were studied. In the second, response surface methodology was used to develop predictive models by central composite design (CCD) for competition between TEs and the nutrients K and N for adsorption onto NM. The addition of NM to the soil solution reduced specifically the concentrations of available As and Cd, but the TE-adsorption capacity of NM decreased as the P concentration increased. The CCD provided more concise and valuable information, appropriate to estimate the behavior of NM sequestering TEs: according to the suggested models, K^+ and NH_4^+ were important factors for Ca, Fe, Mg, Mn, Na, and Zn adsorption ($R^2_{adj} = 95\%$, except for Zn with $R^2_{adj} = 87\%$). The obtained information and models can be used to predict the effectiveness of NM for the stabilization of TEs, crucial during the phytoremediation of contaminated soils.

1. Introduction

The bioremediation of soils contaminated by trace elements (TEs) through the establishment of a vegetation cover (phytostabilisation) is a viable alternative for their recovery and the conservation of the surrounding areas and groundwater. Conditioning the soil is a key factor for the survival and growth of the plants, with nanoparticles being promising materials for the stabilization of inorganic pollutants [1,2], especially for multi-element-contaminated areas. Contaminant-immobilizing amendments decrease TEs bioavailability by inducing adsorption to mineral surfaces, surface precipitation, and ion exchange [3]. Adsorption technology with no chemical degradation is attractive due to its merits of effectiveness, efficiency and economy [4]. Adsorbents like activated carbons, zeolites, clays, industrial by-products, agricultural wastes, biomass or polymeric materials suffer from low adsorption capacities and separation inconvenience [5]. Alternatively, the synthesis and utilization of iron oxide nanomaterials with novel properties and functions has received much attention due to their surface modifiability, excellent superparamagnetic properties, and great biocompatibility [6,7], and especially due to their reactivity and relatively-large specific surface area (tens to hundreds of $m^2\ g^{-1}$). For these reasons, iron nano-oxides are important scavengers of contaminants [8], being a good choice for contaminated soils because of their sorption properties [9]. Named “eco-nanomagnet” by Girginova et al. [10], nano-maghemite (NM) has been investigated due to its abundance and effectiveness at removing the most-toxic form of As (arsenite, As^{3+}) [11] and other elements, like Cu^{2+}, Zn^{2+}, and Pb^{2+} [12], from contaminated water, and as an in situ remediation material [13]. Moreover the potential availability of nutrients and toxic TEs to living organisms will depend on the nature and the strength of the interactions with the nano oxide surfaces, as well as the conditions for the interaction.

In complex systems, such as soil solution, there are ions other than toxic metal ions that may affect the adsorption of metals. Therefore, there is a need to investigate whether the effectiveness of an adsorbent is affected by the nutrient supply in the

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Table 1
Characterization of the contaminated soil from Mokrsko (Czech Republic), with the total element concentrations, and its soil solution (extracted by 10 mmol L^{-1} $CaCl_2$) used for the experiments.

	Total digestion (mg kg^{-1})	Soil solution (mg L^{-1})
pH	6.15	4.66
Al	22,383	–
As	389	0.11
Ca	–	423
Cd	b.d.	0.03
Cu	21	0.04
Fe	23,782	0.05
K	–	7.76
Mg	–	12.68
Mn	499	1.10
Na	–	5.86
Pb	26	–
Zn	93	0.12

soil. On the other hand, low nutrient content is one of the most-limiting problems for the growth of plants in contaminated soils [14] therefore, it is crucial to evaluate how the application of nano-oxides might reduce the bioavailability of nutrients, and how nutrients can alter their effectiveness. The related literature summarizes mainly the use of nanoparticles for the cleanup of drinking-water and their competition with nutrients: for example, As–P competition during Fe–Al nano-oxides adsorption [15], TEs removal by zero-valent iron as affected by $PO_4{}^{3-}$ and $NO_3{}^{-}$ [16], and the use of Fe_3O_4 and Fe_2O_3 for the removal of either As (III) or As (V) from drinking water [17]. However, there is very little information about these processes in contaminated soils and soil solutions, the consequent changes in element concentrations following NM application, or the implications for plant nutrition and growth [18].

In this work, we study the effect of NM on the potential availability of nutrients and TEs in a contaminated soil solution, using a coupled geochemical/statistical approach: the results should have implications for phytoremediation technologies and for studies using NM in hydroponic culture. The nutrients potassium (K), nitrogen (N), and phosphorus (P) were selected because they are the most-important macronutrients, and they are usually supplied to contaminated soil to improve plant growth during phytoremediation tasks. Metals and metalloids were analyzed, with the focus on those with high total concentrations in the soil.

2. Material and methods

The adsorption of TEs by nano-maghemite (NM; γ-Fe_2O_3; <50 nm nanopowder; Sigma–Aldrich) was tested in a soil solution with/without NM and increasing concentrations of nutrients, with the emphasis on the competition between contaminants and nutrients for the sorption sites. Two experimental designs were compared. The first used increasing concentrations of nutrients in a soil solution, with NM interaction, and subsequent statistical comparison. The second followed a central composite design (CCD) approach, which has several advantages over the traditional one-variable-at-a-time approach. It was used to predict the behavior of each element, since CCD is the most-popular class of designs used for fitting a second-order model [19]. The CCD approach can be used to determine the statistically-significant factors affecting a response, and to predict mathematically how a response relates to the values of various factors [20]. The mathematical models can then be utilized to find the optimum response (through the statistical significance of various parameters) and to find the conditions that result in a maximum or minimum value, as appropriate, within the experimental study.

2.1. Soil solution

The Mokrsko–West mesothermal gold deposit is a former mining area affected by high TEs concentrations, located in central Czech Republic [21,22]. Samples from the top soil (0–25 cm; 49°44′18″N 14°19′49″E) were collected, air-dried, sieved through a 2-mm sieve, and homogenized to determine selected initial soil characteristics (Table 1). The pH and electrical conductivity (EC) were measured in saturated soil/water pastes (1:3, w/w). Cations were measured by inductively-coupled plasma-optical emission spectrometry (ICP-OES) (Varian, VistaPro, Australia). A soil solution was obtained by mixing 10 g of soil with 100 mL of 10 mmol L^{-1} $CaCl_2$, to extract the potentially-available TEs in the soil fraction [23]. In order to maintain the pH following the addition of the different nutrients, MES buffer ($C_6H_{13}NO_4S$) was added to the soil solution at a concentration of 1.5 mmol L^{-1}.

2.2. K, N, and P during TEs adsorption by NM

In the first experiment, KNO_3, NH_4NO_3, and KH_2PO_4 were used to add K, N, and P, respectively, to the soil solution before addition of NM. These compounds are typically used for nutritive hydroponic solutions at concentrations of 2–4 mmol L^{-1} [24–26]. Stock solutions of 0.1 mol L^{-1} were prepared for each salt. In order to have three concentrations of each nutrient (0, 3, and 6 mmol L^{-1}), different combinations of volumes of the stocks were added to the soil solution (diluted), in 10-ml tubes, in triplicate. For this, since K and N are common to more than one compound, a set of combinations was designed to study the individual effects of each element (Table 2). The software Visual MINTEQ [27] showed that in these solutions more than 98.8% of the K, N, and P were available in free forms, as K^+, $NO_3{}^-$, $NH_4{}^+$, and $PO_4{}^{3-}$. After the nutrients were mixed with the soil solution, 1 ml of 10% w/v NM in pure water was added to each tube to obtain 1% w/v NM in the soil-nutrients-solution, in the final volume of 10 ml. These dose was selected because usually, 1–2 wt.% of nano-amendment is sufficient for metal stabilization [9]. The resultant pH of the solution was 4.66. Controls without NM (1 mL of pure water added to each tube) were used to determine the effect of NM on the equilibrium. After agitation for 24 h, in darkness, the pH was determined and the samples were centrifuged and filtered using 0.45-μm nylon filters, which were efficient due to the aggregation of the nano particles (not detected in the filtrates). Samples were diluted using HNO_3 and analyzed using ICP-OES (Varian, VistaPro, Australia).

2.3. Central composite design (CCD) for K and N

In this experiment, the response surfaces methodology (RSM) was employed to investigate the influence of K^+ and $NH_4{}^+$ (added as KNO_3 and NH_4NO_3) on the bioavailability of nutrients and TEs after NM application to the soil solution. The nutrients were independent variables and they were factor levels coded as–1 (low), 0 (middle), and +1 (high) (Table 3). Using MINITAB software version 16.1.1. [28], a CCD of 13 runs (in triplicate) was designed for KNO_3 and NH_4NO_3 (from 0 to 6 mmol L^{-1}). The same conditions

Table 2
Concentration of each salt used to create a set of combinations of nutrients in the interaction media used in the first experiment. The name of the combination denotes the final concentration of each element in the soil solution (0, 3 or 6 mmol L^{-1}). The interaction forms were K^+ for K, $NH_4{}^+$ and $NO_3{}^-$ for N, and $PO_4{}^{3-}$ for P.

Name of combination	KNO_3 (mmol L^{-1})	NH_4NO_3 (mmol L^{-1})	KH_2PO_4 (mmol L^{-1})
K0N0P0	0	0	0
K0N3P0	0	1.5	0
K0N6P0	0	3	0
K3N0P3	0	0	3
K3N3P0	3	0	0
K3N3P3	0	1.5	3
K3N6P0	3	1.5	0
K3N6P3	0	3	3
K6N0P6	0	0	6
K6N3P6	0	1.5	6
K6N6P0	6	0	0
K6N6P3	3	1.5	3
K6N6P6	0	3	6