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Articles

Assessment of two low-cost geological materials as adsorbents for arsenic

Evaluación de dos materiales geológicos de bajo costo como adsorbentes para As

Oscar Coreño-Alonso[1], ORCID: https://orcid.org/0000-0003-1966-4061
Leticia Elena González-Gómez[2], ORCID: https://orcid.org/0000-0001-8078-8667
Juan Coreño-Alonso[3], ORCID: https://orcid.org/0000-0001-9800-7814

[1]Facultad de Ingeniería Civil, Universidad de Guanajuato, Guanajuato, México, ocoreno@ugto.mx
[2]Licenciatura en Ingeniería Ambiental, Universidad de Guanajuato, Guanajuato, México, legogo1419@gmail.com
[3]División de Ingenierías, Universidad de Guanajuato, Guanajuato, México, jcorenoalonso@gmail.com

Corresponding author: Juan Coreño, jcorenoalonso@gmail.com

Abstract

Two easily accessible local materials, kaolin, and sediments from the reservoir of a dam, were evaluated to compare their efficiencies as adsorbents for As. The kaolin sample was composed mainly by kaolinite and quartz, while the sediments contained illite, montmorrillonite and quartz. Also, iron, calcium and magnesium minerals were present as minor components. The adsorption experiments were performed using batch equilibrium techniques. The samples were chemically treated using piranha solution, and trimesic acid, to study their effects on the adsorption capacity. The piranha treatment seems to be a good alternative to improve the adsorption capacity of kaolin. However, the intact reservoir sediments showed higher efficiencies than the intact or treated kaolin. On the other hand, the initial uptake of trimesic acid showed only a slightly positive effect on the arsenic uptake of the reservoir sediments. Most of the arsenic adsorption seems to be due to the finest particles of the sediments, composed mainly of iron minerals, while the organic matter contributes scarcely to the arsenic uptake. The influences of pH, contact time, initial arsenic concentration, and chemical treatments were studied. Freundlich and Dubinin-Kaganer-Radushkevich isotherm models were used to evaluate the arsenic uptake capacity of the intact and trimesic acid treated reservoir sediments. Maximum arsenic adsorption was completed almost within five hours of reaction, reaching a measured sorption capacity of 137 mg/kg for the intact sediments, slightly lower than for the trimesic treated sediments.

Keywords: arsenic, aluminosilicates, low-cost adsorbent, piranha reagent, sediment, trimesic acid, kaolinite.

Resumen

Dos materiales locales fácilmente accesibles, caolín y sedimentos de un embalse, se evaluaron para comparar sus eficiencias como adsorbentes para arsénico. La muestra de caolín estaba compuesta sobre todo de caolinita y cuarzo, mientras que los sedimentos constaban de illita, montmorillonita y cuarzo. Componentes en menores proporciones fueron minerales de hierro, calcio y magnesio. Se realizaron experimentos de adsorción por lotes para medir la influencia del pH, tiempo de contacto, concentración inicial de arsénico y tratamientos químicos, los cuales se llevaron a cabo utilizando reactivo piraña y ácido trimésico para estudiar sus efectos en la capacidad de adsorción. El reactivo piraña parece ser una buena alternativa para mejorar la capacidad de absorción del caolín, mientras que la adsorción inicial usando ácido trimésico tiene solo un ligero efecto positivo en los sedimentos del embalse. Los sedimentos sin tratar mostraron mayores capacidades de adsorción que el caolín natural o tratado. Una gran parte de la adsorción parece deberse a las partículas más finas de los sedimentos, compuestas principalmente de minerales de hierro, en tanto que la materia orgánica casi no contribuye a la adsorción. Se emplearon los modelos de Freundlich y Dubinin-Kaganer-Radushkevich para evaluar la capacidad de adsorción de arsénico de los sedimentos intactos y tratados con ácido trimésico. La máxima capacidad de adsorción observada experimentalmente fue de 137 mg/kg para los sedimentos intactos después de cinco horas de reacción, que es ligeramente inferior a la medida para los tratados con ácido trimésico.

Palabras clave: arsénico, aluminosilicatos, adsorbente de bajo costo, reactivo piraña, sedimento, ácido trimésico, caolín.

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Introduction

The continuous intake of arsenic through the direct or indirect consumption of contaminated water is associated with chronic health problems, such as various types of cancer or skin lesions. The World Health Organization (WHO) (WHO, 2010) considers arsenic one of the ten most chemical concerns for public health, establishing a guideline value of 10 µg/l of arsenic in drinking water for human consumption. The presence of arsenic in water may be due to the mobilization under natural conditions; however, anthropogenic pollution creates further impact (Mohan & Pittman, 2007).

In lakes and river waters, As(V) is generally the dominant species, while in groundwaters the ratio of As(III) to As(V) can vary enormously, as a result of large variations in aquifer redox conditions, redox gradients, and history. High concentrations of arsenic in groundwater is a very widespread problem (Mohan & Pittman, 2007).

Several methods for arsenic adsorption in water have been reported. These comprise studies of precipitation and coprecipitation, coagulation, ion exchange, adsorption, among others. In the case of adsorption, many materials have been studied, such as those based on different types of activated carbon, aluminum, or iron compounds, biosorbents, and surface modified adsorbents, like coated sands, or alumina. A recently report published by the United Nations University (UNU) (UNU, 2018) has pointed out that, in spite of the laboratory-level successes on As remediation, there are certain difficulties to transfer this knowledge into sustainable impacts on the ground. Limitations of existing remediation technologies may include high maintenance costs, or the need of specific controlled conditions to be effective. Other methods may generate toxic components, or secondary contaminants that would need additional treatment. On the other hand, the operation costs have also to be considered. At this respect, it is suggested that costs can be reduced by using efficient locally available materials, such as soils and sands, which are already used in Argentina, India and Vietnam (Bundschuh *et al*., 2011; Berg *et al*., 2006; Mondal *et al*., 2017).

In Mexico, arsenic is present at high levels in groundwater in some north-central, north-west, and central regions of the country. In Guanajuato State, Central Mexico, groundwater is the only source of drinking water for a number of cities, and arsenic concentrations higher than the limit of the Mexican Standard for drinking water, 0.025 mg/l, can be found in some drinking water wells (Rodríguez, Morales-Arredondo, & Rodríguez, 2016).

The aim of this work is to assess two local materials from the state of Guanajuato as arsenic adsorbents. Both were evaluated in their natural form, and after surface chemical modification, using piranha reagent and trimesic acid (TMA), as alternatives to improve their arsenic adsorption capacities. One of them is a kaolin, waste material from the natural clay used for pottery production. The other material are sediments from the reservoir of the dam La Esperanza, near the city of Guanajuato. This reservoir suffers a significant siltation problem, thus the possible use of the sediments as arsenic adsorbents could help to relieve it.

Materials and methods

Sediments and chemical treatments

Two surface sediment samples, identified as M1, and M2, were collected from the reservoir of the La Esperanza dam, 3 kilometers from

Guanajuato city, in the state of Guanajuato, México. The samples were selected based on their different reddish coloration, i.e., possible distinct iron content. Gravel, roots and leaves were taken away manually. The resultant sediments were oven-dried at 60 °C, for four days, homogenized, and ground to pass through 200 mesh. Kaolin sample was obtained from Comonfort, Guanajuato, Mexico. Soil particle-size determination was carried out according to the method by Kettler, Doran and Gilbert (2001). The removal of organic matter was performed placing 25 g of each sample in a 500 cm^3 beaker, and adding 50 cm^3 of distilled water, and 25 cm^3 of 30 % H_2O_2. The suspension was placed in a boiling water bath. The treatment was allowed to proceed until the reaction ceased, and the solution became clear. Then, a new portion of H_2O_2 was added without removal of the clear liquid. This treatment was repeated twice. The supernatant was removed, and the samples were washed with distilled water, filtered, and air-dried for one day. For the treatment with piranha reagent, 10 g of the sample were immersed in 50 cm^3 of a piranha solution (5:1 concentrated sulphuric acid/H_2O_2 35 %, v/v), at 80 °C for 2 h. The supernatant was discarded, the samples were washed twice with 100 cm^3 of running water, and finally, with a 1M NaOH solution, until pH around 7 was obtained. Finally, the samples were air-dried for one day. Trimesic acid (TMA) adsorption was conducted following the method reported by Saha, Chakraborty and Das (2009).

Adsorption experiments, and determination of point of zero charge

An stock aqueous solution (100 ppm) of arsenic was prepared from H_3AsO_3 oxidation by chlorine, according to Clifford and Ghurye (2001). The solutions used for each experiment were prepared by dilution of this stock solution. All the adsorption experiments were conducted by the batch technique, using a solid/liquid ratio of 1 g/40 cm^3, at room temperature (25 °C ± 1 °C). The experiments were carried out in 15 cm^3 screw capped vials, containing 10 cm^3 of the desired arsenic solution, and 0.25 g of sediment, and mixed using a tube rotator shaker. After each reaction time, the suspensions were centrifuged, and the supernatant was stored under refrigeration. All experiments were performed in duplicate. To determine the influence of contact time, a set of experiments were carried out at different adsorption times, at natural pH 5.9, and 1.38 ppm initial arsenic concentration. Another set of experiments were performed to study the effect of pH by varying the initial solution pH values (pH 3, 5, 7 and 9), and 1.38 ppm initial arsenic concentration. Isotherms were studied with varying concentrations of arsenic (0.3 to 3.74 ppm), with fixed amount of adsorbent, at natural pH. Since no speciation of As(III) and As(V) was performed, the adsorption of arsenic is considered as total As along the text.

The arsenic uptake, Q (mg/g), and percentage of adsorption were calculated using the next equations:

$$Q = V * \frac{(C_i - C_f)}{m}$$

$$\%\,\text{adsorption} = 100 * \frac{(C_i - C_f)}{C_i}$$

where C_i and C_f are the concentrations (mg/l) of As in the initial and final solutions, respectively, V is the volume of the reacting solutions (l), and m is the weight (g) of the adsorbents.

The point of zero charge (pH_{pzc}) was estimated by using the drift method (Khan & Sarwar, 2007). 0.08 g of the samples were suspended in 40 cm^3 of a 0.1M NaCl varying the initial solution pH values from ~3 to pH ~9, increasing the initial pH around 1 unit for each experiment. The initial pH values were adjusted with 0.001 M NaOH or 0.001 M HCl solutions. The suspensions were stirred for 6h, at 250 rpm, at room temperature. After this time, the suspensions were centrifuged, and final pH of the liquids were measured again to obtain the final pH of each suspension.

Instrumentation

Arsenic in solutions was determined by hydride generation atomic absorption spectrometry, using a PerkinElmer Analyst 100 Spectrometer. Scanning electron microscopy, SEM, was carried out using a JEOL JSM-6010 PLUS/LA device, with incorporated JEOL detector for energy dispersive analysis of X-rays, EDS. For X-ray diffraction, XRD, a Rigaku Ultima IV diffractometer, with Ni filter, and Cu Kα_1 radiation was used. Energy dispersive X-ray fluorescence, XRF, was performed using a Rigaku Nex CG spectrometer, equipped with an X-ray tube with Pd anode. FTIR spectra were recorded using a PerkinElmer Spectrum 100 spectrophotometer in KBR disks.

Results and discussion

Figure 1 corresponds to the powder XRD pattern of the M2 intact sample, M2 treated with hydrogen peroxide (M2HP), and with this treatment followed by piranha reagent (M2PR). The identified phases were: montmorillonite (Krupskaya *et al*., 2017), illite-1 (Gualtieri, 2000), illite-

2 (Drits, Zviagina, McCarty, & Salyn, 2010), and quartz. Similar phases were detected for the intact sample M1. After treatment with hydrogen peroxide, the peak corresponding to montmorillonite disappears. This may be due to an indirect dissolution promoted by hydrogen peroxide, as has been reported for other aluminosilicates (Lavkulich & Wiens, 1970).

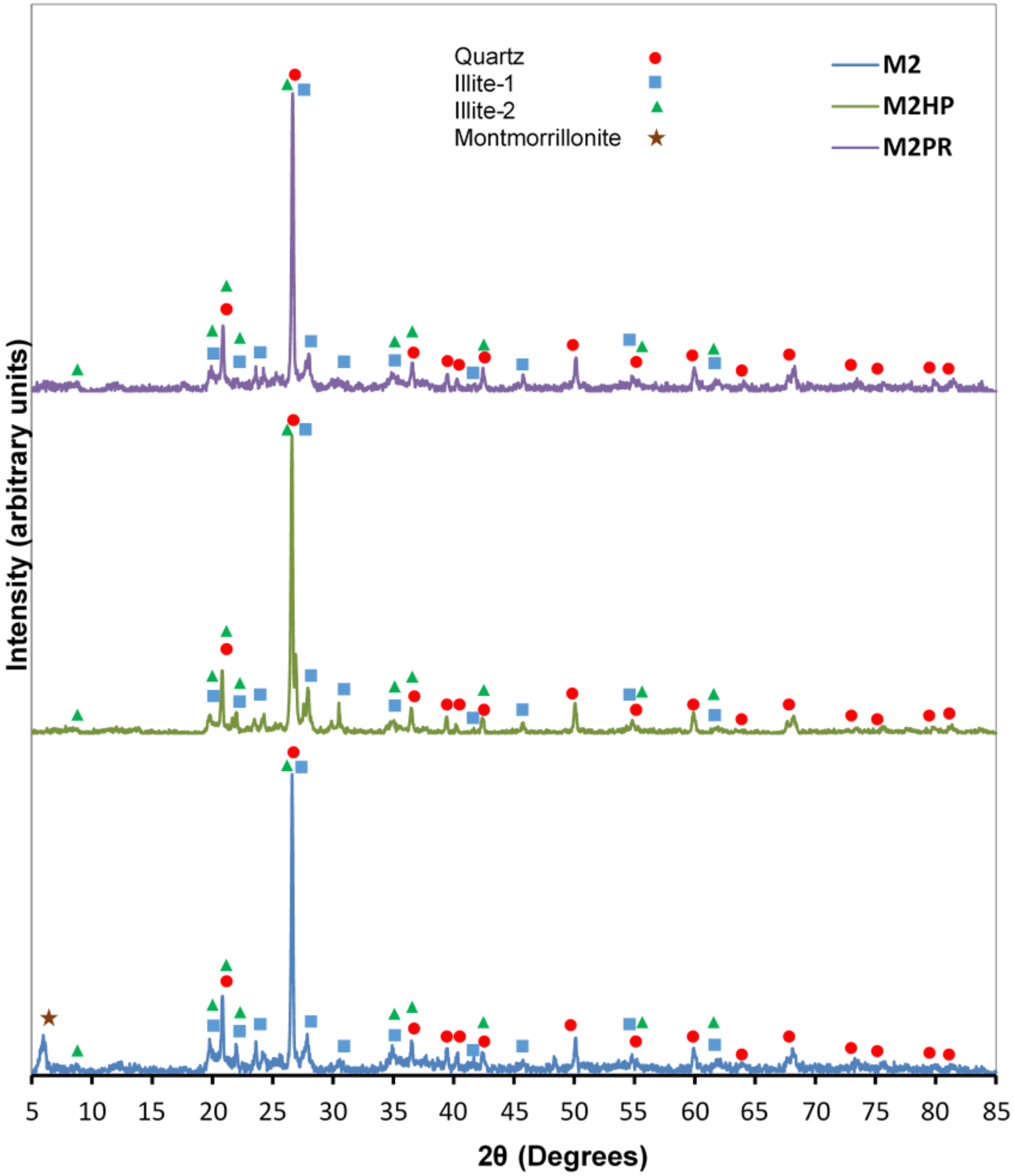
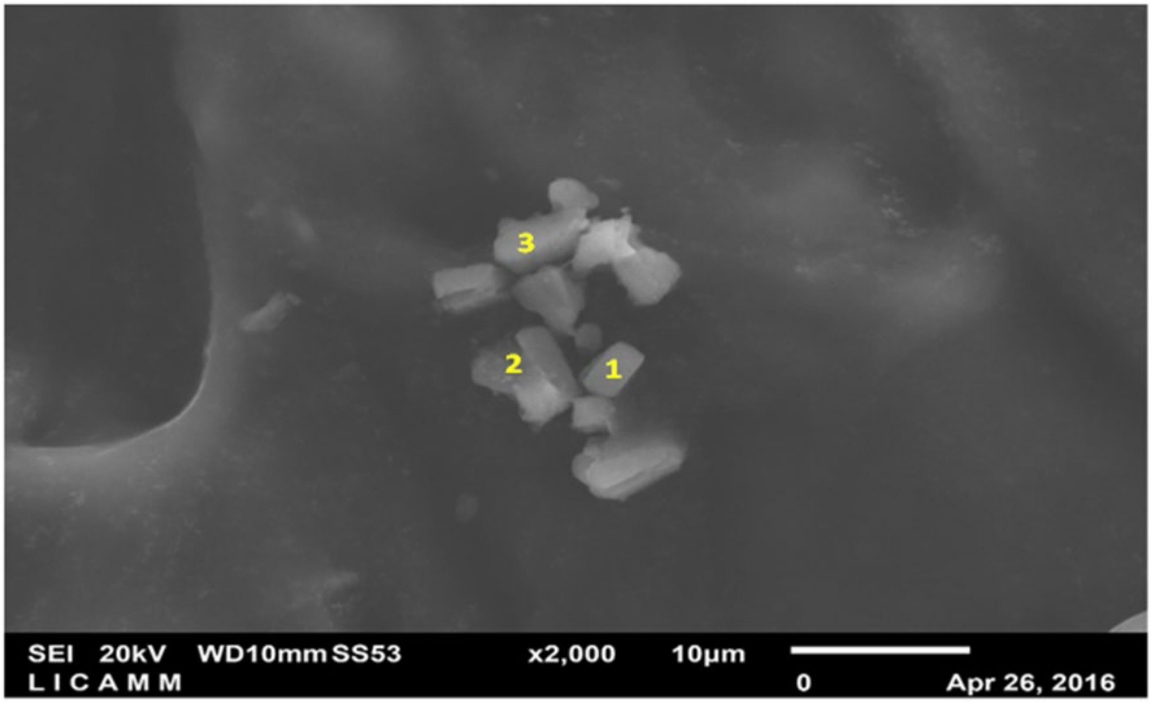


Figure 1. XRD patterns for intact soil M2, hydrogen peroxide treated soil, M2HP and piranha reagent treated sample M2PR.

In addition, the presence of other compounds such as calcium oxide and carbonate, in percentages lower than 5 %, thus not detected by XRD, is assumed. This is deduced from the EDS analysis of some single particles of the sediments shown in Figure 2, and Table 1.



	Particle 1		Particle 2		Particle 3	
Element	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
O	75.45	88.50	64.66	80.81	76.27	88.37
Si	0.0	0.0	7.32	5.21	0.0	0.0
Al	0.0	0.0	0.0	0.0	2.92	2.01
Ca	24.55	11.50	28.03	13.98	20.81	9.62

Figure 2. SEM images of selected particles of the M2 sediments after hydrogen peroxide treatment, M2HP, and their composition determined by EDS analysis.

Table 1. XRF analysis of the intact samples, M1 and M2, and of the samples treated with piranha reagent, M1PR and M2PR, respectively. (Values in weight percent).

Element	M1	M2	M1PR	M2PR
Mg	0.917	0.94	0.59	0.52
Ca	0.88	0.89	0.46	0.51
Fe	4.77	4.7	2.47	2.24
Al	8.22	8.46	8.70	8.78
Si	21.45	21.5	25.50	25.85
K	1.48	1.57	1.81	1.76
O	62.02	61.53	60.40	59.54

Table 1 presents the XFR analysis of the intact, and chemically treated samples. As can be seen, the piranha reagent diminished around 50 % the Fe content, from 4.77 % and 4.7 % to 2.47 % and 2.24 %, for M1 and M2, respectively. Also, the percentage of O lowered 2 %, on average, and the contents of Ca and Mg decreased from approximately 0.9 % to around 0.45 %. On the contrary, the percentages of Si, Al and K increased around 5, 0.4, and 0.25 %, on average, respectively. Arsenic was detected in percentages close to 0.002% in both intact soils. Other present elements (not shown in Table 1) were S, Cl, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, and Ga, in concentrations lower than 0.1 %.

Figure 3 shows the powder XRD pattern of the kaolin sample. This is a clay consisting of about 65 % of kaolinite, being quartz the main accessory phase.

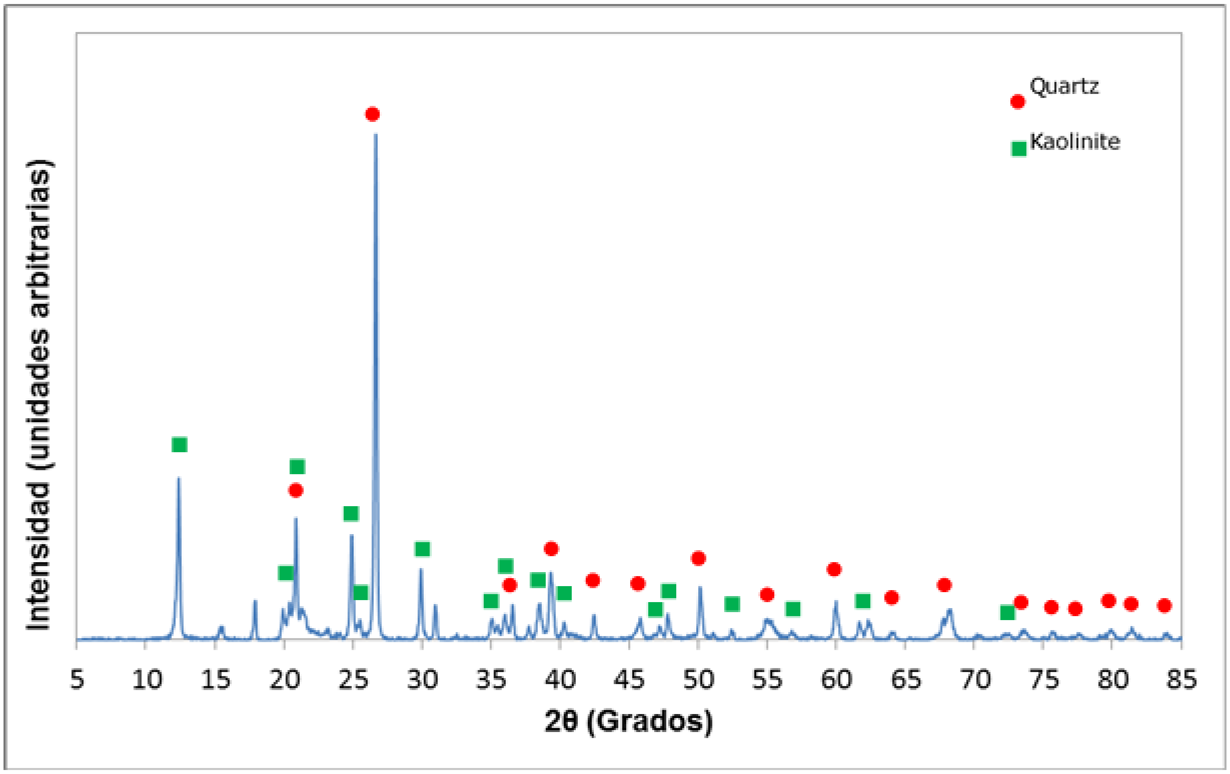


Figure 3. XRD pattern of the kaolin sample.

The piranha reagent is a strong oxidizing agent that can break surface Al-O-Al bonds to form -Al-OH groups (Coreño, Coreño, & Guerrero-Paz, 2018), and it augments the number of -SiOH groups in glass surfaces (Kalani *et al.,* 2007). The effect of this reagent on the sediments can be seen in Table 2. After the treatment, the silt content increase of the samples is close to the percentage of sand decrease for the two samples. Likewise, in a M2PR suspension, no suspended particles were noted after 5 minutes of stirring followed by 3 hours of rest, while in a M2HP suspension, those particles were observed, in addition to the settled ones.

Table 2. Textural analysis of M1 and M2 samples before, and after the piranha treatment (PR).

Component	M1 before PR	M1 after PR	M2 before PR	M2 after PR
Sand (%)	17.87	6.45	23.53	6.51
Silt (%)	73.67	83.71	68.53	84.93
Clay (%)	8.46	9.84	7.94	8.56

On the other hand, the loss of the sediments reddish coloration, attributed to iron compounds, was also observed after the piranha treatment. The piranha reagent dissolved Fe, Ca, and Mg compounds soluble under acidic conditions, such as oxides and carbonates. However, as in the case of the sand fragmentation to form silt particles after the piranha treatment, it could also have dissolved very fine aluminosilicate clay particles.

Table 3 reports the arsenic adsorption capacity for an initial concentration of 0.75 ppm, after 5-h contact time. It can be observed that the arsenic consumption was practically total for the intact sediments, and that it diminished 2 % after the organic matter removal by hydrogen peroxide, although it constitutes 13 % by weight (Table 4).

Table 3. Percentage of arsenic adsorbed for different chemical treatments.

Sample treatment	M1	M2	Kaolin
Intact Soil	99	99	25
Hydrogen peroxide (HP)	97	97	---
HP and trimesic acid	98	98	
Piranha reagent (PR)	13	39	68
PR and trimesic acid	64	45	30

Table 4. Percentage of weight loss of the sediments after chemical treatments.

Sample	Hydrogen peroxide	Piranha reagent
M1	16.6	11.24
M2	9.8	12.36

The adsorption of trimesic acid after hydrogen peroxide treatment did not have an appreciable effect on the arsenic uptake. However, when the piranha reagent was used, the adsorption capacity decreased to 13

% and 39 %, for M1 and M2, respectively, while the weight loss was only 12 %, on average (Table 4).

In the case of the kaolin sample, it showed an adsorption capacity of 25 %, within the range of the sediments treated with piranha reagent, composed mainly by aluminosilicates. After the piranha treatment, the arsenic adsorption on kaolin increased to 68 % (Table 3), which could be due to an increment in the porosity, and surface area. For high surface zeolites (Chutia, Kato, Kojima, & Satokawa, 2009), it has been reported that a higher percentage of mesoporosity favors the arsenate adsorption performance. Factors such as uniform pore size, and an interlinked pore system have also been reported to improve arsenic adsorption, in mesoporous alumina (Kim, Kim, Choi, Rengaraj, & Yi, 2004). For mineral zeolites, whose porosity system is bidisperse, composed mainly by clinoptilolite, it has been proposed that micropores do not take part in the arsenic uptake after HCl treatment (Elizalde-González, Mattusch, Wennrich, & Morgenstern, 2001). It has also been reported that natural laterite clay showed a noticeable increase in arsenic adsorption, after treatment with HCl, attributed to a higher surface area, higher average pore diameter, and volume, and increased amount of active sites. However, the adsorption diminished if the treatment dissolved Fe, and Al compounds of the clay (Maiti, Basu, & De, 2010). Thus, it is possible that kaolinite might have developed certain extent of mesoporosity after the treatment. Besides, it would be expected the formation of -Al-OH groups, as for the sediments, after the break-up of Al-O-Al bonds.

The -Al-OH sites are active towards arsenic adsorption. In the case of arsenate, these sites once positively charged (Equation (1)), can uptake the anion both due to a Coulombic attraction without subsequent chemical interaction (Equation (2)), or by adsorption followed by chemical interaction (Equation (3)) (Chutia *et al.*, 2009; Höll, 2010; Manning & Goldberg, 1997):

$$\text{-Al-OH} + H^+ \longrightarrow \text{-Al-OH}_2^+ \qquad (1)$$

$$\text{-AlOH}_2^+ + H_2AsO_4^- \longrightarrow \text{-Al-OH}_2H_2AsO_4 \qquad (2)$$

$$\text{-AlOH}_2^+ + H_2AsO_4^- \longrightarrow \text{-Al-OH}_2AsO_3 + H_2O \qquad (3)$$

For soils containing iron compounds, arsenate uptake has been related significantly with crystalline and no crystalline iron forms, and to clay content in a smaller extent (Bundschuh *et al.*, 2011; Jiang *et al.*, 2005; Manning & Goldberg, 1997). In the case of iron (hydr)oxides, the adsorption could take place according to Equation (4) (Escudero, Fiol, Villaescusa, & Bollinge, 2009):

$$\text{-FeOH}_2^+ + H_2AsO_4^- \longrightarrow \text{-FeH}_2AsO_4 + H_2O \qquad (4)$$

In the sediment samples M1 and M2, whose clay content is less than 10 %, this would mainly explain the arsenic adsorption. Thus, the negative effect of the dissolution of iron compounds and of very fine aluminosilicate particles, on the arsenic adsorption after the piranha reagent, seems to be much higher than the positive effect due to the possible increment of pore volume, and to the formation of new -AlOH groups.

Figure 4 shows the FTIR spectra for the intact M2 sample (Figure 4a), and after the different treatments (Figures 4b and 4c). The band around 1 640 cm^{-1} is due to strongly adsorbed water on -AlOH groups (Modolo-Segal *et al*., 2018), and the smaller peak in 1 420 cm^{-1} is attributed to the presence of a carbonated mineral (Vaculíková & Plevová, 2005). After the hydrogen peroxide treatment, a small unassigned band was observed at 1 320 cm^{-1} (Figures 4b and 4c). The adsorption of TMA on M2HP sample (M2HP-TMA) originated a small band around 1 380 cm^{-1} (Figure 4c), attributed to the symmetric deformation of the TMA carboxylate groups adsorbed on Al-OH moieties (Borah & Mahiuddin, 2008). These sites have been proposed to enhance phosphate adsorption on TMA adsorbed by alumina (Saha *et al*., 2009). Given the chemical similarity between the phosphate and arsenate anions, it would explain the increase on the arsenic adsorption, after the TMA adsorption on the samples treated with piranha reagent (Scheme 1), which raised to 45 and 65 % for M2PR-TMA and M1PR-TMA, respectively (Table 3).

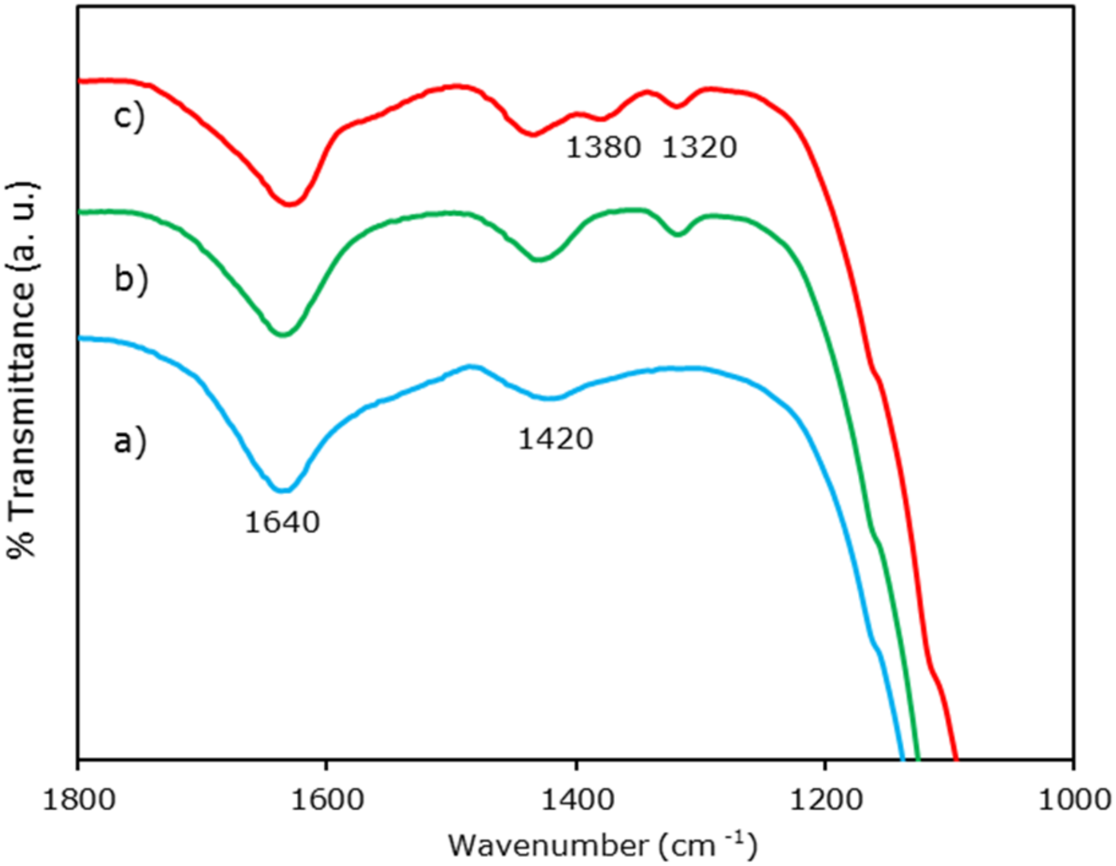
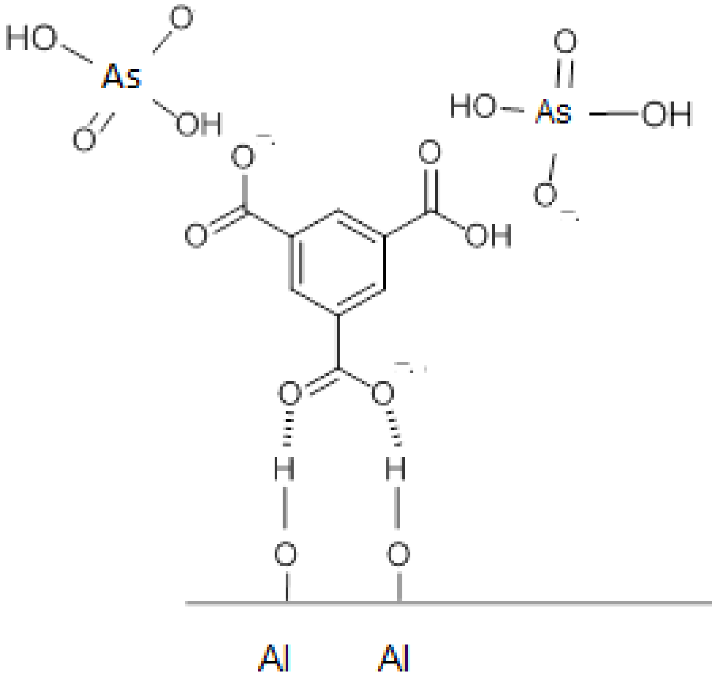


Figure 4. FTIR spectra for the intact M2 sample, M2 after hydrogen peroxide treatment, M2HP, and M2HP after TMA treatment, M2HP-TMA.



Scheme 1.

For kaolin, an increase on As adsorption, higher than 68 %, would have been expected after the TMA adsorption. However, it was only 5 % higher than the intact kaolin (Table 3). Reported As(V) adsorption capacities on samples containing 90% of kaolin, and ~10 % illite varied from 24 to 30 mg/kg at pH 5 and 7, respectively (Cornu, Breeze, Saada, & Baranger, 2003). In the present case, the measured capacity was 7.5 mg/kg, very possibly due to its higher quartz content, ~35 %, and to a low surface area, and pore volume, although an increment to 20.4 mg/kg was observed, after the piranha treatment, possibly due to a raise of those characteristics.

The intact reservoir sediments M1, and M2, showed four times higher As removal efficiencies than kaolin (Table 3). Samples M1, and M2 didn’t show appreciable differences on composition, and their As uptake capacities were equal, and close to M1HP-TMA and M2HP-TMA. Thus, As adsorption was evaluated as a function of time, pH, and variable initial As concentration, only for the M2, and for M2HP-TMA samples.

The effect of initial pH on arsenic adsorption for M2, and M2HP-TMA samples is shown in Figure 5. The M2 arsenic uptake values are around 10 % higher than the measured for M2HP-TMA, except for pH 7, where it is 7 % lower. At this pH, the M2HP-TMA sample reached a maximum adsorption, 25 and 15 % higher than the observed at pH 3, and pH 9, respectively. The pK_a^2 value of arsenic acid is ~6.9, and the pH_{pzc} are ~6.7, and ~6.3 for M2, and M2HP-TMA, respectively (Figure 6). The pH_{pzc} is the pH value of an adsorbent suspension where the net surface charge is zero. Thus, above pH 7 it would be expected a lower arsenic adsorption because the predominant species is $HAsO_4^{=}$, while the adsorbents surfaces becomes negatively charged, which increases the electrostatic repulsion between them. The arsenic uptake showed a noticeable decrement at pH 9, for M2HP-TMA. In the case of M2, there was only ~2 % increment from pH 7 to pH 9, while it raised 10 % from pH 3 to pH 7.

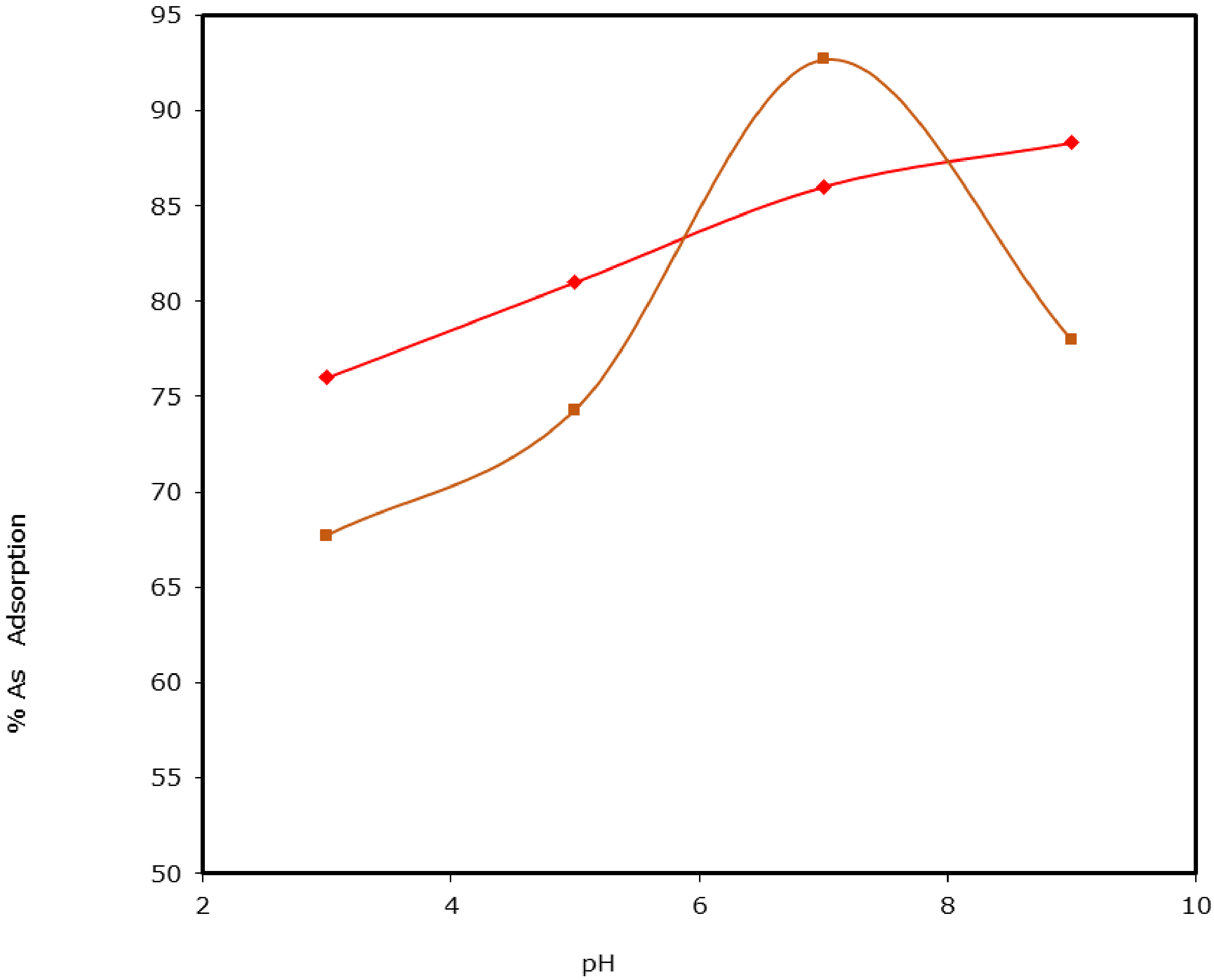


Figure 5. Effect of initial pH on arsenic adsorption for M2 and M2HP-TMA, using a 1.38 ppm initial arsenic concentration.

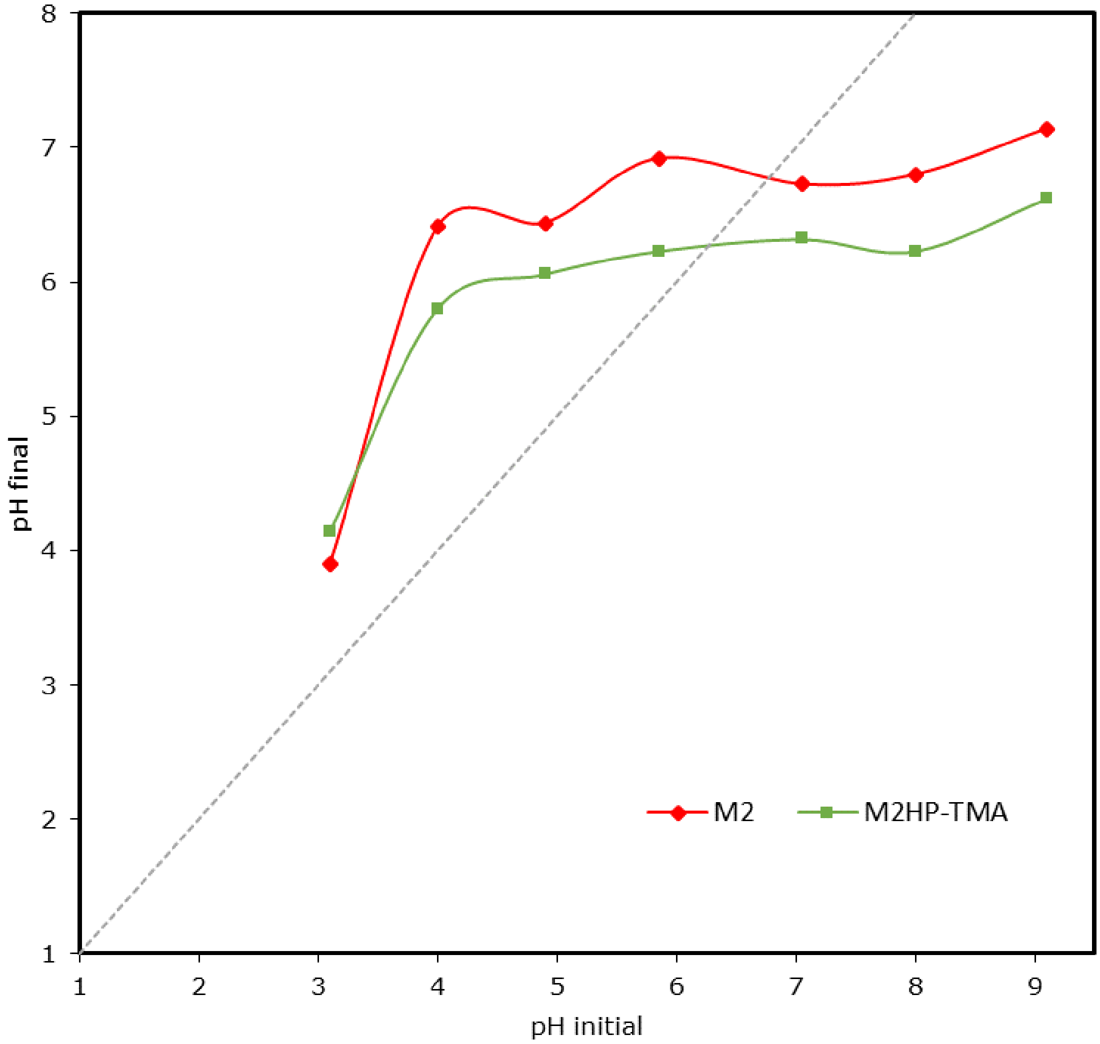


Figure 6. Determination of pH_{pzc} for M2 and M2HP-TMA.

Arsenic adsorption capacity of the M2 sample, as a function of time, using a 1.38 ppm initial arsenic concentration, at the natural initial pH 5.9, is presented in Figure 7. There is a sharp adsorption increase within the first 60 minutes, and it raises gradually up to five hours reaction time.

The pseudo-second-order reaction model has been applied to the adsorption of pollutants from aqueous solutions that involve covalent forces, or ion exchange (Ho, 2006). The linear form of this rate expression (Equation (5)) was applied to the previous results (Figure 7):

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

where k_2 is the equilibrium rate constant of pseudo-second-order, and q_e, and q_t (mg/g) are the amounts of arsenic sorbed at equilibrium, at time t. The value for the k_2 constant is 1.11 g/mg min, and the calculated q_e, inverse of the slope, is 0.051 mg/g, which is close to the maximum experimental adsorption capacity, 0.049 mg/g.

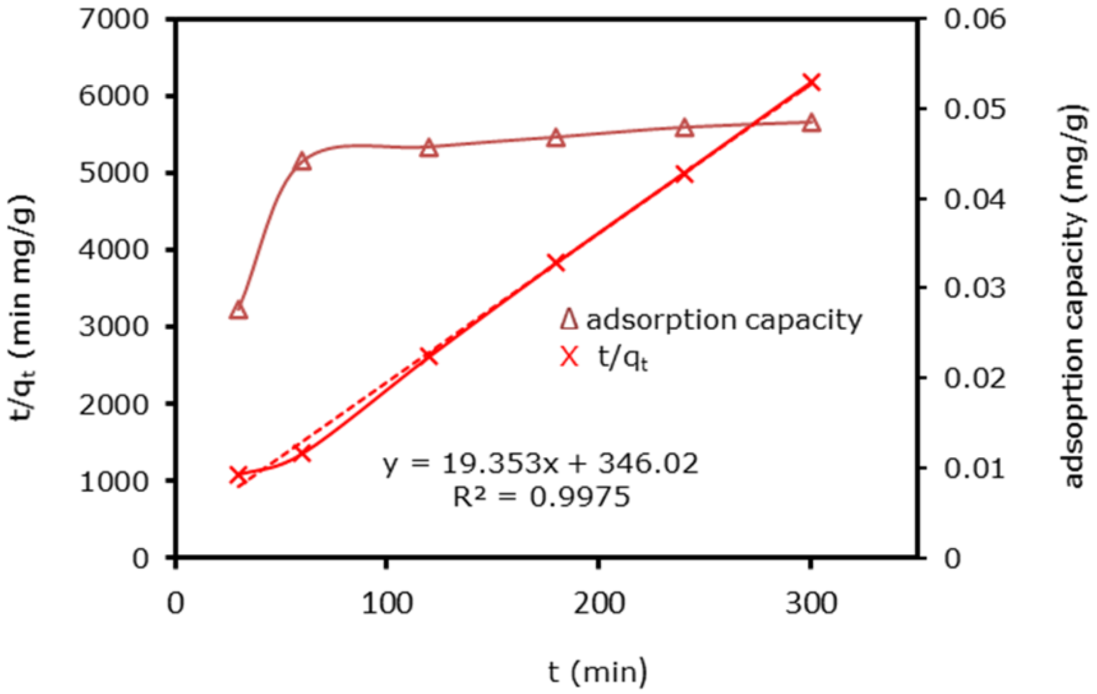


Figure 7. Arsenic adsorption as function of time for M2 sample and linear fit using the pseudo-second-order kinetic.

The effect of varying arsenic concentrations (0.3 to 3.74 ppm) was evaluated using 10 cm^3 of the arsenic solution, and 0.25 g of sediment, after 5-h reaction time, for the intact M2, and M2 treated with hydrogen peroxide, and TMA (M2HP-TMA) samples. The initial natural pH of the suspension were 5.9, and 3.1 for the M2, and M2HP-TMA, respectively. Figure 8 presents the linear fits of the experimental data applying the Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm model, for M2, and M2HP-TMA. Besides, the Freundlich model was used for the two samples (Figure 9). Both are empirical models that have been widely applied in heterogeneous systems, for organic and inorganic compounds (Erdem, Karapinar, & Donat, 2004). The linearized equations for these models can be written as (Foo & Hameed, 2010):

$$\ln Q_e = \ln X_m - \beta \varepsilon^2 \quad = \text{(DKR)}$$

$$\log Q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \; = \text{(Freundlich)}$$

Where Q_e is the amount of adsorbed arsenic by weight of adsorbent, in mg/g, and C_e is the concentration in the liquid phase, in mg/dm^3, in the equilibrium. In the Freundlich model, K_f, and n are empirical constants. In the DKR equation, X_m is the maximum sorption capacity, β is the activity coefficient (mol^2 /J^2), $\varepsilon = RT \ln(1 + 1/C_e)$, R = 8.314 J/K·mol, and T the temperature in Kelvin.

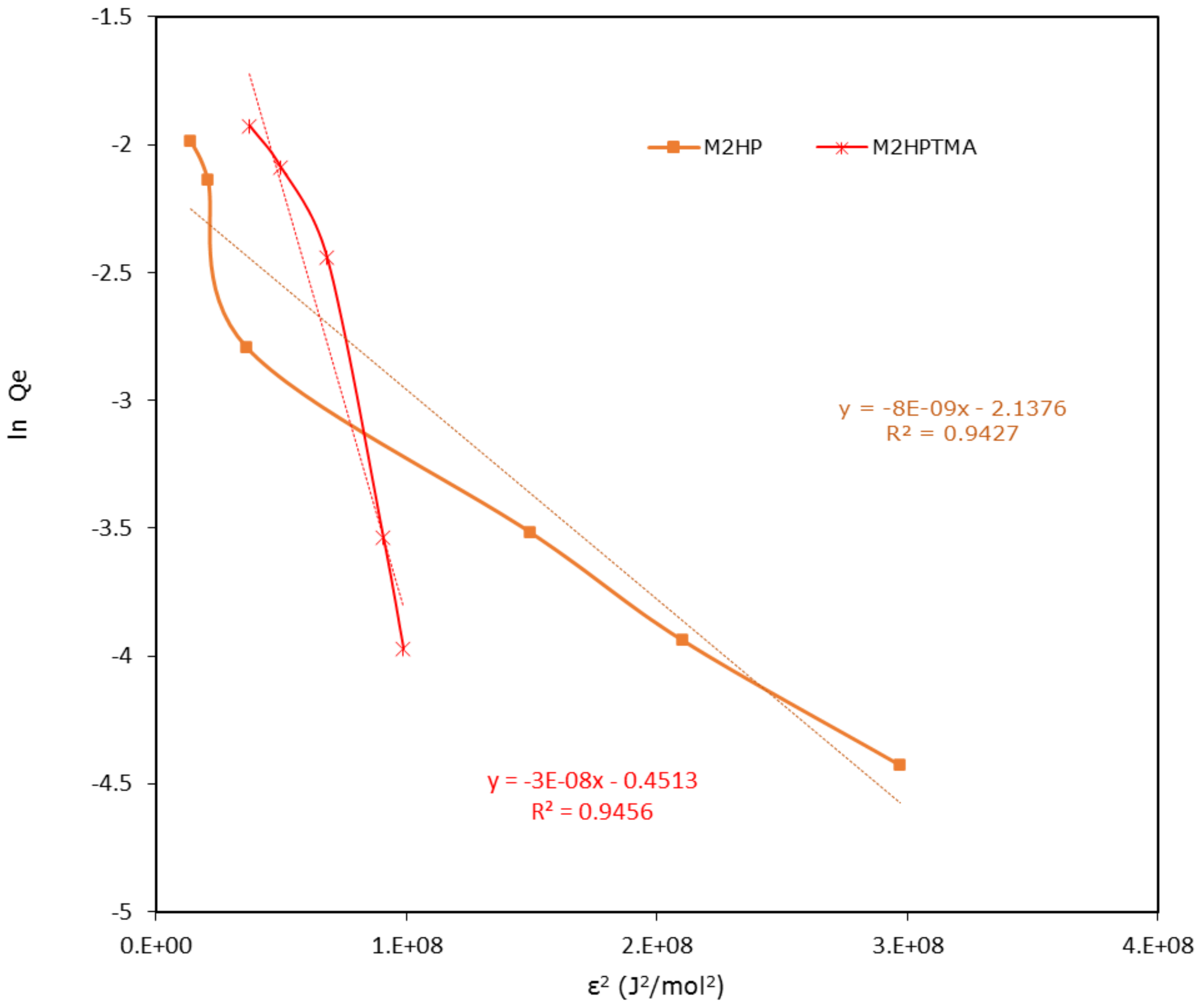


Figure 8. Linear fits of experimental data using DKR linear isotherm model for M2 and M2HP-TMA at 25 °C.

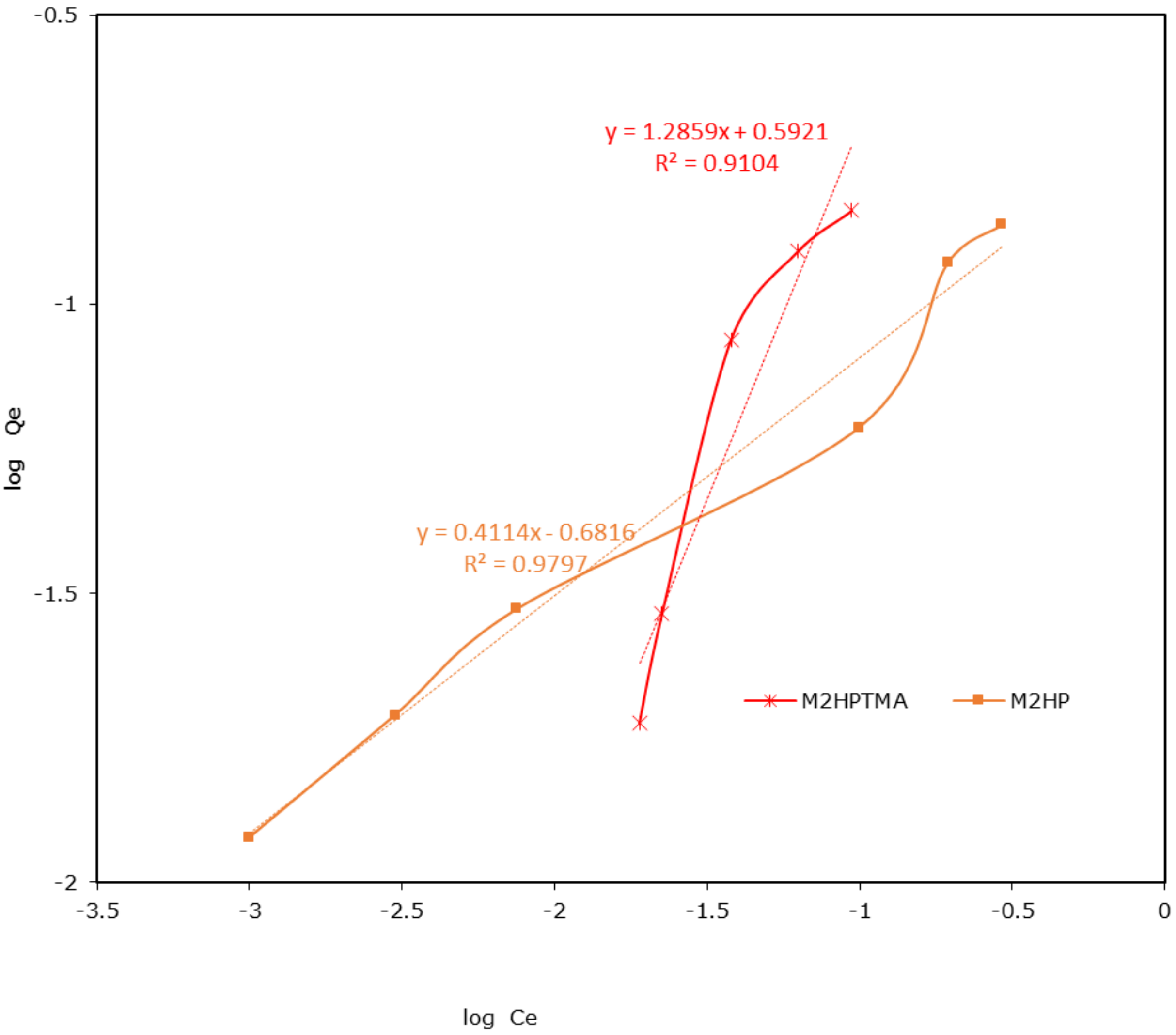


Figure 9. Linear fits of experimental data using Freundlich linear isotherm model for M2, and M2HP-TMA at 25 °C.

For M2HP-TMA, the estimated X_m, 0.64 mg/g, is rather high, compared with the highest measured amount, 0.145 mg/g. However, for

M2, X_m = 0.12 mg/g, is near the maximum capacity observed experimentally, 0.137 mg/g. It is 6 % lower than the highest sorption determined for M2HP-TMA, and it falls within the range reported for some Chinese soils (Jiang *et al*., 2005). Besides, from this model, it is possible to estimate the average adsorption energy, E, from the relation: $E=1/(2\beta)^{1/2}$. A value of E less than 8 kJ/mol indicates physisorption, while values between 8-16 kJ/mol are characteristic of mechanisms of ion exchange (Chutia *et al.,* 2009; Erdem *et al*., 2004). The estimated E for M2HP-TMA and M2 were 4.1 and 7.9 kJ/mol, respectively, which would indicate physisorption for the former, while for the latter, E is very close to the lower limit for the ion-exchange mechanism (Equation (3)). The slopes 1/n were 0.41 and 1.28 for M2, and M2HP-TMA, respectively. In this model, the slope 1/n can be interpreted as a measure of the strength of adsorption (Puttamat & Pavarajarn, 2016; Boparai, Joseph, & O'Carroll, 2011; Foo & Hameed, 2010). Isotherms with $1/n<1$ reflect a high affinity between adsorbate and adsorbent, that would be in accordance with the ion exchange process, suggested by the E value, and the pseudo-second-order reaction model, for M2. On the other hand, M2HP-TMA showed $1/n>1$, which has been observed also for phosphate uptake on TMA adsorbed on alumina (Saha *et al*., 2009).

Although the adsorption capacity of the M2 soil sample is low compared with other adsorbents, especially synthetic materials, it is higher than the reported for iron-coated sand, which has been proposed as a low-cost and efficient As adsorbent (Thirunavukkarasu, Viraraghavan, & Subramanian, 2003). On the other hand, the use of this local and abundant soil as adsorbent could also help to mitigate the siltation reservoir problem, while the residues might be used by the local bricks manufacturers as a raw material, as has been recently proposed for waterworks sludge (Fang *et al*., 2019). However, further studies are necessary to assess its efficiency using unsieved soil, natural water, and natural conditions such as pH, presence of other anions, and influence of microbial activity.

Conclusions

The native sieved reservoir sediments seem to be a potential alternative to solve the arsenic water contamination for cities in the state of Guanajuato, Mexico. They showed an experimental maximum adsorption capacity of 137 g/kg, and they are abundant local materials. Besides, their use would help to diminish the siltation in the reservoir. The treatment with TMA increases slightly the arsenate adsorption capacity of this material. On the other hand, the studied kaolin, an abundant waste material without commercial use closer to some of the affected areas, showed lower arsenic capacity uptake, although the piranha reagent treatments almost triples it. However, further work is still needed in this respect.

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