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Comparative study of As(V) removal by ferric coagulation and oxy-hydroxides adsorption: laboratory and full-scale case studies

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ABSTRACT

This research attempts to evaluate the efficiency of the two main arsenic removal processes, i.e. Fe(III) coagulation and iron oxy-hydroxides adsorption, by combining laboratory-scale experiments and results from operating full-scale water treatment units, located in several places of Greece. The proposed experimental procedure showed that the removal ability of Fe (III) coagulation is proportional to the added iron salt dose and appears to be much more efficient than the adsorption process applied in columns filled with iron oxy-hydroxide solid media. Furthermore, the comparison with the results obtained from large-scale water treatment plants indicated the possibility to predict the required quantities of chemicals' addition, or adsorbents in scaling-up the laboratory or pilot-scale systems, respectively. However, apart from the effectiveness of each method, the variation in water flow rates, the residual arsenic concentrations, and the specific requirements for operation and maintenance should be also considered as important criteria for the selection of the optimum arsenic removal process.

Keywords: Arsenic removal; Ferric oxy-hydroxides; Coagulation; Adsorption; Case studies

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1. Introduction

Arsenic pollution of water sources, arising by geochemical or anthropogenic origins, is considered as a serious health problem affecting the consumption of drinking water from large populations worldwide [1,2]. Among the proposed techniques for the removal of this toxic element, arsenic sorption by ferric oxy-hydroxides is the most extensively applied, especially for the removal of As(V), due to a number of reasons including high effectiveness, low cost, and simplicity of application [3]. The capacity of sorption is mainly determined by the surface charge and the specific surface area of the used oxy-hydroxides, thus amorphous structures of this material are preferable. In practice, there are two competitive technologies taking advantage of the affinity of As(V) oxy-anions with the Fe(III) cations, i.e. adsorption onto granular ferric oxy-hydroxides, or on-site precipitation of

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ferric oxy-hydroxides by the addition of appropriate iron salts.

The operation of columns filled with an iron oxy-hydroxide adsorbent is considered as a relatively selective treatment process, the simplest among the convenient available arsenic removal technologies, requiring minimum operation and maintenance effort [4]. Ionic strength, as well as the presence of other inorganic ions, such as sulfate, nitrate, chloride, and bicarbonate, generally have very little effect on the iron oxy-hydroxides adsorption capacity [5], whereas there are considerable interferences caused by the presence of phosphate or silicate anions, which compete with arsenic for the same iron adsorption sites [6,7] and by the pH value. Coagulation of iron salts appears to present larger effectiveness-to-cost ratio, especially in large-scale drinking water treatment units. The main mechanisms operating in this case for arsenic removal include the adsorption onto the hydrolysis products of Fe(III) and the occlusion in the formed agglomerates. Several studies have been reported for removing arsenic from drinking water by coagulation, most of them by using $FeCl_3$ [8,9]. Iron coagulation process is a well-known treatment technology, involving commonly found and widely available chemicals, while their dose can be predicted at any pH value in the range between 6 and 8 for initial concentrations up to 1,000 μg As(V)/L [10]. However, the handling of produced sludge, along with the management of dewatered product, are considered as the main disadvantages of this process, contributing significantly to the increase of the respective treatment cost.

In general, there is always an uncertainty about the optimum method to be applied in each occasion, which differs in flow rate demands and initial arsenic content of the source (ground) water to be treated. In this work, the aforementioned mainly applied techniques were comparatively evaluated by laboratory tests and operating water treatment units regarding their sorption capacity. Laboratory-scale experiments by $FeClSO_4$ coagulation were performed by using a two-stage continuous flow process, while the corresponding adsorption rapid small-scale column tests (RSSCT) were applied by using the two most commonly applied commercially available adsorbents: granular ferric hydroxide (GFH) and BAYOXIDE (E33). Additionally, selected results from the full-scale coagulation and adsorption drinking water treatment units were also collected and evaluated from various plants, located at different regions around Greece, facing arsenic concentrations higher than the legislative permissible maximum contaminant level (MCL) of 10 μg/L.

2. Materials and methods

2.1. Water samples

The major physicochemical parameters, concerning arsenic removal of the waters evaluated in this study, are presented in Table 1. Tap water of Thessaloniki city spiked with 100 μg As(V)/L was used for laboratory-scale coagulation and adsorption experiments, after its appropriate dechlorination, using an activated carbon column. On-site measurements for adsorption and coagulation processes evaluation were performed in several full-scale water treatment plants, located in regions of Macedonia (North Greece), suffering from As contamination, including Kymina and Malgara (30 km west of Thessaloniki, close to Axios river), Triglia (60 km south-east of Thessaloniki) and Mitrousi (Serres), as well as in the waters of the spring "Bourboulithra" at Melivoia (30 km north-east of Larissa) and "Daidalos," a private well at the island of Kos (Fig. 1).

2.2. Reagents and adsorbents

The As(V) test solutions for laboratory experiments were freshly prepared by proper dilution of the stock solution (1,000 mg/L prepared from $Na_2HAsO_4 \cdot 7H_2O$) in tap water. The $FeClSO_4$ was selected as the most cost-effective source of Fe(III) for the coagulation tests as well as to allow direct comparison with the full-scale treatment plants of this study. A 1,000 mg/L Fe(III) stock solution (at pH 0.7) was prepared by diluting 8 g of 12.5% w/w $FeClSO_4$ and 5 mL of reagent grade concentrated H_2SO_4 in 1 L of distilled water. Working standards were freshly prepared by proper dilution of the stock solution and addition of sufficient drops of reagent grade concentrated H_2SO_4 to keep the solution pH value below 1.

The adsorbents evaluated in this study were the commercially available: (a) GFH that was supplied by SIEMENS and (b) the E33 (BAYOXIDE) that was supplied by Severn Trent. GFH consisted of akaganeite with an iron content 55 ± 1% w/w on dry basis, a specific surface area 270 m^2/g, a point of zero charge 5.2, and around 45% w/w of moisture. E33 is identified as goethite with an iron content 52 ± 1% w/w on dry basis, a specific surface area 130 m^2/g, a point of zero charge 7.8, and less than 5% moisture. The surface charge density of the adsorbents determined by the potentiometric mass titration method was found to be 0.89 and 0.28 mmol OH^-/g for GFH and E33, respectively.

2.3. Fe(III) coagulation tests

The laboratory pilot system for coagulation tests is described in Fig. 2. The major components are a

Table 1
Major physicochemical parameters of waters studied

Parameter	Thessaloniki[a]	Malgara[b]	Kymina[b]	Mitrousi[b]	Triglia[b]	Daidalos[b]	Melivoia[c]
pH	7.3	7.9	7.7	7.9	7.1	7.7	7.6
Redox, mV	280	82	105	118	230	130	205
Conductivity, μS/cm	590	795	1,050	455	1,550	1,320	425
Total Hardness, mg/L $CaCO_3$	284	174	285	87	595	138	195
HCO_3^-, mg/L	360	258	260	262	640	470	226
TOC, mg/L	0.9	0.8	1.1	0.6	0.7	0.6	0.15
Fe, mg/L	<0.05	0.18	0.09	0.22	<0.05	0.06	<0.05
Mn, mg/L	<0.02	0.23	0.19	0.13	<0.02	<0.02	<0.02
NH_4^+, mg/L	<0.05	1.2	1.1	0.7	<0.05	0.2	<0.05
PO_4^{3-}, mg/L	0.30	0.45	0.35	0.60	0.35	0.35	0.05
SO_4^{2-}, mg/L	14	<2	5	8	29	32	14
SiO_2, mg/L	20	26	26	14	32	61	12
Sb, μg/L	<1	<1	<1	<1	<1	<1	21
Cr, μg/L	<1	<1	<1	<1	4	<1	<1
Total As, μg/L	100	20	44	19	208	33	41
As(III), μg/L	<1.5	14	26	15	21	25	4
Maximum flow rate, m^3/h	–	75	100	50	100	20	60

[a] Tap water spiked with As(V).
[b] Ground water.
[c] Spring water.

Fig. 1. Location of examined drinking water treatment plants around Greece.

peristaltic pump for raw water sample feeding at 50 L/h, a 3 L rapid mixing tank equipped with a propeller stirrer rotating at 300 rpm, a 14 L flocculation tank equipped with four-paddled stirrer rotating at 30 rpm and a sand filtration column with diameter 0.08 m containing 0.7 m of silica with particle size 0.4–0.8 mm. Since all reactions (adsorption, occlusion, and co-precipitation) leading to arsenic removal by $FeClSO_4$ coagulation are completed during both rapid mixing and flocculation stages, the overall "reaction time" was estimated to be 20.4 min. The concentration of $FeClSO_4$ solution ranged between 100 and 1,000 mg/L corresponding to a Fe(III) dose of 0.5–5 mg/L which was added by a peristaltic chemical feed pump running at 0.4 L/h. Pilot-scale experiments were run for at least 4 h. For the tests, water samples from Mitrousi, after biological oxidation of natural arsenic (19 μg As(V)/L),

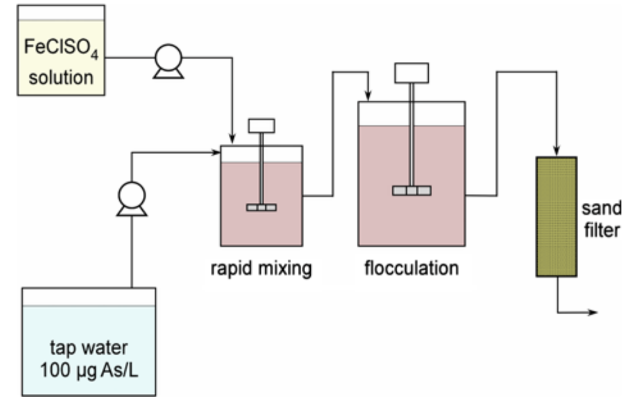

Fig. 2. Schematic diagram of laboratory Fe(III) coagulation system.

Table 2
Characteristics of filtration media in full-scale experiments

Parameter	Anthracite	Silica sand
Matrix	Coal	Silica
Physical form	Dry, crushed	Natural granules
Specific gravity, g/mL	1.6	2.6
Bulk density, g/mL	0.8	1.6–1.8
Size range, mm	1.4–2.5	0.4–0.8
Uniformity coefficient	<1.8	<1.6
Bed depth, m	0.4–0.5	0.7–0.8
Backwash rate, m/h	30–40	30–40

and tap water from Thessaloniki spiked with 100 μg As(V)/L were used (Table 1).

In full-scale experiments, concerning Kymina, Malgara, Triglia, and Daidalos water treatment plants, in-line addition of Fe(III) dose ($FeClSO_4$) was practiced resulting in a reaction time around 10, 12, 22, and 6 min, respectively, while the filtration rate (empty bed velocity) was estimated to 6, 8, 6, and 8 m/h. Filtration beds consisted of sand and anthracite and their characteristics are presented in Table 2. Fe(III) doses, as well as the Fe(III) concentrations in treated water samples, were determined by flame atomic absorption spectrophotometry, using a Perkin Elmer instrument model AAnalyst 800.

2.4. Adsorption tests

RSSCT were applied to evaluate the adsorbents' performance in laboratory and to produce the breakthrough curves under fixed-bed conditions. The columns (diameter 1.1 cm) were filled with 17 cm of the respective media adsorbent, which was equal to 20 g of dry GFH or 8 g of dry E33 with particle sizes 0.25–0.50 mm. Water spiked with 100 μg/L As(V) was passed through the columns at a flow rate 0.8 L/h. Under these experimental conditions, the empty bed contact time (EBCT) of small-scale column was 1.2 min, which is equivalent to 3 min EBCT of a relevant large-scale column (Table 3). For comparison reasons, full-scale adsorption column measurements were collected from Mitrousi treatment plant, using GFH (column dimensions: $D = 2.5$ m, $H = 0.9$ m) with 5 min EBCT, while results for E33 were taken from Melivoia adsorption unit (column dimensions: $D = 2.85$ m, $H = 1$ m) with 6 min EBCT.

2.5. Arsenic determination

Initial and residual (total) arsenic concentrations were determined by graphite furnace atomic absorption spectrophotometry, using a Perkin-Elmer instrument model AAnalyst 800. The detection limit of the method was 1.5 μg As(V)/L.

Table 3
Experimental conditions employed in RSSCTs

Parameter	Value
EBCT small scale, min	1.2
Equivalent EBCT of large scale, min	3
Hydraulic loading rate, m/h	8.4
Media height (L), cm	17
Particle size range, mm	0.25–0.50
Geometric mean of particles (d_p), mm	0.35
L/d_p	49
Column (media) diameter (D), cm	1.1
D/d_p	31
Column cross-sectional area, cm^2	0.95
Media mass, g	20 (GFH) 8 (E33)
Bed volume, mL	16
Bed volumes per hour	50
Flow rate, L/h	0.8
Backwash flow rate, L/h	1.8
$R_e \cdot S_c$	~2000
pH	7.2 ± 0.1
Temperature, °C	20 ± 1

2.6. Leaching tests

Dried saturated spent adsorbents from RSSCTs, as well as from full-scale water treatment plants of Mitrousi and Melivoia, and also dried sludge samples from Triglia plant, were subjected to standard leaching procedure EN 12457 used in European Union [11] and to US toxicity characteristic leaching procedure (TCLP) [12] to evaluate their compliance with the regulations for environmentally safe disposal of arsenic-loaded (spent) solids.

3. Results and discussion

3.1. Laboratory Fe(III) coagulation tests

The experimental results obtained from the treatment of tap water from Thessaloniki by coagulation showed an important decrease of arsenic removal efficiency as the treatment pH increases (Fig. 3(a)), in agreement with the data previously published [9,10,13]. In the range of residual arsenic concentration (C_e) with practical significance and interest for drinking water treatment purposes (2–20 μg/L), the specific removal ability q, in μg As(V)/mg Fe(III), vs. C_e resulted in a Freundlich-type curve $q = K_F C_e^{1/n}$, where K_F and n are constants related to adsorption capacity

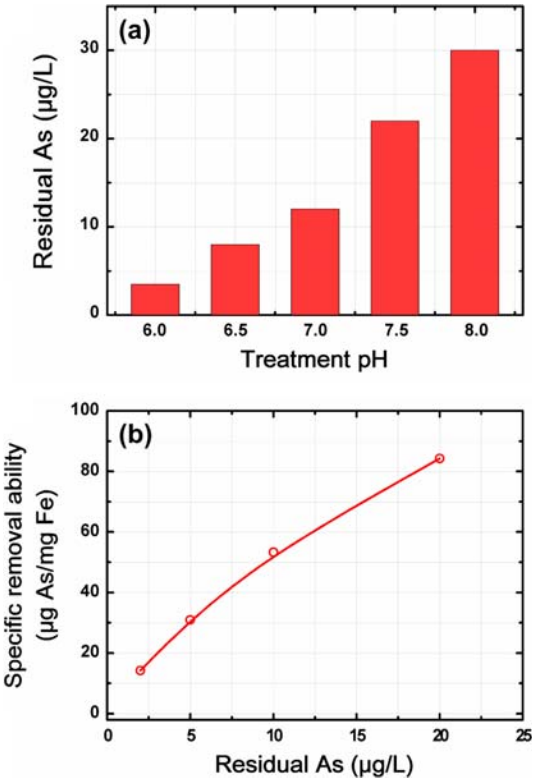

Fig. 3. Fe(III) coagulation experiments (a) influence of pH on As removal, $C_o = 100\,\mu g$ As(V)/L, Fe(III) doses = 1 mg/L and (b) Freundlich-type correlation between specific removal ability and C_e at pH 7.3.

and intensity, respectively (Fig. 3(b)). The validity of Freundlich model for a given pH value supports that the removal ability is independent to the initial arsenic content (C_o) [10]. In contrast, from Fig. 3(b) it is concluded that as C_e decreased, the value of q also decreased, which in turn resulted in higher Fe(III) dose demand for a given C_o. Using tap water from Thessaloniki city (initial pH 7.3), the q-value reaches 68 μg As/mg for the equilibrium As(V) concentration of 15 μg/L and reduces to 29 μg As/mg for the equilibrium As(V) of 5 μg/L (Table 4). Therefore, at low arsenic concentrations the specific removal ability is determined by the targeted C_e, since the available surface sites of iron precipitates are far from the saturation stage. The significantly lower removal ability (18 μg As/mg) observed for Mitrousi water at the equilibrium As(V) of 10 μg/L in comparison to that of Thessaloniki tap water (49 μg As/mg) directly reflects the strong influence of water pH.

3.2. Laboratory adsorption tests

The two commercially available (and mostly used for arsenic removal) adsorbents, i.e. E33 and GFH, were evaluated according to their breakthrough curves derived after the operation of packed bed columns in RSSCT experiments (Table 3). Fig. 4(a) indicates the evolution of arsenic concentration in the outflow of the columns with the volume of treated water passed. A column filled with GFH appears to treat similar volumes of water, while keeping residual arsenic concentration lower than 10 μg/L, in comparison to E33. However, considering the different mass content of each adsorbent column used to reach the same operational bed volumes of treated water and by introducing the breakthrough curve in terms of adsorption capacity (Fig. 4(b)), which directly reflects the cost of treatment, E33 comes out to be much more effective, reaching the q-value of 7.5 μg As/mg Fe (or 3.9 μg As/mg E33), before overcoming the MCL of 10 μg As/L. The corresponding value to obtain residual arsenic concentration 5 μg/L was 6.3 μg As/mg Fe (or 3.2 μg As/mg E33), while the GFH efficiency was found at 1.5 μg As/mg Fe (or 0.9 μg As/mg GFH), i.e. around one-forth of that of E33. Since surface charge density of GFH (0.89 mmol OH^-/g) was found greater than that of E33 (0.28 mmol OH^-/g) it is concluded that the secondary formation of the adsorbents grains seems to greatly influence their practical adsorption capacity observed in RSSCTs as well as in full-scale treatment plants.

In any case, the adsorption ability of solid adsorbents was still 6–10 times lower, than that of the freshly precipitated Fe(III) solution. The apparent reason for this significantly higher specific arsenic removal for the case of *in situ* formed (hydrous) hydroxides, is that the arsenate ions can form surface complexes on the short-chain polymers of $Fe(OH)_y{}^{z+}$, as they are gradually transformed from Fe(III) cations into $Fe(OH)_3$ floc (solid) particles, which can be subsequently separated by filtration. Pre-formed $Fe(OH)_3$ and granular ferric oxide/hydroxide media simply do not possess the similar extensive "surface area," when compared with the *in situ* formed oligomeric and polymeric species ($Fe(OH)_y^{z+}$).

3.3. Full-scale case studies

The results from the currently operating medium-size drinking water treatment plants are shown in Table 4. Wherever As(III) was co-existing with As(V) the indicated oxidation process, either biological [14] or chemical [15], was applied before treatment.

3.3.1. Coagulation–filtration

Arsenic removal in Malgara, Kymina, Triglia, and Daidalos drinking water treatment plants was performed by means of coagulation–filtration process, adding

Table 4
Specific iron consumption of $FeClSO_4$ coagulation and maximum adsorption capacity of iron oxy-hydroxide adsorbents for As(V) removal

Water sample	C_e (μg As(V)/L)	$FeClSO_4$ coagulation		Adsorption		As(III) oxidation	As after oxidation[a] (μg/L)
		Laboratory	Full-scale	RSSCT (lab-scale)	Full-scale		
		q (μg As(V)/mg Fe)		q (μg As(V)/mg Fe)			
Thessaloniki	15	68		GFH: 3.4 [or 1.9][b] E33: 9.1 [or 4.7][b]		–	100
Thessaloniki	10	49		GFH: 2.9 [or 1.6][b] E33: 7.5 [or 3.9][b]		–	100
Thessaloniki	5	29		GFH: 1.5 [or 0.9][b] E33: 6.3 [or 3.2][b]		–	100
Malgara	5		13			Biological	18
Kymina	5		17			Biological	44
Mitrousi	10	18			GFH: 3.1 [or 1.7][b]	Biological	19
Triglia	5		36			Ozone	208
Daidalos	5		14			Biological	29
Melivoia	15				E33: 9.8 [or 5.1][b]	–	41

[a] As(III) ≤ 2 μg/L.

[b] μg As/mg adsorbent (in dry basis).

$FeClSO_4$. Although, the residual arsenic concentration (C_e) varied between 2 and 10 μg/L, i.e. within the legislative MCL, the respective q-values for $C_e = 5$ μg/L are shown in Table 4 for comparison reasons.

The removal capacity values achieved at the full-scale treatment plants were found close to that predicted by recent proposed empirical expressions [10] for the specific quality characteristics of water samples and especially pH values and phosphate concentrations. In particular, the q-values ranged between 13 μg As(V)/mg Fe for the water of Malgara (pH 7.9) and 36 μg As(V)/mg Fe for the water of N. Triglia (pH 7.1) (Table 4). In addition, the observed 20% lower q-value (14 μg As(V)/mg Fe at pH 7.7) at Daidalos treatment plant, when compared to that of Kymina (17 μg As/mg at pH 7.7), directly reflects the moderate influence of different silicate concentrations [16] on Fe(III) removal capacity for pH values higher than 7.5, since the respective phosphate concentrations were found to be similar. Using the spot price of 0.25 €/kg for 12.5% w/w $FeClSO_4$ commercially available solution, the cost for 1 kg of Fe is estimated to be as low as 2 €/kg, which contributes to the low treatment cost of this method. As a result, the coagulation–filtration process was proved more efficient for the removal of As(V), when combining also the low cost of $FeClSO_4$ used, even for the case of Triglia, where the initial arsenic concentration was higher than 200 μg/L.

However, in both laboratory and full-scale experiments a significant increase of residual iron concentration was observed by increasing the filtration rate. More specifically, in all cases filtration rates below 5 m/h resulted in residual iron concentration well below 0.05 mg/L, while for filtration rates between 5 and 8 m/h the residual iron concentration fluctuated below the MCL 0.2 mg/L for iron. For filtration rates above 8 m/h, iron concentration overpassed MCL suggesting that a thorough investigation should be performed considering the optimization (increase) of filtration rate along with the subsequent precipitate separation. In addition, sand filter beds showed significantly low capacity for ferric oxy-hydroxides restrain, which ranged between 300 and 400 g Fe/m^3 of filter bed and resulted in turn to the consumption of more than 5% of the treated water for the backwash (cleaning) of sand filters. Conclusively, the relatively low filtration rate and the water loss along with the management of the sludge produced during the sand filters' backwash are considered as the main drawbacks of coagulation–sand filtration arsenic removal process.

The operational cost, as a sum of reagent, energy, labor, and depreciation cost, was estimated to be around 0.09 ± 0.02 €/m^3, with the reagent cost to count in a significantly lower level than 0.01 €/m^3 (10% of total running cost) for Daidalos, Kymina, and Malgara treatment plants, where the backwash water is directly disposed to the sewage. Triglia's plant had a higher operational cost 0.14 ± 0.02 €/m^3 mainly attributed to the precipitate treatment, which includes handling of backwash water, thickening, and

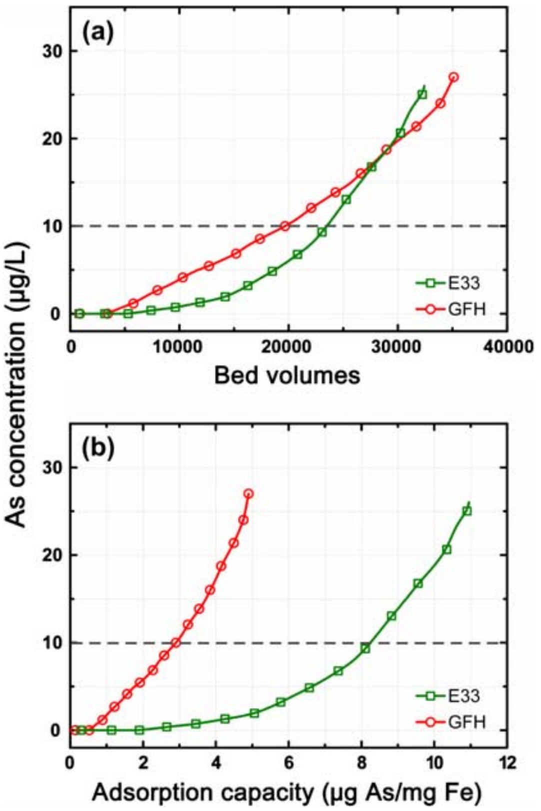

Fig. 4. Breakthrough curves of RSSCT experiments corresponding to E33 and GFH adsorbents in terms of (a) bed volumes and (b) adsorption capacity.

dewatering of the sludge, since the reagent cost remains close to 0.01 €/m^3.

3.3.2. Adsorption

The information concerning the adsorption capacity of E33 and GFH sorbent materials in full-scale units, collected from the drinking water treatment plants of Melivoia and Mitrousi, respectively, is consistent with the RSSCT tests, which actually simulate the operation of larger scale adsorption columns. The results proved that in general, the adsorption efficiency of E33 was significantly higher than GFH (Table 4), while the adsorption efficiency of both adsorbents was more than five times lower, when compared with the coagulation–filtration process. The marginally higher adsorption capacity of E33 at Melivoia plant ($q = 9.8$ μg As(V)/mg Fe), in comparison to that of RSSCT experiments ($q = 9.1$ μg As(V)/mg Fe) despite the higher pH of the water to be treated (7.6 instead of 7.3), should be mainly attributed to waters' lower phosphate content (0.05 instead of 0.30 mg/L), as well as to the extended contact time (6 min instead of 3 min). Considering the spot commercial price of 9 €/kg GFH on dry basis (Mitrousi) and that of 12.5 €/kg E33 (Melivoia) the cost of iron in adsorbents was calculated to be 16 €/kg Fe and 24 €/kg Fe, respectively. The total operational cost at both water treatment plants practicing arsenic adsorption was estimated to be around 0.16 ± 0.02 €/m^3, with the cost of adsorbents to count in around 0.09 ± 0.02 €/m^3, contributing with more than 50% in the total running cost. The lower initial arsenic concentration of Mitrousi water counterbalances the lower adsorption capacity of GFH while Melivoia's treatment plant (E33) taking the advantage of gravity for water filtration, operates at almost no energy cost.

The preceded cost analysis verified the higher operational cost of adsorption process in comparison to coagulation–filtration. The reagent contribution to the treatment cost by the adsorption process using ferric oxy-hydroxides was estimated to be more than five times higher, than that of the coagulation–filtration process, counting also in more than 50% of the total running cost. In contrast, the adsorption process was proved to be much simpler, with lower labor cost and almost no water loss, since adsorption beds were preventively backwashed only once a month, while the sand filter's beds (following coagulation) had to be backwashed more than once per day. Labor cost is determinative to coagulation–filtration treatment and due to its inelasticity the smaller the unit is built the higher the contribution of labor cost to operational one becomes. Therefore, the expenses for the adsorbent were significantly counterbalanced by the lower labor cost [4], while quality assurance cost as well as energy and depreciation cost remained marginally lower than that of the coagulation–filtration process. Considering the aforementioned discussion, it is concluded that coagulation–filtration seems to be more attractive either for the higher water flows (e.g. Kymina) optimizing labor cost or for the high initial arsenic concentration taking the advantage of the lower reagent cost. In contrast, adsorption process is cost effective for lower initial arsenic concentration (<<50 μg/L), since the adsorbent cost is the dominant one in operational cost. By applying, for example, the adsorption data of E33 in this study and by practicing two adsorption columns in series, a cost of 0.35 ± 0.5 €/m^3 was estimated for the treatment of Triglia's water, which clearly consolidates the results of this study.

3.4. Spent media disposal

The spent adsorbents should comply with the environmental regulations for safe disposal after their

Table 5
Leaching characteristics of the spent media from RSSCTs and from full-scale plants

Process	Material	RAC[a] (μg/L)	Arsenic content		Leaching procedure	
			(μg As/mg Fe)	(μg As/mg media)	EN 12457 (mg As/kg media)	TCLP (μg/L)
RSSCT	GFH	25	4.7	2.6	0.04	7
RSSCT	E33	25	10.4	5.4	0.16	135
Melivoia	E33	15	9.8	5.1	0.24	150
Mitrousi	GFH	10	3.1	1.7	0.03	8
Triglia	Dry iron hydroxide	5	36	13	0.45	20

[a] Residual As concentration at the end of experiment.

use. In case of landfill disposal, specific leaching procedures were designed to predict whether the contained pollutants, such as arsenic, are likely to be mobilized from the deposited wastes, moving into the surrounding ground waters, resulting in contamination problems. The tests EN 12457 and TCLP are well-defined standard leaching procedures that have been developed from European Union and US EPA, respectively. Regarding the EN 12457 standard leaching test, the required criterion for the characterization of a waste as inert (for safe disposal) is that the leachate should contain less than the MCL of 0.5 mg As/kg of media. Regarding the TCLP test, when the leachate contains lower than 5 mg/L of arsenic, then the waste is identified as non-hazardous under US federal regulations and can be legally land filled.

Regarding leaching of arsenic, both GFH and E33 spent media, either after the RSSCT experiments, or produced from the full-scale water treatment plants, as well as the spent sludge from the coagulation–filtration plant of Triglia, were proved to be inert according to EN 12457 procedure and non-hazardous according to TCLP test (Table 5). The higher arsenic concentration leached from the E33 spent adsorbent in comparison to the respective GFH media should be probably attributed to its higher arsenic-loaded content. Surprisingly, two out of the three examined spent media overstepped the EN 12457 MCL for inert wastes due to the leaching of toxic metals other than arsenic, fulfilling, however, the respective one for non-hazardous wastes. In particular, the total chromium leached (9 mg Cr/kg) from the spent sludge of Triglia marginally fulfilled the respective MCL (10 mg Cr/kg) for non-hazardous wastes, while the leaching of antimony (0.15 mg/kg) from the spent E33 media of Melivoia overpassed the EN 12457, respective MCL for inert wastes (0.06 mg/kg). Complementary to this study, the total antimony content 0.04 μg Sb/mg E33, which determined at the residual concentration of 21 μg Sb/L equal to initial one (Table 1) of Melivoia spent media was found to be equivalent with the respective published [17] for GFH (0.06 μg Sb/mg GFH) ensuring that the commercial ferric oxy-hydroxides examined in this study are practically unsuitable for the removal of antimony, unlike to allegation of the producers.

4. Conclusions

The comparison between the Fe(III) coagulation and the adsorption water treatment processes, considering the examination of commercially available ferric oxy-hydroxides and sorbents (E33 or GFH) in laboratory, as well as in full-scale treatment level, indicated the superiority of the first method to reduce As(V) below the regulated MCL, in terms of the spent iron (cost). In addition, it was shown that the removal ability during the *in situ* precipitation of iron-hydroxides by $FeClSO_4$ was at least six times higher, than the corresponding adsorption process. However, water flow rate, initial arsenic concentration along with labor, and maintenance requirements, should also be considered for the installation of the optimum drinking water treatment process. On the view of environmental disposal safety, spent materials from both methods complied with the regulation for arsenic leaching.

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