Table 1. The arsenic concentrations of water before and after filtered through Mesopaper.

	Gansu ($\mu\text{g L}^{-1}$)		Innner Mongolia ($\mu\text{g L}^{-1}$)		Hunan ($\mu\text{g L}^{-1}$)	
	One layer	Two layer	One layer	Two layer	One layer	Two layer
Startup	729	729	1658	1658	86580	86580
0.2 L	3	0	26	0	47849	1125
0.4 L	5	0	82	5	79454	27277
0.6 L	13	0	557	38	80745	53796
0.8 L	21	0	685	80	77566	65696
1.0 L	33	0	843	129	82520	68370

And then, 1 liter (L) water sample was prepared and poured through the Mesopaper, with 0.2 L every time. The arsenic concentrations were determined at accumulated filtration volume of 0.2 L, 0.4 L, 0.6 L, 0.8 L and 1 L. In this study, we tested the arsenic removal efficiency of one layer and two layers of Mesopaper, respectively.

2.4 Arsenic leaching experiment

The major activated media for Mesopaper to remove arsenic is the nano-scale powder. And then, we directly tested the arsenic leaching rate of nano-scale powder equipped with enough arsenic. 2 g nano-scale powder that had been adsorbed nearly 3.56 mg arsenic were weighted and putted into 100 mL solutions with different pH values of 3, 5, 7 and 9, respectively. After stirring for 5 minutes, the supernatant liquid was extracted to determination of arsenic concentrations.

2.5 Arsenic determination

The arsenic concentrations of all water samples in this report were measured using hydride generation-atomic fluorescence spectroscopy (HF-AFS).

3 RESULTS AND DISCUSSION

3.1 Arsenic removal efficiency

Table 1 displays the removal effect of As by Mesopaper. It was obvious that the arsenic concentrations of the three samples were all significantly decreased after filter through one layer and two layers of Mesopaper. In Gansu samples, for example, more than 90% arsenic was adsorbed by one-layer Mesopaper and the final arsenic concentrations was below $10 \mu\text{g L}^{-1}$ at the sampling point of 0.2 L and 0.4 L. In addition, our findings have also suggested that the arsenic removal efficiency for two layers of Mesopaper was

Table 2. The arsenic leaching rate of nano-scale powder.

pH values	Arsenic concentration ($\mu\text{g L}^{-1}$)	Arsenic leaching rate (%)
3	150	0.42
5	10	0.03
7	7.5	0.02
9	10	0.03

Note: The arsenic leaching rate were calculated as [(arsenic concentration * 100 mL)/3.56 mg].

significantly higher than that shown in one layer. We supposed that the better efficiency might be associated with the relatively much more nano-scale powder and large surface area presented in two layers of Mesopaper. Together, all above findings have suggested that the Mesopaper has highly effective in treatment of field arsenic-contaminated water.

3.2 Arsenic leaching rate

As it listed in Table 2, the arsenic leaching rate in solutions with pH values of 3, 5, 7 and 9 were all relatively low. The findings give evidence on that the nano-scale powder used in Mesopaper has no secondary arsenic pollution.

4 CONCLUSIONS

The Mesopaper has high effectiveness in treatment of field arsenic-contaminated water and without secondary arsenic pollution.

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Decrease of arsenic in water from the Pampean plain (Argentina) by calcium salts addition

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ABSTRACT: Arsenic (As) presence in groundwater from Argentinean Pampean plain is favored by high pH and Na-HCO₃ type waters. Our hypothesis was that by adding Ca to the aquifer system, pH could decrease due to calcite precipitation and As may be retained in solid phase (sediments). Batch experiments were performed on natural sediments in contact with a Na-HCO₃ solution, where CaSO₄ or CaCl₂ were added. Ca salts addition decreased down to 0.3 points of pH solution and as a result, As concentration in solution decreased. Two mechanisms are proposed. One is that a small decrease in pH enhanced As adsorption on Fe oxides. The second is that calcite precipitated and could trap As inside its structure.

1 INTRODUCTION

High arsenic (As) groundwater concentrations remain a critical concern in the Pampean plain of Argentina (Nicolli *et al.*, 2012). Groundwater from the Pampean aquifer presents a Na-HCO₃ hydrochemical signature and pH values higher than 7.5. Stratigraphic sequence in the area is composed of loess sediments which are interbedded with numerous petrocalcic layers (known as calcrete or tosca) indicating semi-arid paleoclimatic conditions (Zárate & Tripaldi, 2012). Natural occurrence of high As-bearing carbonates was reported in the literatures (Alexandratos *et al.*, 2007; Winkel *et al.*, 2013), suggesting that As retention by calcite precipitation could be a natural process in the groundwater systems of the Pampean plain. The aim of this work is two-fold: (1) to assess a potential As removal treatment based on the addition of Ca salts that induce the calcite precipitation, pH decrease, and As retention; (2) to propose the aforementioned mechanisms as the ones responsible for the high As concentrations that were measured in some tosca layers.

2 METHODS/EXPERIMENTAL

In order to verify the effectiveness of the proposed geochemical mechanisms, the experiment was simulated with the model PHREEQC (Parkhurst, 1995), by adding Ca salts to a Na-HCO₃ initial solution. This simulation allowed calculating the Ca mass needed to produce a decreasing of pH from 9 to 7.

Prior to batch experiments, a synthetic Na-HCO₃ solution was prepared with miliQ water and NaCl (EMSURE), MgCl₂ (Sigma-Aldrich) NaHCO₃ (Merck) and CaSO₄ (Merck) salts. Solution pH was adjusted with KOH.

Table 1. Textural and mineralogical characteristics of selected samples.

Sample	Minerals	Texture	Type
M12	Calcite, quartz, Na rich anorthite, Na-montmorillonite	Silt 54%, Sand 26%, Clay 20%	Tosca
M22	Quartz, calcite, Ca rich albite, Na-montmorillonite	Sand 55%, Silt 35%, Clay 10%	Sandy loess
M41	Quartz, Na rich anorthite, Na-montmorillonite	Silt 58%, Sand 27%, Clay 16%	Silty loess

Sediment samples were obtained from a 70 m deep borehole located in Tres Arroyos city, Buenos Aires province, Argentina (Sierra *et al.*, 2016). Selected samples correspond to 12, 22 and 41 m depth (M12, M22 and M41, respectively). Main features of selected samples are shown in Table 1. Sediment samples showed similar composition, although M41 is the only sample where calcite was not observed (Table 1). Previous studies showed that samples M12 and M41 are of silt grain size whereas M22 is a fine sand (Sierra *et al.*, 2016).

Five suspensions were prepared with the following solids: M12, M22, M41, M41Fe (1% of ferrihydrite added) and MQz (pure quartz sand, considered as a blank). Six 50 mL-tubes were filled with 2 g of each sample, which were washed with MiliQ-water, centrifuged and dried.

Then, 10 mL of NaHCO₃ synthetic solution with 500 µg L⁻¹ of As were added to each tube. After 24 h shaking, 3 and 7 mmol of CaSO₄ and CaCl₂ salts were added, respectively. After 48 h shaking, final pH was measured. Samples were centrifuged at 4500 rpm

Figure 1. pH variations on samples through the experiments.

Figure 2. Retained As percentages on samples through the experiments.

during 15 min and filtered with nylon membrane of $0.2\mu\text{m}$ pore. Aliquots of 5 mL were collected from each tube and acidified with HNO_3 10%. Arsenic concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS). Chloride interference was verified with an As blank solution.

3 RESULTS AND DISCUSSION

PHREEQC calculations yielded a decrease from 9.1 to 7.1 pH units in one liter of water by adding 7.9 mM of CaSO_4 or 7.5 mM of CaCl_2 .

After 48 h, samples equilibrated with Na-HCO_3 solution at an approximate pH of 8.5 without salts addition (Fig. 1). This is because carbonates, which are present in almost all samples, have buffer properties. In this sense, quartz sample (MQz) had no initial change in pH due to its low reactivity with solution. After salts addition, pH showed a slight decrease, with a maximum of 0.3 units, compared with that obtained from PHREEQC.

Regarding As retention in absence of Ca salts, samples M12, M22 and M41 retained 13, 11 and 19% of total initial As, respectively (Fig. 2). Ca addition enhanced the As retention in all samples, which increased to 51, 48 and 57%, respectively.

The addition of CaCl_2 showed slightly more efficiency than CaSO_4 in the As retention. Sample M41Fe achieved 87% of As retention in the absence of Ca salts due to the presence of ferrihydrite, which increases the specific surface area practically adsorbing the initial mass of As (Dixit & Hering, 2003). The Ca salts

addition in this sample raised the As retention in a 10% only. Sample MQz denoted an As retention of 30% by adding Ca salts, suggesting that the precipitated calcite could retain As into its structure or may adsorbed on its surface.

4 CONCLUSIONS

Ca salts addition to a synthetic water sample, similar to Pampean groundwaters, generated only a slight pH decrease. However, As retention on solid samples increased up to the double of its retaining capacity.

Although a decrease in pH favored As sorption on Fe oxides, calcite precipitation retained almost 30% of total As.

Arsenic uptake by calcite may be explained by entering calcite structure or by adsorbing on calcite surface.

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