
This is the **submitted version** of the journal article:

Inchaurrondo, Natalia; Di Luca, Carla; Haure, Patricia; [et al.]. «Evaluation of low-cost geo-adsorbents for As(V) removal». Environmental Technology and Innovation, Vol. 21 (February 2021), art. 101341. 21 pàg. Elsevier BV. DOI 10.1016/j.eti.2020.101341

This version is available at <https://ddd.uab.cat/record/307063>

under the terms of the  license

1 Evaluation of low-cost geo-adsorbents for As(V) removal

2

3 Natalia Inchaurredo^{1,*}, Carla di Luca¹, Patricia Haure¹, Gregor Žerjav², Albin Pintar², Cristina
4 Palet³

5

6 ¹*Department of Chemical Engineering, Institute of Materials Science and Technology*
7 *(INTEMA), University of Mar del Plata and National Research Council (CONICET), Av. J. B.*
8 *Justo 4302, 7600 Mar del Plata, Argentina*

9 ²*Laboratory for Environmental Sciences and Engineering, Department of Inorganic Chemistry*
10 *and Technology, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia*

11 ³*Centre Grup de Tècniques de Separació en Química, Department of Chemistry, Universitat*
12 *Autònoma de Barcelona, 08193 Barcelona, Catalunya, Spain*

13

14 **Abstract** – Four low-cost iron-bearing geo-adsorbents were tested for As(V) removal without
15 pretreatment: Montanit300[®] (M), diatomite (D), pumice (P) and black sand (BS). The solids
16 were carefully characterized by different analytical techniques (SEM-EDX, TPD-pyridine, N₂
17 Physisorption, XRD and point of zero charge). The adsorption of As(V) was evaluated through
18 isotherms and kinetic studies (bottled water matrix, pH₀=8, 25g/L of solids), and experiments
19 addressing pH effect (pH₀=3.6, 7.5, 11) and the presence of interfering anions (Cl⁻, SO₄²⁻, NO₃⁻
20 , PO₄³⁻). Experimental results were fitted to the Freundlich and Langmuir sorption isotherms.
21 Under the employed conditions, P showed negligible adsorption, M and D presented adsorption
22 capacities around 0.02 mg/g and, in spite its lower surface area, BS displayed the highest value
23 (0.045 mg/g), which relates to a higher density of Fe species. M and D samples were easily
24 regenerated (80-100 % desorption) through a basic treatment (0.01 M NaOH) and presented

*Corresponding author. *E-mail address:* ninchaurredo@gmail.com.

1 fast adsorption kinetics (1 h for D and seconds for M). BS showed a slow adsorption kinetic
2 (24 h) and poor regeneration (only 50% desorption). Sample M (natural zeolite) resulted a
3 promising option due to its remarkably fast adsorption kinetic, easy regeneration and adsorption
4 capacity suitable for systems with relatively low As concentrations.

5

6 **Keywords:** geo-adsorbents, As(V) removal, adsorption mechanism, Fe-bearing minerals

7

8 **1. Introduction**

9 **The occurrence of arsenic in underground and surface water resources is of great concern**
10 **since it represents a high risk for human health. Arsenic has been linked to skin and**
11 **vascular diseases, liver, bladder, lung, kidney and prostate cancer (Palma-Lara et al.**
12 **2020). Hence, the World Health Organization has suggested a limit of 10 ppb for drinking**
13 **water (WHO, 2011). The presence of As in the environment is commonly triggered by**
14 **biological activity, geochemical and weathering reactions, volcanic emissions and**
15 **anthropogenic activities such as petroleum refineries, mining/smelting operations,**
16 **manufacture of certain ceramics or glass, and the use of pesticides and fertilizers (Litter**
17 **et al. 2010). In Argentina, the presence of arsenic in water is a serious problem which**
18 **centers the attention of many research groups, focusing their studies on arsenic**
19 **distribution in different areas of the country and water remediation (Litter et al. 2010).**

20 The removal of arsenic in large scale is usually achieved by coagulation/precipitation reactions
21 using Fe or Al salts, generating a great amount of sludge as unwanted waste. **Therefore, the**
22 **implementation of cleaner processes such as membrane filtration, bioremediation or**
23 **adsorption technologies has been impelled. Among them, the adsorption process results a**
24 **very promising alternative owing to its easy operation; reduced cost; no chemical**
25 **requirement; no sludge generation; low energy consumption and regeneration capability**

1 **(Burakov et al. 2018). Based on these features, a wide diversity of materials have been**
2 **studied as adsorbents for the removal of organic and inorganic pollutants: granular**
3 **activated carbon (GAC) (Kalaruban et al. 2019); activated alumina (Ghosh and Gupta**
4 **2012); waste carbonaceous materials (Singh et al. 2020); polymeric adsorbents (Wei et al.**
5 **2018; Liu et al. 2020); magnetite nanoparticles (Gu et al. 2018; Wang et al. 2018); iron**
6 **oxide based sorbents (Siddiqui and Chaudhry 2017); bio-adsorbents and biochar (Gupta**
7 **et al. 2015; Suhas et al. 2016; Zhao et al. 2020). In particular, the adsorption technology**
8 **is highly appropriate when sophisticated and expensive techniques cannot be applied,**
9 **which is the situation of populations with low economical resources. Accordingly, several**
10 **strategies have emerged, such as the preparation of adsorbents from waste materials**
11 **(Gupta et al. 2015; Ahmaruzzaman and Gupta 2011) or the use of cost-effective naturally-**
12 **occurring adsorbent materials (Asere et al. 2019), which is the topic of the present study.**

13 Several authors investigated the use of soils (Maji et al. 2007; Boglione et al. 2019),
14 diatomites (Danil de Namor et al. 2012), sand (Bajpai and Chaudhuri 1999; Thirunavukkarasu
15 et al. 2003), clays (Manning 1996; Zehhaf et al. 2015), and zeolites (Elizalde-González et al.
16 2001) in adsorption processes. However, most studies focused on the modification of these
17 natural adsorbents through diverse techniques (impregnation, acid/base treatments) and the
18 usage of the raw materials has not been studied in equal depth.

19 Oxides and hydroxides of iron, aluminum and manganese, which have shown high
20 affinity towards As, exist ubiquitously in natural environments. **Therefore, the use of these**
21 **raw materials without preliminary modifications is an interesting and practical option**
22 **that could decrease the cost of the adsorption process and ease its implementation. The**
23 **element which best associates with As in geo-adsorbents is Fe, due to its high abundance**
24 **and strong binding affinity (Siddiqui and Chaudhry 2017; Smedley and Kinniburgh 2002).**
25 Accordingly, this study focuses on the screening and comparison of four natural Fe-bearing

1 materials of different characteristics: pumice, diatomite, black sand, and Montanit300[®], for
2 As(V) removal. These materials have been previously tested as catalysts in the Fenton-Like
3 reaction, showing promising results regarding the mineralization of organic pollutants
4 (Inchaurrondo et al. 2018).

5 Diatomite is a sedimentary rock composed of microfossils of aquatic algae. It **contains**
6 a large quantity of silica in its structure and the acid sites **present** on its surface are associated
7 to clay impurities with a high content of Al or Fe, **elements** which have shown high affinity
8 towards As in adsorption processes (Danil de Namor et al. 2012). Several studies have reported
9 the use of diatomite for arsenic removal, but generally modified by iron and/or manganese
10 addition (Danil de Namor et al. 2012). In this work, we propose to study the raw material, since
11 the Fe present in its structure proved to be available and active for the catalytic oxidation of
12 organic compounds (Inchaurrondo et al. 2018).

13 **Pumice is a highly porous volcanic rock with an elevated silica content, which has**
14 **been tested for the adsorption of different organic and inorganic pollutants (Çifçi and**
15 **Meriç 2016), typically as a support material or modified through different techniques.** In
16 comparison to other studied samples (Çifçi and Meriç 2016), the pumice chosen in this work
17 presents a rather high content of Al and Fe species (**Inchaurrondo et al. 2018**).

18 Natural aluminosilicate Montanit300[®] (Montana Žalec, Slovenia) is mostly composed
19 of quartz and natural zeolites like clinoptilolite and heulandite. Some authors studied the
20 application of synthesized or modified zeolites for As removal, frequently through the addition
21 of iron (Bilici Baskan and Pala 2011; Shevade and Ford 2004; Šiljeg et al. 2012). As mentioned
22 before, the use of the raw material has not been studied in equal depth. Natural zeolites have
23 shown a good ion-exchange capacity for cations, releasing non-toxic ions (K⁺, Na⁺, Ca²⁺ and
24 Mg²⁺) to the environment. In the case of anions, the retention in zeolites cavities has been

1 connected to strong interactions with extra-framework cations and Brønsted acid sites
2 (Uzunova and Mikosch 2016).

3 The black sand used in this study was collected in Praia Preta, Ilha Grande (Brazil) and
4 it is essentially composed of ilmenite, hematite and quartz (**Inchaurrondo et al. 2018**). **The**
5 **use of quartz sand (inert support) modified through the addition of iron has been reported**
6 **for arsenic removal at laboratory or higher scale (Thirunavukkarasu et al. 2003). In**
7 **contrast** to the quartz sand frequently studied, a composition rich in Fe species characterizes
8 the sample chosen in this work, which is expected to promote As removal.

9 **The novelty of this work lies in the comparison of cost-effective geo-adsorbents, all**
10 **widely available, but with different surface structure and composition, in order to select**
11 **the most efficient material based on adsorption capacity, kinetics and regeneration**
12 **capability. The comparison of the materials was performed taking into consideration that**
13 the adsorption process depends on the surface characteristics (specific surface area, surface
14 acidity and point of zero charge) and composition of the adsorbents, the water pH and the
15 presence of interfering ions.

16

17 **2. Experimental**

18

19 *2.1. Materials*

20 Na₂HAsO₄·7H₂O (Aldrich), NaOH, HNO₃ (70% wt/wt, Cicarelli), NaCl (100%, WWR
21 Chemicals), NaNO₃ (99%, Aldrich), Na₂SO₄ (99%, Panreac), Na₂HPO₄·7H₂O (Aldrich),
22 CH₃COONa·3H₂O (>99%, Panreac) and CH₃COOH (>99% ACS, Aldrich) were used as
23 received.

24

25 *2.2. Natural materials employed*

1 Pumice (P) and diatomite (D) were acquired from a native supplier (Argentina, Marysol). The
2 black sand (BS) was collected from Praia Preta (Ilha Grande, Brazil) and the natural
3 aluminosilicate Montanit300[®] (M) was obtained from Montana Žalec, Slovenia. All samples
4 were carefully washed with distilled water, dried during 48 h at room temperature and 24 h at
5 60°C, and then ground into dust to **minimize** diffusional restrictions.

6

7 *2.3. Characterization of the natural materials*

8 The characterization methodology concerning the point of zero charge (pH_{PZC}), powder X-ray
9 diffraction (XRD), emission scanning electron microscope and energy-dispersive X-ray
10 analysis (SEM-EDX), specific surface area and pore size distribution by N₂ Physisorption and
11 density of acid sites by temperature programmed desorption (TPD) of pyridine, were reported
12 in previous studies by Inchaurredo et al. (Inchaurredo et al. 2018; Inchaurredo et al. 2017).

13

14 *2.4. Batch experiments*

15 Adsorption tests were performed with a solid concentration of 25 g/L. The suspensions were
16 shaken on a rotary mixer at room temperature. Aiming to test a more realistic condition, the As
17 solutions were prepared using a bottled water matrix (Font Vella, Barcelona), which according
18 to its label contained: 143 mg/L bicarbonates, 12.5 mg/L Na, 11.3 mg/L Mg, 42 mg/L Ca, with
19 a conductivity of 286 $\mu\text{S}/\text{cm}$. For the sake of comparison, As(V) adsorption experiments were
20 also performed over a ultrapure Milli-Q water matrix. The solid adsorbents were separated by
21 filtration (RC 0.45 μm syringe filter).

22 As(V) adsorption isotherms were obtained at the equilibrium pH value reached naturally
23 for each adsorbent. The As(V) isotherms were evaluated at a concentration range between 0.5
24 and 6 mg/L.

1 The kinetic studies were performed considering different time intervals according to the
2 above method. The initial concentration of arsenic was set at 1 mg/L and the sampling time was
3 adjusted according to the rate of As removal for each solid sample.

4 To determine whether the natural adsorbents can be reused, desorption tests were
5 performed by adding the used adsorbent (charged with As(V)) to NaOH (0.01 M) or HNO₃
6 (0.01 M) solutions in Milli-Q water, with a solid concentration of 25 g/L, as in the adsorption
7 tests. Afterwards, the suspensions were shaken for 24 h and separated by filtration (RC 0.45
8 µm syringe filter).

9 The influence of **the** initial pH value on measured data was assessed in adsorption tests
10 with 1 mg/L As solutions. The value of the starting pH was adjusted with NaOH (0.1 M) or
11 acetate buffer (0.02 M) to regulate at pH=11 or pH=3.7, respectively.

12 Additionally, the influence of anion interference was studied for As(V) solutions of 1
13 mg/L prepared with Milli-Q water, by using an As:anion molar ratio of 1:25. The investigated
14 anions were Cl⁻, SO₄²⁻, NO₃⁻ and PO₄³⁻.

15 At the end of the experiments, the final pH value was registered to be reported
16 throughout the work as **the adsorption equilibrium pH** (pH_{eq}).

17

18 *2.5. Analytical measurements*

19 Arsenic concentration was determined by Inductively Coupled Plasma Mass Spectrometry,
20 ICP-MS (XSERIES 2 ICP-MS, Thermo Scientific, USA).

21 The reported values are the average of at least two measurements, and error bars
22 represent the standard deviation.

23

24 **3. Results and discussion**

25

1 3.1. Characterization of adsorbents

2 The materials were characterized in a previous study, where the natural samples were used for
3 catalytic purposes in the heterogeneous Fenton-like reaction (Inchaurreondo et al. 2018;
4 Inchaurreondo et al. 2017).

5 Table 1 presents BET specific surface area and TPD-pyridine results for all the studied
6 samples. Two of the materials selected, black sand and pumice, presented rather low surface
7 areas (0.5-1 m²/g). On the other hand, Montanit300[®] and diatomite showed significantly higher
8 values, 36 and 133 m²/g, respectively. Regarding the TPD-pyridine experiments, the adsorption
9 of pyridine was very low, which was related to the relatively reduced BET specific surface areas
10 observed. In the case of diatomite, its higher surface area enabled an increased hydroxyl groups
11 exposure to pyridine and therefore, the amount of acidic sites (mmol/g) measured **was higher**
12 **than the values obtained with the other samples**. Montanit300[®] showed a higher density of
13 acidic sites (mmol/m²) which correlates to its higher content of Al and Fe (Table 2).

14 **The point of zero charge was similar between samples, in the case of pumice (8.7),**
15 **diatomite (8.5) and Montanit300[®] (8.9). The black sand showed a lower value: pH_{pzc} = 7.9.**

16 The SEM-EDX results (Table 2) showed a majority of Si, Al and Fe oxides, with minor
17 mineral impurities, such as Ca, Ti, Na, Mn, K and Mg. Pumice, diatomite and Montanit300[®]
18 samples presented a composition mostly based on SiO₂. On the other hand, the black sand
19 showed a composition quite different, centered in the presence of Fe and Ti oxides.

20 According to XRD results, pumice is primarily composed of an **abundant amorphous**
21 **phase of SiO₂**, plagioclase (feldspar, which composition ranges from NaAlSi₃O₈ (Albite) to
22 CaAl₂Si₂O₈ (Anorthite)), quartz crystals, phyllosilicates, cristobalite and calcium carbonate
23 (Inchaurreondo et al. 2018). The black sand showed the presence of quartz, ilmenite (titanium-
24 iron oxide mineral, weakly magnetic) and hematite (common iron oxide, Fe₂O₃) (Inchaurreondo
25 et al. 2018). **The Montanit300[®] sample exhibited the presence of natural zeolites, mainly**

1 heulandite $(\text{Ca}_{3.6}\text{K}_{0.8}\text{Al}_{8.8}\text{Si}_{27.4}\text{O}_{72}\times 26.1\text{H}_2\text{O})$ and clinoptilolite
2 $(\text{(Na,K,Ca)}_6\text{(Si,Al)}_{36}\text{O}_{72}\times 20\text{H}_2\text{O})$, but also quartz and phyllosilicates (Inchaurredo et al.
3 2018). The diffractogram of diatomite showed the presence of albite ($\text{NaAlSi}_3\text{O}_8$), nontronite
4 (Fe(III) rich member of the smectite group in clay minerals) and quartz as main components
5 (Inchaurredo et al. 2017). It was also identified the amorphous silica phase (opaline silica)
6 characteristic of diatom frustules.

7

8 *3.2. Preliminary As(V) adsorption results*

9 Preliminary As(V) adsorption studies were performed in 24-h tests, using Milli-Q water at
10 initial pH=7.5, with As(V) concentration of 6 mg/L. These preliminary screening tests were
11 executed in order to choose the materials with higher adsorption capacity.

12 Pumice showed negligible adsorption (0.0037 mg/g) under the given experimental
13 conditions. According to the characterization results, pumice presents not only a lower surface
14 area but also a lower content of Fe impurities, specie that promote arsenic adsorption. Pumice
15 is mostly composed of amorphous silica; therefore, its surface is covered by inert silanol groups,
16 which have shown low affinity towards arsenic (Shevade and Ford 2004). Consequently,
17 pumice was not considered for further studies.

18 Among the materials tested, black sand showed the highest adsorption capacity (0.021 mg/g).
19 However, unlike the other materials, its final equilibrium pH value was found to be lower than
20 its pH_{PZC} ($\text{pH}_{\text{eq}} = 7.5$). The hydroxyl functional groups form on the hydrated surface of the
21 studied minerals can protonate ($\text{pH} < \text{pH}_{\text{PZC}}$) or deprotonate ($\text{pH} > \text{pH}_{\text{PZC}}$), causing variations in
22 the surface charge, which depends on the pH of the aqueous medium. This analysis must be
23 correlated to the speciation state of the arsenic molecules, which also depends on solution pH.
24 The equilibrium dissociation constants of H_3AsO_4 (As (V)) are: $\text{pK}_{\text{a}1}=2.19$, $\text{pK}_{\text{a}2}=6.94$, and
25 $\text{pK}_{\text{a}3}=11.5$. In the case of black sand, $\text{pH}_{\text{eq}} < \text{pH}_{\text{PZC}}$ favored the adsorption of arsenic since the

1 arsenate anion ($\text{pH}_{\text{eq}} > \text{pK}_{\text{a}2}$) interacted through coulombic forces with the positively charged
2 surface.

3 The different adsorption capacities observed for diatomite (0.013 mg/g) and
4 Montanit300[®] (0.0062 mg/g) samples could relate to the different equilibrium pH values
5 reached: 9.9 for Montanit300[®] and 8.6 for diatomite. Then, Montanit300[®] reached equilibrium
6 at a much more basic pH value, which is detrimental for the arsenic adsorption process.

7 To further compare the behavior of the materials under similar conditions, the
8 subsequent isothermal measurements were performed at equal equilibrium pH using a more
9 realistic water matrix elaborated with bottled water.

10

11 *3.3. As(V) isotherms in a bottled water matrix*

12 Isotherms were determined using bottled water at initial pH=8. The ions present in the water
13 matrix buffered the pH variations caused by the addition of the solid samples. The final
14 equilibrium pH value reached for all examined samples remained between 7.8 and 8.2. To
15 assure equilibrium, the contact time was prolonged up to 48 h, **which agrees with the kinetic**
16 **results obtained (see section 3.4). Results are presented in Fig. 1.**

17 The outcomes suggest that the surface area is not the governing factor for As(V)
18 adsorption, **but** the chemical composition of the adsorbents.

19 Previous studies have shown that the major surface functional groups in soils and natural
20 inorganic materials are the siloxane groups linked to the plane of oxygen atoms bound to the
21 silica tetrahedral layer present on phyllosilicates, and the OH-groups associated with the edges
22 of inorganic minerals such as metal oxides, oxyhydroxides, hydroxides, kaolinite and
23 amorphous materials (Sparks 2003). Spectroscopic analyses of the crystal structures of oxides
24 and clays showed that different types of OH-groups have different reactivity (Sparks 2003).
25 Therefore, the composition of the samples, such as the content of amorphous SiO₂, Al or Fe

1 clay impurities or oxides, determines the capacity and strength of adsorption.

2 On the subject of the removal mechanism on hydroxyl sites, arsenic adsorption may
3 proceed through ligand exchange with OH^- and OH_2^+ functional groups, leading to complex
4 formation. For example, partial dissociation of H_3AsO_4 releases H^+ ions which form H_2O with
5 OH^- and leave space for arsenate binding (Siddiqui and Chaudhry 2017). Also, the
6 complexation may proceed through either physisorption or chemisorption processes and As
7 may attach the oxide surface via intramolecular or extra-molecular interactions (Siddiqui and
8 Chaudhry 2017), which will be discussed later.

9 The highest adsorption capacity was shown by the black sand, which presented the
10 lowest superficial area, but a composition quite different compared to diatomite and
11 Montanit300[®], which are mostly based on Si oxides. As mentioned previously, silanol surface
12 groups show low affinity towards As (Shevade and Ford 2004). The black sand presented a
13 high content of Fe species (mainly ilmenite and hematite) and according to several authors,
14 iron-containing compounds present higher affinity towards arsenate compared to non-iron
15 compounds (Youngran et al. 2007). For example, Elizalde-Gonzalez et al. (2001) related the
16 adsorption capacity of clinoptilolite rich tuffs to the iron content of the samples. Taking into
17 account these characteristics and adsorption results, it can be deduced that **the** iron species
18 present in black sand are responsible for the highest adsorption observed. However, a small
19 quantity of red sludge was detected. Hence, co-precipitation of secondary oxides with the target
20 metal(loid) (e.g., $\text{FeAsO}_4 \times \text{H}_2\text{O}$, $\text{FeAsO}_4 \times 2\text{H}_2\text{O}$, and $\text{Fe}_3(\text{AsO}_4)_2$) could be a key step in the
21 removal of As using this material (Komárek et al. 2013).

22 Montanit300[®] and diatomite showed similar adsorption capacity per mass unit of
23 adsorbent. However, if the uptake of arsenic is considered per square meter of adsorbent,
24 Montanit300[®] showed a higher affinity. The lower adsorption onto diatomite could be due to
25 the lower density of reactive hydroxyl edge sites in spite of its larger specific surface area.

1 Montanit300[®] showed a higher density of acidic sites (mmol/m²) and content of Fe and Al. The
 2 relatively high concentration of terminal Al–OH or Fe–OH species present in natural zeolites
 3 with medium/low Si/Al ratio, has been linked to its greater ability for ligand exchange;
 4 moreover, those surface groups may represent the principal reactive sites for the adsorption of
 5 As(V) (Shevade and Ford 2004).

6 The isotherms of the three materials fit the Freundlich model (Equation 1), which
 7 describes non-ideal and reversible adsorption.

$$8 \quad q_e = K_F * C_e^n \quad (1)$$

9 The adsorption coefficient, K_F , is connected to the adsorption strength. The exponent n
 10 defines the isotherm curvature and the saturation speed . When $n < 1$ the isotherm shows a
 11 relative high adsorbent loading at low adsorbate concentrations, which corresponds to favorable
 12 isotherms.

13 According to the Freundlich model (Table 3), all materials presented favorable
 14 isotherms ($n < 1$). As expected, the black sand exhibited higher K_F , while diatomite and
 15 Montanit300[®] samples presented similar values. These results are directly related to the
 16 adsorption capacities observed.

17 Additionally, the Langmuir equation was evaluated (Equation 2). This model assumes
 18 that the adsorbent surface presents a fixed number of accessible sites with the same energy
 19 (Langmuir 1918). However, this model is not valid for heterogeneous surfaces found in soils
 20 (Sparks 2003) and **should only be** used for qualitative comparisons.

$$21 \quad q_e = \frac{Q_m * K_L * C_e}{1 + K_L * C_e} \quad (2)$$

22 Q_m (mg/g) is defined as the maximum saturated monolayer adsorption capacity and K_L
 23 (L/mg) is related to the adsorbent/adsorbate affinity. Consequently, good adsorbents display
 24 high Q_m and a steep initial sorption isotherm slope (high K_L).

1 As it was observed for the Freundlich model, the Langmuir parameters obtained for
2 black sand were remarkably better, since they showed a higher maximum saturated monolayer
3 adsorption capacity (Q_m) and affinity towards the adsorbate (K_L) (Table 3). Diatomite and
4 Montanit300[®] presented similar parameters. As described previously, if the parameters are
5 considered per square meter of adsorbent (Q'_{max}), Montanit300[®] showed higher affinity towards
6 As(V) compared to diatomite, which is related to its higher density of acidic sites (mmol/m²)
7 and content of Fe and Al.

8 The maximum saturated monolayer adsorption capacity values observed in this study
9 ($Q_{max}=0.065-0.033$ mg/g) are in agreement with some of the results obtained with other
10 materials of natural origin and used without any pretreatment, **such as presented in Table 4.**
11 **The higher adsorption values observed for some of these natural materials are related to**
12 **their amorphous nature (higher surface area and density of hydroxyl sites) and higher**
13 **aluminum and/or iron content. In addition, water matrix and pH may differ between tests.**
14 **Since the adsorption capacities are much lower for unmodified natural materials, a**
15 **greater amount of adsorbent may be required to achieve the recommended arsenic levels.**
16 **Then, these materials are suited for systems with relatively low As concentrations (µg/L**
17 **levels) such as leachates from altered rocks (Tabelin et al. 2014). Moreover, the higher**
18 **adsorbent load requirement can be compensated by the lower cost of these raw materials**
19 **and the avoidance of the environmental impact (CO₂ emission) related to the modification**
20 **or synthesis of more sophisticated materials**

21

22 3.4. As(V) kinetics curves

23 Previous studies have reported the existence of a wide time scale for soil chemical reactions,
24 which ranges from microseconds to years (Sparks 2003). Ion association (ion pairing,
25 complexation, and chelation-type reactions in solution), ion exchange and some sorption

1 reactions may take **remarkable short times**, ranging from microseconds **to** milliseconds. On
2 the other hand, mineral solution (precipitation/dissolution reactions including discrete mineral
3 phases) and mineral crystallization reactions can take years. Moreover, these reactions can
4 occur simultaneously and consecutively (Sparks 2003). Taking this into consideration, kinetic
5 studies were performed to study the feasibility of adsorption processes with the proposed
6 materials, hoping to obtain short reaction times. Tests were executed with As(V) concentration
7 of 1 mg/L in a bottled water matrix. The obtained results are presented in Fig. 2.

8 The adsorption of arsenic was practically instantaneous in the case of Montanit300[®]. **A**
9 **fast solute removal** as well as a low equilibration time are connected to highly favorable
10 sorptive interactions. The faster uptake could be connected to a higher surface area, in contrast
11 to the black sand and also a higher density of acidic sites (mmol/m²), in comparison to
12 diatomite. Furthermore, Montanit300[®] presents a higher content of Fe and Al. As mentioned
13 before, a higher concentration of terminal Al–OH species in low Si/Al ratio zeolites enhances
14 ligand exchange reactions (Shevade and Ford 2004). Another likely mechanism for the removal
15 of anions in zeolites could involve the interaction with extraframework cations (such as
16 Na⁺, Ca²⁺ or Mg²⁺), forming the corresponding salt in the voids of the zeolite (Uzunova and
17 Mikosch 2016).

18 As it can be seen in Fig.2-b, diatomite reaches equilibrium after only one hour, probably
19 due to its high surface area and pore volume. The black sand reaches equilibrium after
20 approximately 24 h. In spite of showing a high content of Fe species, its surface area is very
21 low.

22 After the first hour, diatomite, Montanit300[®] and black sand showed similar adsorption
23 values of 0.005, 0.006 and 0.005 mg/g, respectively. After two days, black sand reached a final
24 equilibrium value of 0.016 mg/g (2.7 times higher).

1 To evaluate the sorption rates, empirical pseudo-first (Equation 3) and pseudo-second
2 order (Equation 4) equations were adopted to model the experimental data (Table 3).

$$3 \frac{dq_t}{dt} = k_1 * (q_e - q_t) \quad (3)$$

$$4 \frac{dq_t}{dt} = k_2 * (q_e - q_t)^2 \quad (4)$$

5 The constants k_1 (1/min) and k_2 (g/(mg min)) are the pseudo-first order and the pseudo-
6 second order rate constants, respectively, while q_t and q_e are the arsenic adsorption amounts
7 (expressed in mg/g) at any time (t (min)) and at equilibrium, respectively.

8 Since adsorption was instantaneous in the case of Montanit300[®], the results did not fit
9 any of the two models. Black sand and diatomite fit reasonably both models (Table 3). The
10 kinetic constant obtained for black sand is quite low and even though the adsorption capacity
11 is higher, a slow kinetic is an unfavorable characteristic for an appropriate adsorbent material.
12 The red sludge observed could be associated to the slower kinetics shown by the formation of
13 surface precipitates (Sparks 2003).

14 In the case of Montanit300[®], the uptake of arsenic was instantaneous (seconds or
15 milliseconds). Similar studied materials such as natural or modified zeolites, presented much
16 larger equilibration times, from minutes to hours or days (Bilici Baskan and Pala 2011;
17 Elizalde-González et al. 2001; Jiménez-Cedillo et al. 2009; Shevade and Ford 2004; Šiljeg et
18 al. 2012).

21 3.5. pH effect in As(V) adsorption

22 The pH effect was addressed in order to understand the nature of **the** arsenic-adsorbent
23 interactions. The adsorption capacity and final equilibrium pH are presented in Figs.3 a)-b).
24 According to these results, in the case of diatomite, the adsorption capacity is less influenced
25 by pH changes, since a relative variation of only 16% was measured for adsorption levels at

1 different pH values. Arsenic removal may not be strongly related to electrostatic interactions in
2 this case. Black sand and Montanit300[®] showed higher adsorption levels under acidic pH. Low
3 pH values generate the protonation of surface hydroxyl groups to $-\text{OH}_2^+$, which facilitates the
4 ligand exchange since H_2O is easier to displace from metal binding sites than OH^- (García-
5 Sanchez et al. 2002). This effect was more notorious in the case of black sand, which also
6 sustains significant levels of adsorption even under neutral or slightly basic pH conditions (7.5-
7 8.0), which is a common value in underground and surface water resources. The fact that there
8 is still some adsorption when the pH value is higher than pH_{PZC} , can be attributed to a specific
9 inner sphere bonding of arsenate to the surface of the solid.

10 The adsorption capacity drastically drops at pH values higher than 8 in the case of
11 Montanit300[®]. The pH dependency indicates a strong electrostatic attraction mechanism, which
12 means that arsenic oxyanions are mostly adsorbed non-specifically by strong electrostatic
13 interactions.

14

15

16

17 *3.6. Anions interference*

18 The influence of different anions in the adsorption of As(V) using a Milli-Q water matrix is
19 shown in Fig. 4. It is important to highlight that different equilibrium pH values were reached
20 at the end of the tests for each material: 9.7 for Montanit300[®], 7.4 for black sand and 8.6 for
21 diatomite.

22 Phosphate and arsenate present similar structure (charge and same tetrahedral
23 configuration) and compete for binding sites (Youngran et al. 2007), which explains the 90 %
24 removal reduction registered for all the materials tested with ultrapure water spiked with
25 phosphate.

1 Under the employed operating conditions, the addition of the other anions, NO_3^- , SO_4^{2-}
2 and Cl^- did not cause a significant variation on As(V) adsorption in comparison to PO_4^{3-} .
3 Relative variabilities of 14, 12 and 6%, were registered regarding arsenic removal in Milli-Q
4 water or NO_3^- , SO_4^{2-} and Cl^- containing solutions, for Montanit300[®], diatomite and black sand,
5 respectively. Other authors observed similar results, although this observation depends on both
6 concentration and pH values. The complexes formed with these anions (nitrate, sulphate and
7 chloride) resulted much weaker than those formed with arsenate (Youngran et al. 2007).

8

9 *3.7. Desorption tests*

10 Desorption tests using HNO_3 and NaOH (Table 5), showed that the black sand is difficult to
11 regenerate (only 17 to 49 % recovered). The arsenic that was not leached was probably either
12 strongly adsorbed (inner sphere complex) or co-precipitated with iron oxide species. The
13 adsorption through inner-sphere complexation is not greatly influenced by the alteration of
14 solution ionic strength, compared to outer-sphere complexation (Hua 2018). However, the pH
15 dependency observed before indicates a strong electrostatic attraction mechanism step.
16 Consequently, it is possible that the arsenic oxyanions are predominantly adsorbed non-
17 specifically by a strong electrostatic interaction, followed by inner-sphere complexation
18 between arsenic oxyanions and OH-groups on the surface of the adsorbent (Hua 2018).

19 Diatomites showed a high and equal level of As desorption under acidic or basic pH.
20 This is very well related to the observed insensitivity of the material towards pH changes. The
21 arsenic sorption through weak physical interactions may be the main mechanism responsible of
22 this behavior.

23 In the case of Montanit300[®], arsenic was totally desorbed under alkaline conditions. As
24 it was observed in tests where the pH effect was assessed, arsenic adsorption was highly
25 inhibited under basic pH values. Therefore, this behavior can be explained by taking into

1 consideration the electrostatic interaction and ion exchange mechanism that may prevail in the
2 case of this material.

3

4 **4. Conclusions**

5 Four different iron-bearing geo-adsorbents were selected to be tested for As(V) removal
6 without any pretreatment: Montanit300[®] (M), diatomite (D), pumice (P) and black sand (BS).

7 The following conclusions were drawn:

- 8 ➤ Surface area was not the dominating factor for adsorption capacity, but the chemical
9 composition of the adsorbents.
- 10 ➤ P exhibited negligible adsorption due to its lower content of Fe or Al impurities and
11 surface area.
- 12 ➤ BS presented a low surface area, but the highest content of Fe species, which resulted
13 in the highest adsorption capacity (0.045 mg/L) with a slow kinetic (24 h).
- 14 ➤ M and D presented similar adsorption capacities (0.02 mg/g).
- 15 ➤ M showed the fastest solute removal (seconds), which was related to its higher density
16 of acidic sites (mmol/m²).
- 17 ➤ Only phosphate ions showed a negative effect on the adsorption process.
- 18 ➤ The pH effect was only relevant for BS and M (adsorption increased under acidic pH).
- 19 ➤ Desorption was achieved for D (80-85 %) and M (100 %) samples, but not for BS (50%).
- 20 ➤ M showed the most promising features: remarkably fast adsorption kinetic and easy
21 regeneration.
- 22 ➤ The materials are suited for systems with relatively low As concentrations (µg/L levels)
23 such as leachates from altered rocks.

24

25 **Acknowledgements** - This work was supported by CONICET, UNMdP, Marie Skłodowska-
26 Curie Actions: Research and Innovation Staff Exchange (RISE) under the title “Advanced

1 multifunctional materials applied to remove arsenic in Argentinian groundwater”
 2 (NANOREMOVAS project n.645024). We also want to express our gratitude to Dr. P.
 3 Caracciolo for his technical support.

4

5 References

- 6 • Ahmaruzzaman, M., Gupta, V.K., 2011. Rice husk and its ash as low-cost adsorbents in water
 7 and wastewater treatment. *Ind. Eng. Chem. Res.* 50, 13589–13613.
 8 [dx.doi.org/10.1021/ie201477c](https://doi.org/10.1021/ie201477c).
- 9 • Asere, T.G., Stevens, C.V., Laing, G.D., 2019. Use of (modified) natural adsorbents for arsenic
 10 remediation: A review. *Science of The Total Environment.* 676, 706–720.
 11 <https://doi.org/10.1016/j.scitotenv.2019.04.237>.
- 12 • Bajpai, S., Chaudhuri, M., 1999. Removal of Arsenic from Ground Water by Manganese
 13 Dioxide–Coated Sand. *Journal of Environmental Engineering.* 125, 782–784.
 14 [https://doi.org/10.1061/\(ASCE\)0733-9372\(1999\)125:8\(782\)](https://doi.org/10.1061/(ASCE)0733-9372(1999)125:8(782)).
- 15 • Bentahar, Y., Hurel, C., Draoui, K., Khairoun, S., Marmier, N., 2016. Adsorptive properties of
 16 Moroccan clays for the removal of arsenic (V) from aqueous solution. *Applied Clay Science*
 17 119, 385–392. <https://doi.org/10.1016/j.clay.2015.11.008>.
- 18 • Bilici Baskan, M., Pala, A., 2011. Removal of arsenic from drinking water using modified
 19 natural zeolite. *Desalination.* 281, 396–403 <https://doi.org/10.1016/j.desal.2011.08.015>.
- 20 • Boglione, R., Griffa, K., Panigatti, M.C., Keller, S., Schierano, M.C., Asforno, M., 2019.
 21 Arsenic adsorption by soil from Misiones province, Argentina. *Environ. Technol. Innov.* 13, 30–
 22 36. <https://doi.org/10.1016/j.eti.2018.10.002>.
- 23 • Burakov, A.E., Galunin, E.V., Burakova, I.V., Kucherova, A.E., Agarwal, S., Tkachev, A.G.,
 24 Gupta, V.K., 2018. Review: Adsorption of heavy metals on conventional and nanostructured
 25 materials for wastewater treatment purposes: A review. *Ecotoxicology and Environmental*
 26 *Safety.* 148, 702–712. <https://doi.org/10.1016/j.ecoenv.2017.11.034>.
- 27 • Çifçi, D.İ., Meriç, S., 2016. A review on pumice for water and wastewater treatment.
 28 *Desalination and Water Treatment.* 57, 18131–18143.
 29 <https://doi.org/10.1080/19443994.2015.1124348>.
- 30 • Danil de Namor, A.F., El Gamouz, A., Frangie, S., Martinez, V., Valiente, L., Webb, O.A.,
 31 2012. Turning the volume down on heavy metals using tuned diatomite. A review of diatomite
 32 and modified diatomite for the extraction of heavy metals from water. *Journal of Hazardous*
 33 *Materials.* 241–242, 14–31. <https://doi.org/10.1016/j.jhazmat.2012.09.030>.
- 34 • Elizalde-González, M.P., Mattusch J., Wennrich R., Morgenstern P., C., 2001. Uptake of
 35 arsenite and arsenate by clinoptilolite-rich tuffs. *Microporous and Mesoporous Materials.* 46,
 36 277–286. [https://doi.org/10.1016/S1387-1811\(01\)00308-0](https://doi.org/10.1016/S1387-1811(01)00308-0).
- 37 • García- Sanchez, A., Alvarez-Ayuso, E., Rodriguez-Martin, F., 2002. Sorption of As(V) by
 38 some oxyhydroxides and clay minerals. Application to its immobilization in two polluted
 39 mining soils. *Clay Minerals.* 37, 187–194. <https://doi.org/10.1180/0009855023710027>.
- 40 • Ghosh, D., Gupta, A., 2012. Economic justification and eco-friendly approach for regeneration
 41 of spent activated alumina for arsenic contaminated groundwater treatment. *Resources,*
 42 *Conservation and Recycling.* 61, 118–124. <https://doi.org/10.1016/j.resconrec.2012.01.005>.
- 43 • Gu, H., Xu, X., Zhang, H., Liang, C., Lou, H., Ma, C., Li, Y., Guo, Z., Gu, J., 2018. Chitosan-
 44 coated-magnetite with covalently grafted polystyrene based carbon nanocomposites for
 45 hexavalent chromium adsorption. *Eng. Sci.* 1, 46–54. doi: 10.30919/espub.es.180308.
- 46 • Gupta, V.K., Nayak, A., Agarwal, S., 2015. Bioadsorbents for remediation of heavy metals:
 47 Current status and their future prospects. *Environ. Eng. Res.* 20(1): 1-18.
 48 <http://dx.doi.org/10.4491/eer.2015.018>.

- 1 • Hua, J., 2018. Adsorption of low-concentration arsenic from water by co-modified bentonite
2 with manganese oxides and poly(dimethyldiallylammonium chloride). *Journal of*
3 *Environmental Chemical Engineering*. 6, 156–168. <https://doi.org/10.1016/j.jece.2017.11.062>.
- 4 • Inchaurredo, N., Maestre, A., Žerjav, G., Pintar, A., Ramos, C., Haure, P., 2018. Screening of
5 catalytic activity of natural iron-bearing materials towards the Catalytic Wet Peroxide Oxidation
6 of Orange II. *Journal of Environmental Chemical Engineering*. 6, 2027–2040.
7 <https://doi.org/10.1016/j.jece.2018.03.001>.
- 8 • Inchaurredo, N., Ramos, C.P., Žerjav, G., Font, J., Pintar, A., Haure, P., 2017. Modified
9 diatomites for Fenton-like oxidation of phenol. *Microporous and Mesoporous Materials*. 239,
10 396–408. <https://doi.org/10.1016/j.micromeso.2016.10.026>.
- 11 • Jiménez-Cedillo, M.J., Olguín, M.T., Fall, Ch., 2009. Adsorption kinetic of arsenates as water
12 pollutant on iron, manganese and iron–manganese-modified clinoptilolite-rich tuffs. *Journal of*
13 *Hazardous Materials*. 163, 939–945. <https://doi.org/10.1016/j.jhazmat.2008.07.049>.
- 14 • Kalaruban, M., Loganathan, P., Nguyen, T.V., Nur, T., Johir, M.A.H., Nguyen, T.H., Trinh,
15 M.V., Vigneswaran, S., 2019. Iron-impregnated granular activated carbon for arsenic removal:
16 Application to practical column filters. *Journal of Environmental Management* 239, 235-243.
17 <https://doi.org/10.1016/j.jenvman.2019.03.053>.
- 18 • Komárek, M., Vaněk, A., Ettler, V., 2013. Chemical stabilization of metals and arsenic in
19 contaminated soils using oxides – A review. *Environmental Pollution*. 172, 9–22.
20 <https://doi.org/10.1016/j.envpol.2012.07.045>.
- 21 • Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum.
22 *Journal of the American Chemical Society*. 40, 1361–1403.
23 <https://doi.org/10.1021/ja02242a004>.
- 24 • Litter, M.I., Morgada, M.E., Bundschuh, J., 2010. Possible treatments for arsenic removal in
25 Latin American waters for human consumption. *Environmental Pollution*. 158, 1105–1118.
26 <https://doi.org/10.1016/j.envpol.2010.01.028>.
- 27 • Liu, B., Liu, Z., Wu, H., Pan, S., Cheng, X., Sun, Y., Xu, Y., 2020. Effective and simultaneous
28 removal of organic/inorganic arsenic using polymer-based hydrated iron oxide adsorbent:
29 Capacity evaluation and mechanism. *Science of The Total Environment*. 742, 140508.
30 <https://doi.org/10.1016/j.scitotenv.2020.140508>.
- 31 • Maji, S.K., Pal, A., Pal, T., 2007. Arsenic removal from aqueous solutions by adsorption on
32 laterite soil. *Journal of Environmental Science and Health, Part A*. 42, 453–462.
33 <https://doi.org/10.1080/10934520601187658>.
- 34 • Manning, B.A., 1996. Modeling Arsenate Competitive Adsorption on Kaolinite,
35 Montmorillonite and Illite. *Clays and Clay Minerals*. 44, 609–623.
36 <https://doi.org/10.1346/CCMN.1996.0440504>.
- 37 • Mar, K.K., Karnawati, D., Sarto, Putra, D.P.E., Igarashi, T., Tabelin, C.B., 2013. Comparison
38 of Arsenic Adsorption on Lignite, Bentonite, Shale, and Iron Sand from Indonesia. *Procedia*
39 *Earth and Planetary Science*. 6, 242–250 . <https://doi.org/10.1016/j.proeps.2013.01.033>.
- 40 • Palma-Lara, I., Martínez-Castillo, M., Quintana-Pérez, J.C., Arellano-Mendoza, M.G., Tamay-
41 Cach, F., Valenzuela-Limón, O.L., García-Montalvo, E.A., Hernández-Zavala, A., 2020.
42 Arsenic exposure: A public health problem leading to several cancers. *Regulatory Toxicology*
43 *and Pharmacology*. 110, 104539. <https://doi.org/10.1016/j.yrtph.2019.104539>.
- 44 • Shevade, S., Ford, R.G., 2004. Use of synthetic zeolites for arsenate removal from pollutant
45 water. *Water Research*. 38, 3197–3204. <https://doi.org/10.1016/j.watres.2004.04.026>.
- 46 • Siddiqui, S.I., Chaudhry, S.A., 2017. Iron oxide and its modified forms as an adsorbent for
47 arsenic removal: A comprehensive recent advancement. *Process Safety and Environmental*
48 *Protection*. 111, 592–626. <https://doi.org/10.1016/j.psep.2017.08.009>.
- 49 • Šiljeg, M., Foglar, L., Gudelj, I., 2012. The removal of arsenic from water with natural and
50 modified clinoptilolite. *Chemistry and Ecology*. 28, 75–87.
51 <https://doi.org/10.1080/02757540.2011.619531>.
- 52 • Singh, E., Kumar, A., Khapre, A., Saikia, P., Kumar Shukla, S., Kumar, S., 2020. Efficient
53 removal of arsenic using plastic waste char: Prevailing mechanism and sorption performance.
54 *Journal of Water Process Engineering*. 33, 101095. <https://doi.org/10.1016/j.jwpe.2019.101095>.

- 1 • Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of
2 arsenic in natural waters. *Applied Geochemistry*. 17, 517–568. [https://doi.org/10.1016/S0883-2927\(02\)00018-5](https://doi.org/10.1016/S0883-2927(02)00018-5).
- 3 • Sparks, D. L., 2003 ‘Environmental Soil Chemistry’, 2nd. Ed. Elsevier-Academic Press, New
4 York.
- 5 • Suhas, Gupta, V.K., Carrott, P.J.M., Singh, R., Chaudhary, M., Kushwaha, S., 2016. Review
6 Cellulose: A review as natural, modified and activated carbon adsorbent. *Bioresource*
7 *Technology*. 216, 1066–1076. <http://dx.doi.org/10.1016/j.biortech.2016.05.106>.
- 8 • Tabelin, C.B., Igarashi, T., Arima, T., Sato, D., Tatsuhara, T., Tamoto, S., 2014.
9 Characterization and evaluation of arsenic and boron adsorption onto natural geologic materials,
10 and their application in the disposal of excavated altered rock. *Geoderma* 213, 163–172.
11 <https://doi.org/10.1016/j.geoderma.2013.07.037>.
- 12 • Thirunavukkarasu, O. S., Viraraghavan, T. and Subramanian, K. S., 2003. Arsenic Removal
13 from Drinking Water using Iron Oxide-Coated Sand. *Water, Air, & Soil Pollution*. 142, 95–111.
14 <https://doi.org/10.1023/A:1022073721853>.
- 15 • Uzunova, E.L., Mikosch, H., 2016. Adsorption of phosphates and phosphoric acid in zeolite
16 clinoptilolite: Electronic structure study. *Microporous and Mesoporous Materials*. 232, 119–
17 125. <https://doi.org/10.1016/j.micromeso.2016.06.019>.
- 18 • Wang, B., Wu, T., Angaiah, S., Murugadoss, V., Ryu, J-E., Wujcik, E.K., Lu, N., Young, D.P.,
19 Gao, Q., Guo, Z., 2018. Development of nanocomposite adsorbents for heavy metal removal
20 from wastewater. *ES Mater. Manuf.* 2, 35-44. doi: 10.30919/esmm5f175.
- 21 • Wei, H., Ma, J., Shi, Y., Cui, D., Liu, M., Lu, N., Wang, N., Wu, T., Wujcik, E.K., Guo, Z.,
22 2018. Sustainable cross-linked porous corn starch adsorbents with high methyl violet
23 adsorption. *ES Mater. Manuf.* 2, 28-34. doi: 10.30919/esmm5f162.
- 24 • World Health Organization. Arsenic in Drinking-water. Background document for development
25 of WHO Guidelines for Drinking-water Quality (2011).
- 26 • Youngran, J., Fan, M., Van Leeuwen, J., Belczyk, J.F., 2007. Effect of competing solutes on
27 arsenic(V) adsorption using iron and aluminum oxides. *Journal of Environmental Sciences*. 19,
28 910–919. [https://doi.org/10.1016/S1001-0742\(07\)60151-X](https://doi.org/10.1016/S1001-0742(07)60151-X).
- 29 • Zehhaf, A., Benyoucef, A., Quijada, C., Taleb, S., Morallón, E., 2015. Algerian natural
30 montmorillonites for arsenic(III) removal in aqueous solution. *International Journal of*
31 *Environmental Science and Technology*. 12, 595–602. <https://doi.org/10.1007/s13762-013-0437-3>.
- 32 • Zhao, J., Boada, R., Cibin, G., Palet, C., 2020. Enhancement of selective adsorption of Cr
33 species via modification of pine biomass. *Science of The Total Environment*. 143816.
34 <https://doi.org/10.1016/j.scitotenv.2020.143816>.
- 35
- 36