

Iron coated pottery granules for arsenic removal from drinking water

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ABSTRACT

A new media, iron coated pottery granules (ICPG) has been developed for As removal from drinking water. ICPG is a solid phase media that produces a stable Fe–Si surface complex for arsenic adsorption. Scanning electron microscopy (SEM) was used to document the physical attributes (grain size, pore size and distribution, surface roughness) of the ICPG media. Several advantages of the ICPG media such as (a) its granular structure, (b) its ability to absorb As via the $F(0)$ coating on the granules' surface; (c) the inexpensive preparation process for the media from clay material make ICPG media a highly effective media for removing arsenic at normal pH. A column filtration test demonstrated that within the stability region (flow rate lower than 15 L/h, EBCT >3 min), the concentration of As in the influent was always lower than 50 µg/L. The 2-week system ability test showed that the media consistently removed arsenic from test water to below the 5 µg/L level. The average removal efficiencies for total arsenic, As(III), and As(V) for a 2-week test period were 98%, 97%, and 99%, respectively, at an average flow rate of 4.1 L/h and normal pH. Measurements of the Freundlich and Langmuir isotherms at normal pH show that the Freundlich constants of the ICPG are very close to those of ferric hydroxide, nanoscale zero-valent iron and much higher than those of nanocrystalline titanium dioxide. The parameter $1/n$ is smaller than 0.55 indicating a favorable adsorption process [K. Hristovski, A. Baumgardner, P. Westerhoff, Selecting metal oxide nanomaterials for arsenic removal in fixed bed columns: from nanopowders to aggregated nanoparticle media, *J. Hazard. Mater.* 147 (2007) 265–274]. The maximum adsorption capacity (q_e) of the ICPG from the Langmuir isotherm is very close to that of nanoscale zero-valent iron indicating that zero-valent iron is involved in the process of the As removal from the water. The results of the toxicity characteristic leaching procedure (TCLP) analysis revealed that the media was non-hazardous, as shown by the ND (non-detectable) result for arsenic. The mechanism of As adsorption by ICPG has not been determined. Formation of Fe–Si complexes on the surface of the ICPG system may be responsible for the tight bonding of the As to the ICPG media.

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1. Introduction

Arsenic has been known for centuries as a toxic element. The main source of arsenic in drinking water is arsenic-rich rocks through which the water has percolated. Arsenic may also be derived from mining or industrial activity in some areas [2]. Arsenic in ground water is largely the result of minerals dissolving from weathered rocks and soils. Anthropogenic As stems from industrial wastes including those from the production of pesticides and fertilizers, and from mining, smelting and agricultural industries [3–6]. Drinking arsenic-rich water over a long period can result in various adverse health effects including skin problems, skin cancer, cancers of the bladder, kidneys and lungs, and diseases of the blood vessels of the legs and feet, and possibly also diabetes, high blood pressure

and reproductive disorders [6]. Arsenic contamination of drinking water resources is a global crisis [7].

A system for removing arsenic from drinking water in developing countries should meet several critical requirements: (1) efficient removal of both As(V) and As(III); (2) long life expectancy, high absorptive capacity, and high rate of adsorption and selectivity; (3) sufficient mechanical strength and large surface area to allow granular packing; (4) high physical integrity in water flow (does not disintegrate); (5) low cost and easy maintenance; (6) short hydraulic retention time (HRT); (7) safe disposal; (8) limited secondary problems such as changes in pH, hardness or microbiology that affect the quality of water. The most common arsenic removal technologies can be grouped into the following four categories: (a) oxidation and sedimentation; (b) coagulation and filtration; (c) sorptive media filtration; and (d) membrane filtration [8–12]. Oxidation of As(III) to As(V) is usually needed for effective removal of arsenic from groundwater by most treatment methods. The oxidation process also converts noncharged arsenite to charged

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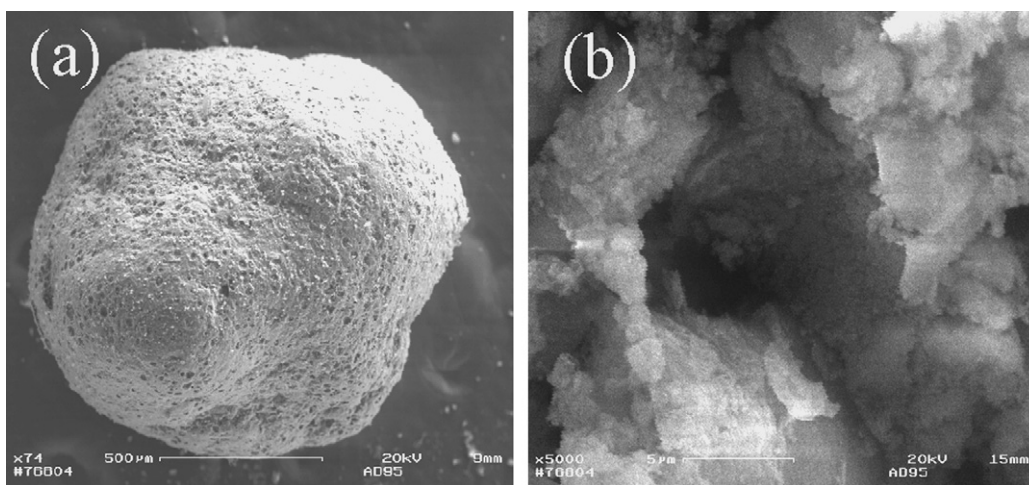


Fig. 1. Scanning electron micrograph of ICPG granule: (a) Whole particle (500 μm bar); (b) close up of ICPG pore (5 μm bar).

arsenate, which can be easily removed from water. In the process of coagulation, As is removed from solution by three mechanisms: precipitation, co precipitation, and adsorption. Sorptive media filtration is a process in which dissolved As is removed by attachment to the sorptive media at the molecular level. The commonly used sorptive media are modified activated carbon and iron-coated sand. Arsenic can also be removed by synthetic membrane filters with pore sizes appropriate for the removal of As. Analysis of these techniques shows that none of these techniques can presently satisfy all eight criteria mentioned above [9].

In this report, we describe a new method for the removal of arsenic from water based on the iron coated pottery granules (ICPG) recently developed at the University of Hawaii. The ICPG media is a highly porous material comprising iron, clay, and carbon.

2. Experimental

2.1. Synthesis of the iron coated pottery granules (ICPG)

The complete procedure for producing such granules is described in the patent submitted recently [13]. Briefly, the ICPG media is made of highly porous pottery granules that are coated with zero-valent iron powder. There are three key stages in the

manufacturing of ICPG media, resulting in the formation of surfaces with a solid phase of Fe–Si complexes: (1) Production of porous, large surface area pottery granules when a proprietary mixture of clay (i.e., kaolinite, 97% pure, with an average size of 1.36 μm), carbon source material (i.e., potato starch), liquid wax and water is fired in an anoxic chamber at first to 110 °C for 2 h and then further to 600 °C for 3 h; (2) the granule pottery is rehydrated and then 30 (w/w) zero-valent iron powder with a particle size less than 70 μm is added to the granules with constant agitation. The granules are mixed with iron powder for 20 min and placed into an iron bucket; and (3) the iron coated granules are re-fired, at first between 80 °C and 150 °C and then at around 500 °C for several hours. The re-firing process strengthens the granules.

2.2. Determination of As removal

The adsorption characteristics of As on the ICPG were studied under equilibrium and dynamic conditions. The ICPG media have been tested in column filter configurations for measuring efficiency of arsenic removal. An 0.8-L glass column, filled with 0.574 kg of ICPG media, was used as an up-flow reactor. Hawaii groundwater with added arsenic (sodium arsenite $150 \pm 1 \mu\text{g/L}$ and sodium arsenate $150 \pm 1 \mu\text{g/L}$) was used as the arsenic-laced test water. The test

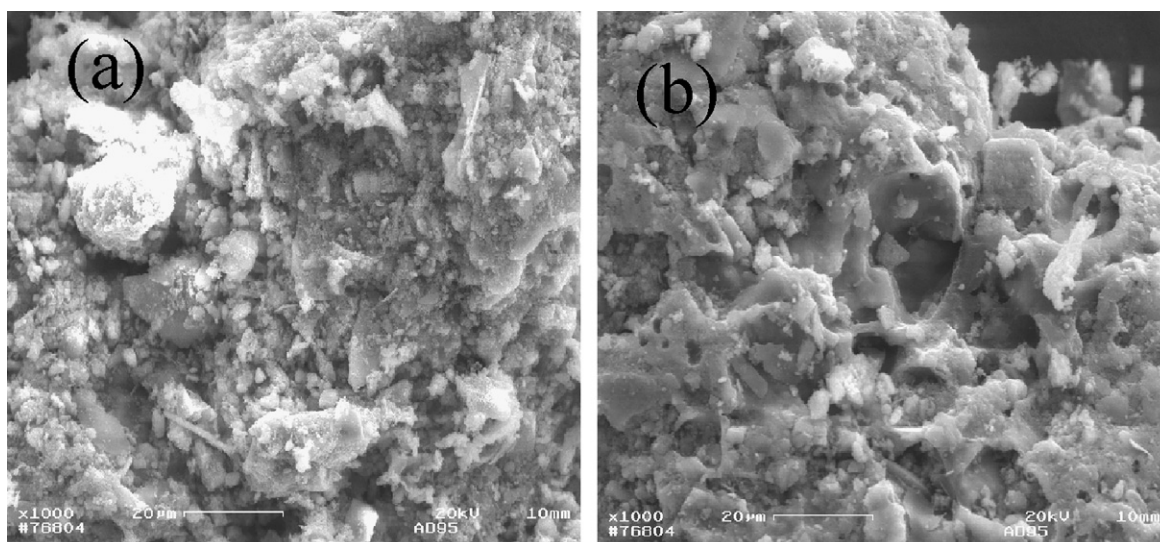


Fig. 2. Scanning electron micrograph of ICPG granule: (a) Unused granule and (b) granule after three months in column flow-through service.

Table 1
Laboratory up-flow column filter performance data for ICPG media.

Flow rate (L/h)	1.8	2.1	3.1	3.5	3.8	4.1	6.1	8	10	12	14.5
Empty bed contact time (min)	26.7	22.9	15.5	13.7	12.6	11.7	7.9	6.0	4.8	4.0	3.3
Effluent residual As ($\mu\text{g/L}$)	0	0	0	4	9	17	20	27	26	39	47
As removal rate (%)	100.0	100.0	100.0	98.7	97.0	94.3	93.3	91.0	91.3	87.0	84.3

water had a pH in the range of 6.5–7.5 and contained 20.8 mg/ml of Ca, 20.99 mg/ml Mg, 0.17 mg/ml Al and 69.3 mg/ml Si. The arsenic and other element concentrations of the test water were analyzed at the Agricultural Diagnostic Service Center (ADSC), University of Hawaii, using inductively coupled plasma-atomic emission spectrophotometry (ICP-AES; Thermo Jarrell Ash, model Atomscan 16) following EPA method 3005A, [14]. The detection limit for these analyses on the ICP was 0.002 $\mu\text{g/ml}$.

Determination of the approximate total arsenic adsorption capacity of the ICPG media in a 24-h isotherm test was also conducted by Shaw Environmental, Inc. (Cincinnati, Ohio). The following isotherm protocol has been adapted. One liter of the arsenic test solution was prepared in a series of plastic reagent bottles as in the column experiment described above. The initial total concentration of the As concentration was 0.132 mg/L (50% As(III) and 50% As(V)). It was also verified that dissolved oxygen levels were below 0.2 mg/L. Increasing adsorbent dosages (M) were added to each successive sample (Table 2). The adsorbent-dosed samples were placed on a shaker table and stirred for 24 h. After 24 h, each sample was analyzed for total arsenic concentration. The pH and dissolved oxygen were also measured.

Evaluation of the ICPG media over a 2-week period to determine the system's ability to achieve a reduction in total arsenic to less than 50 micrograms per liter ($\mu\text{g/L}$) in the treated water was conducted by Shaw Environmental, Inc. (Cincinnati, Ohio). Each day, a fresh batch of test water was prepared for use in the study. A 600-L polyethylene tank was filled with dechlorinated City of Cincinnati tap water. The target-dissolved oxygen (DO) level in the tank water was 1.0 ± 0.5 mg/L when the test commenced. The pH of the test water was adjusted with concentrated hydrochloric acid to approximately 4.8 the day before the test. Overnight, the pH typically rose to 7.0 ± 0.5 . If the pH was outside of this range, it was re-adjusted to be within this range directly before the test by adding either sodium hydroxide or hydrochloric acid as necessary. The average flow rate was 4.1 L/h. Sodium arsenite (As(III)), sodium arsenate heptahydrate (As(V)), and ferrous chloride tetrahydrate (Fe(II)) were added 15 min prior to commencing

the test each morning. The target concentrations of arsenic and iron in the influent water are as follows: As(III) – 150 $\mu\text{g/L}$, As(V) – 150 $\mu\text{g/L}$, and Fe(II) – 2 mg/L. The test water tank was kept under a nitrogen blanket and stirred throughout the duration of the test. Samples of influent test water and effluent treated water were collected daily for metals analysis: total arsenic, As(III), As(V), iron, calcium, aluminum, magnesium, sodium, and silicon. Metals were analyzed using a PerkinElmer Optima 2100 Series Inductively Coupled Plasma (ICP) instrument with Optical Emission Spectrometer. Arsenic speciation was performed using a solid phase extraction cartridge (SPEC) – Waters Corporation Sep-Pak Plus Accell Plus QMA cartridges 37–55 μm – followed by analysis of the As(III)-bearing filtrate by ICP. Table 5 shows the average and standard deviation of the influent and effluent metal concentrations over the 2-week test period. Samples of influent test water and effluent were collected for anions (sulfate, chloride, nitrate, phosphate) once daily over the 2-week test period. Anions were analyzed using a Dionex ICS 2500 ion chromatograph (IC). The anion concentrations are provided in Table 6. Table 6 shows the average and standard deviation of the influent and effluent anion concentrations over the 2-week test period.

3. Results

3.1. Grain's morphology

The surface morphology of the ICPG granules was examined by scanning electron microscopy (SEM, Zeiss 960). The ICPG granule size is between 0.3 mm and 2.36 mm. The typical surface of the ICPG particle is highly porous, with pore diameters ranging from 10 μm to 20 μm (Fig. 1a and b). Fig. 2a and b compare the surface features of unused ICPG with those of exhausted (by arsenic adsorption) ICPG at a magnification of 1000 \times . The iron and clay substrate on ICPG surfaces initially forms a rough surface structure for arsenic adsorption (Fig. 2a). Extensive flow-through exposure (for 96 h) during arsenic adsorption appears to smooth the surface structure somewhat (Fig. 2b). Arsenic adsorption occurs at the surface of the media, presumably including the inside surface area of the pores in the media granules.

To determine the porosity of ICPG media, N_2 sorption experiments have been conducted using an Automated Gas Sorption system from Quantachrome Instruments [15]. The samples were degassed for 4 h at 210 $^\circ\text{C}$ before each isotherm measurement. The porosity of the ICPG media was found to be 75–80%. The BET specific surface area was 212 m^2/g , and the total pore volume 0.28 cm^3/g . BET specific surface area is evaluated from the Brunauer–Emmett–Teller (BET) equation describing the physical adsorption of gas molecules on a solid surface [16]. For comparison, the BET surface area of the iron-containing mesoporous carbon (IMC) [17] is twice as high (401 m^2/g) as that of ICPG, however, porosity is one half (44%) that of ICPG, indicating that the matrix of the ICPG is denser than that on IMC. These properties infuse the ICPG media with high permeability and adsorptive potential.

3.2. Column filtration test

The ICPG filtration column was operated continuously to purify sample groundwater. Arsenic removal efficiency as a function of

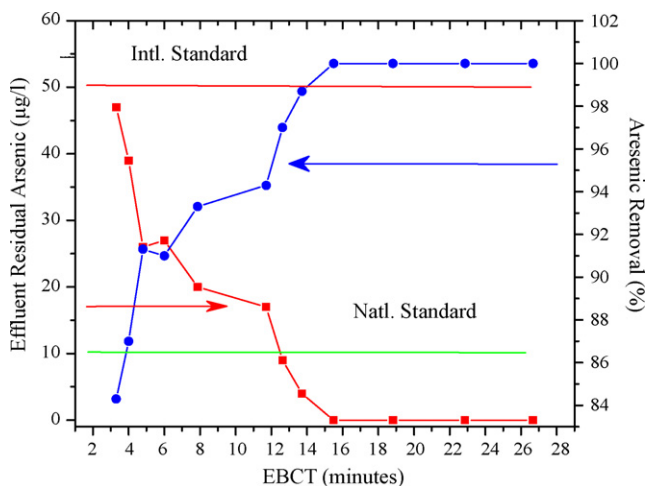


Fig. 3. Effluent residual arsenic (solid squares); arsenic removal rate (solid circles) as a function of EBCT.

Table 2

Results of the of the equilibrium experiment. The control measurement (first row in the table) is an average of two measurements.

M (mg)	C _e (mg/L)	X/M (mg/g)	pH
0	0.132	0	5.65
15.4	0.110	1.429	5.77
49.1	0.073	1.202	5.91
105.5	0.027	0.995	6.01
108.7	0.031	0.929	6.07
232.6	0.011	0.520	6.36

the flow rate was analyzed by adjusting the flow rate. During the filtration test the total influx concentration of the As was kept constant (sodium arsenite 150 µg/L and sodium arsenate 150 µg/L, all measured as arsenic) and the effluent concentration of the As was analyzed by ICP-AES. In each EBCT set, the system was tested for one week at steady state effluent with a constant flow rate. Table 1 and Fig. 3 show the results of the column filter test. In Fig. 3a, the average of the effluent of As (collected in the first and in the last day of the 1-week test) is represented as a function of the empty bed contact time (EBCT). The EBCT is the volume of the adsorbent ($Q = 0.8$ L) divided by the flow rate, V ($EBCT = Q/V$). Fig. 3 also shows the crucial EBCT necessary for the effluent quality to meet the U.S.A. national (10 µg/L) and international (50 µg/L) standards. In the test, when EBCT was less than 3 min or the flow-rate greater than 15 L/h, the system performance was not stable. However, within the stability region (flow rate lower than 15 L/h, EBCT > 3 min), the concentration of As in the influent was always lower than 50 µg/L. The crucial EBCT for effluent meeting the 10 µg/L was 12.6 min. For EBCT higher than 15 min, the concentration of the effluent As concentration was less than the detection limits of the ICP-AES system (2 µg/L). Fig. 3 also shows the efficiency of the As removal as a function of EBCT. The efficiency of the total arsenic removal was determined according to the following formula:

$$\% \text{Arsenic removal} = \frac{\text{total As}_{\text{in}} - \text{total As}_{\text{out}}}{\text{As}_{\text{in}}} \times 100. \quad (1)$$

The evaluation of the reliability of the ICPG media was carried out by employing a 1-L column loaded with 0.72 kg of ICPG. This system (at EBCT = 13.7) was able to treat 14,000 L before reaching the break-through load for arsenic. Since the ICPG medium is Fe- and Al-rich, Fe and Al concentrations in the effluent were monitored throughout the column filter tests. Results showed that no Al or Fe were leached (less than 0.5 µg/L) from the media after 5 days of operation.

3.3. Adsorption capacity test

Table 2 shows the results of the equilibrium experiment. To evaluate the sorption capacity of the ICPG media Freundlich equilibrium and Langmuir equilibrium isotherms were used to describe arsenic removal onto solids. The Freundlich equation has the form [18,19]:

$$q_e = \frac{X}{M} = K_F C_e^{1/n} \quad (2)$$

where q_e is the mass of solute sorbed per unit dry weight of solid (mg/g), $X = C_0 - C_e$ is the amount of compounds adsorbed from a unit volume of solution, M is the weight of adsorbent, C_0 is the concentration of arsenic in the untreated solution (control measurements in Table 2), C_e is the concentration of arsenic in the treated water, K_F is the Freundlich sorption coefficient (mg/g)(L/mg)^{1/n} and $1/n$ is a dimensionless constant. The arsenic adsorption data, obtained at pH 7.0 (Table 2) and fitted with the logarithmic form (red line) of the Eq. (2) are shown in Fig. 4. The two Freundlich isotherm constants (i.e. K_F and $1/n$) obtained from fitting

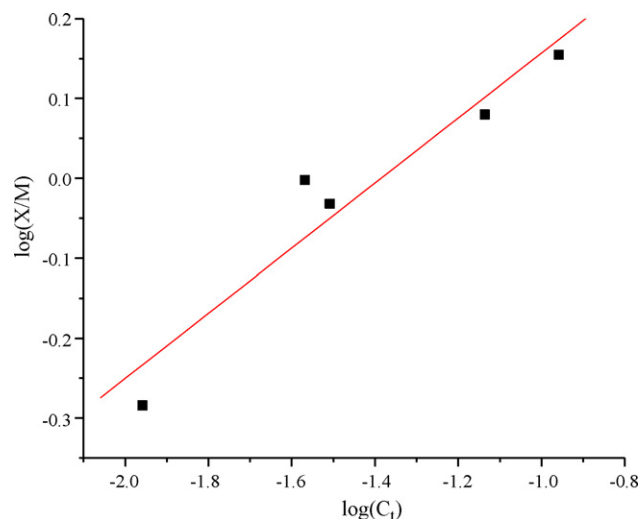


Fig. 4. Adsorption isotherm obtained for arsenic sorption by ICPG using Freundlich equation.

the experimental data to Freundlich equation isotherms (Fig. 5) are tabulated in Table 3. The sorption coefficient, K_F , was found to be $3.6 (\pm 1.3)$ (mg/g)(L/mg)^{1/n}, and the adsorption intensity $1/n = 0.41 (\pm 0.07)$. Numbers in the brackets are standard deviations. In the Freundlich isotherm model, K_F is a measure of the adsorption capacity (larger K_F indicates a larger overall capacity), whereas the parameter $1/n$ is a measure of the strength of adsorption, representing the concentration of arsenic in a saturated column. The adsorbent capacity of the media was found to be 1.17 mg As/g adsorbent).

For the Langmuir adsorption isotherm we used a linearized form (see [20]):

$$\frac{1}{q_e} = \frac{1}{K_L q_{\text{max}} C_e} + \frac{1}{q_{\text{max}}}, \quad (3)$$

where constants q_{max} (mg/g) and K_L (L/mg) are the Langmuir parameters. The constant q_{max} represents the maximum adsorption capacity and K_L is the dissociation coefficient of the solute-adsorbent complex, which represents the affinity between the solute and the adsorbent [21]. The Langmuir isotherm constants obtained from fitting the experimental data to linearized Langmuir isotherm (Fig. 5) are tabulated in Table 4. Results of

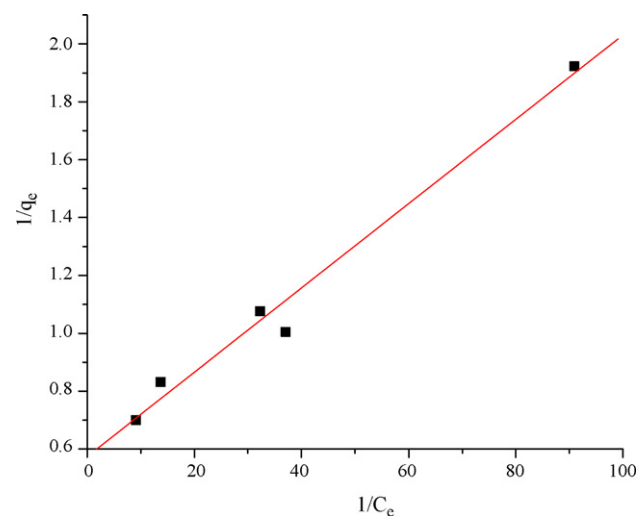


Fig. 5. Adsorption isotherm obtained for arsenic sorption by ICPG using Langmuir equation (linearized form).

Table 3
Arsenate adsorption Freundlich isotherm parameters for ICPG compared with other adsorbents.

Adsorbents	K_F (mg/g)	$1/n$ (L/mg)	pH	Duration (h)	Reference
ICPG	3.6	0.41	7.0	24	This study
Ferric hydroxide	3.5	0.28	7.0	24	[39]
Nanocrystalline titanium dioxide	0.5–0.75	0.19–0.53		22	[40]
Nanoscale Fe(0)	3.5	0.31	7.0	12	[41]
Algae <i>Lessonia nigrescens</i>	2.96	0.35	6.5	24	[21]

Table 4
Arsenate adsorption Langmuir isotherm parameters for ICPG compared with other adsorbents.

Adsorbents	q_{max} (mg/g)	K_L (mg/L)	pH	Duration (h)	Reference
ICPG	1.74	39.3	7.0	24	This study
Nanoscale Fe(0)	1.8	135		12	[41]
Algae <i>Lessonia nigrescens</i>	28.2	69.4	6.5	24	[21]
Fe oxide-coated sand	0.029	83.0	7.5	2	[42]
Uncoated sand	0.006	2.0	7.5	2	[42]
Kaolinite	0.86		5.0	3	[43]

Table 5
Average and standard deviation of the influent and effluent metal concentrations.

Metal	Influent (mg/L)	Effluent (mg/L)
Arsenic (total)	0.324 ± 0.013	0.005 ± 0.003
Arsenic(III)	0.031 ± 0.029	0.001 ± 0.002
Arsenic(V)	0.293 ± 0.031	0.004 ± 0.003
Iron	1.974 ± 0.106	0.395 ± 0.0525
Calcium	34.20 ± 1.94	32.88 ± 1.47
Aluminum	0.215 ± 0.023	0.23 ± 0.126
Magnesium	11.66 ± 0.51	11.45 ± 0.45
Sodium	32.80 ± 1.33	31.11 ± 2.96
Silicon	2.364 ± 0.297	4.011 ± 0.972

another isotherm study with different adsorbents are also presented in Tables 3 and 4 for comparison. Adsorbent capacity q_e^0 was determined from the Eq. (2) for the equilibrium concentration ($C_e = 50 \mu\text{g/L}$) and was found to be equal to 1.17 mg/g.

3.4. 2-week system ability test

The average removal efficiencies for total arsenic, As(III), and As(V) during the 2-week test period were 98%, 97%, and 99%, respectively (Table 5). Although equal concentrations of As(III) and As(V) were added to the feed water, it was observed that As(III) oxidized rapidly to As(V) at the influent sample location. In addition to arsenic, the unit also removed most of the iron from the influent test water. Silicon concentration in the effluent water increased slightly compared to the influent. Data on the concentrations of the anions in the treated water revealed that there were no significant changes in the concentrations of the anions in the treated effluent water relative to the influent test water (Table 6). There was a nearly 40% reduction in nitrate concentration; however, high statistical error in the measured nitrate concentration precludes drawing an emphatic conclusion. We are going to conduct a comprehensive study on nitrate removing by ICPG media from drinking water in the future.

Table 6
Average and standard deviation of the influent and effluent anion concentration.

Anion	Influent (mg/L)	Effluent (mg/L)
Sulfate	75.8 ± 6.7	66.7 ± 6.8
Chloride	95.7 ± 9.9	94.3 ± 4.8
Nitrate	1.96 ± 0.71	1.14 ± 0.36
Phosphate	0.35 ± 0.15	0.094 ± 0.141

3.5. Toxicity characteristic leaching procedure (TCLP)

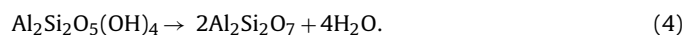
A sample of the used ICPG media associated with the ICPGF was submitted to a contract analytical laboratory (Severn Trent Laboratories, North Canton, Ohio) for TCLP analysis. The purpose of this analysis is to determine the hazardous or non-hazardous nature of the used media for disposal considerations. Exhausted media was tested by Standard method of toxicity characteristic leaching procedure which is designed to determine the mobility of both organic and inorganic constituents present in liquid, solid, and multiphase wastes). The results of the TCLP analysis revealed that the media is non-hazardous, as shown by the ND (non-detectable) result for arsenic [22]. The media can be classified as non-hazard waste suitable for regular landfill waste disposal.

4. Discussion

The Freundlich constants of the ICPG obtained in this study are based on a pseudo equilibration time of 24 h (see [23]) and, therefore, in Table 3 Freundlich constants are given only for those adsorbents that were obtained under similar conditions (a pseudo equilibration time of 24 h and 22 h, respectively). The Freundlich constants of the ICPG are very close to those of the ferric hydroxide, nanoscale zero-valent iron and much higher than those of nanocrystalline titanium dioxide. Parameter $1/n$ is smaller than 0.55 indicating a favorable adsorption process [1]. The maximum adsorption capacity (q_e) of the ICPG from the Langmuir isotherm is very close to that of nanoscale zero-valent (Table 4) indicating that the zero-valent iron is involved in the process of the As removing from the water. It is interesting that Freundlich constants of the bioadsorbent (*Algae Lessonia nigrescens*) is close to those of ICPG (Table 3), however Langmuir isotherm parameter q_{max} for bioadsorbent is 20 times as high as that of ICPG (Table 4) [1]. Some of the techniques that are widely used for As removal from the drinking water were not included into the Table 4 because often parameters of the Freundlich and Langmuir isotherms are measured under conditions that are different from those used in this work: for instance equilibrium time. However, it is easy to identify advantages of the ICPG media over other major technologies such as alum coagulation, iron coagulation, lime softening, and iron coated sand discussed in the recent review written by Mohan and Pittman [12]. For instance, Alum coagulation, produces toxic sludge and has low removal of arsenic and pre-oxidation may be required if arsenic is presents as arsenite [12]. The ICPG media does not produce toxic sludge and achieves high arsenite (97%) and arsenate (99%) removal. For the iron coagulation method, sedimentation and filtration are needed because of extra iron ions in the effluent water [12]. In contrast, iron does not leach out to water in ICPG media. In the lime softening method, chemicals are available commercially but readjustment of pH is required because lime increases pH of water up to 10, whereas the ICPG method can be operated under normal pH for both arsenite and arsenate adsorption without changing pH of the water. Iron coated sand is an inexpensive method and removes both As(III) and As(V), but it is not standardized and produces toxic solid waste. The ICPG media can be easily standardized and does not generate toxic waste.

The absorbent capacity $q_e^c = 1.17$ mg/g determined for ICPG from the test experiments conducted by Shaw Environmental, Inc. (Cincinnati, Ohio) was found to be nearly 10 times lower than the values of the absorbent capacity measured in the feasibility studies conducted by the University of Hawaii. At the University of Hawaii, the ICPG granules have been tested in 24 h batch experiments. Hawaii groundwater with an arsenic dosage was used for testing: sodium arsenite 150 $\mu\text{g/L}$ and sodium arsenate 150 $\mu\text{g/L}$. The water's pH was in the range of 6.5–7.5 and contained 20.8 mg/L of Ca, 20.99 mg/L of Mg, 0.17 mg/L of Al and 69.3 mg/L of Si. The performance results for arsenite (As(III)) adsorption capacity of ICPG media are 12.5 mg/g, 19.8 mg/g, and 27.1 mg/g at pH of 4.0, 7.0 and 10, respectively, and for the arsenate As(V) the adsorption of ICPG are 41 mg/g, 32 mg/g and 21 mg/g at pH of 4.0, 7.0 and 10, respectively. The discrepancy between preliminary studies conducted at the University of Hawaii and the test conducted by Shaw Environmental, Inc. (Cincinnati, Ohio) can be related to the difference in water compositions used for these tests. The Cincinnati tap water used by Shaw Environmental, Inc. contains high concentration (ppb amounts) of anions (sulfate, chloride, nitrate, phosphate) that can compete with As for the adsorption sites affecting real capacity of media adsorption. The effect of the anions on the adsorption capacity of the ICPG is beyond the scope of the current work and will be a subject of the future research.

The mechanism of As adsorption by ICPG has not been determined. The nature of the final product that appears to fix arsenic so strongly in the ICPG system is also not known. A detailed study of the As adsorption mechanism of the ICPG system via characterization of pristine and exhausted ICPG media is a major objective of future research; however, we can consider possible mechanisms of As removal by ICPG. The ICPG media consists mostly of kaolinite. Kaolinite is a layer-structured silicate with a chemical composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and undergoes a series of phase transformations upon thermal treatment in air at atmospheric pressure [24]. Endothermic dehydroxylation (or, alternatively, dehydration) begins at 550–600 °C to produce disordered metakaolin, $\text{Al}_2\text{Si}_2\text{O}_7$ [25,26]



Extensive research has led to a general consensus that metakaolin is not a simple mixture of amorphous silica (SiO_2) and alumina (Al_2O_3), but rather a complex amorphous structure that retains some longer-range order (but not strictly crystalline) due to stacking of its hexagonal layers [27,28]. Therefore, three elements Al, Si, and Fe could be responsible for As removal. Zero-valent iron has been found recently to be extremely promising for removal of arsenic from groundwater [29–32]. The mechanism of arsenic removal by Fe(0) has been suggested to involve adsorption of As(III) and As(V) onto iron oxides formed *in situ* as a result of corrosion reactions with Fe(0). To verify the role of the Fe(0) coating of the pottery granules, a filtration test was conducted where pottery granules were not coated with Fe(0). It has been demonstrated that the pottery granules without Fe(0) coating were able to remove As, but only for a short period of time (2–3 h), while those coated with Fe(0) can sustain the high removal efficiency over extended time periods (greater than three months). Unlike zero-valent iron treatment, the ICPG technology does not require chemical additions or post-As removal filtration, as is usually required for iron leachate removal.

The removal mechanism by the ICPG media might be similar to that described by Zeng [33] who developed a method for preparation of granulated iron(III)-based binary oxide adsorbents, which consisted mainly of amorphous hydrous ferric oxide (FeOOH) with silica as a binding agent. The key step in the method was the simultaneous generation of hydrous ferric oxide (FeOOH) sol and silica sol *in situ* in one reactor. It has been also reported that polymerization

of H_4SiO_4 on FeOOH surfaces can occur to form Fe–Si surface complexes, typically in the form of Fe–O–Si(OH)₃ [34]. The formation of Fe–Si surface complexes was reported by Zhang and Itoh [35]. They synthesized an adsorbent for aqueous arsenic removal by loading iron(III) oxide onto melted municipal solid waste incinerator slag. The simultaneous *in situ* generation of amorphous hydrous ferric oxide sol and a silica sol eventually led to the formation of Fe–Si surface complexes which tightly bonded the iron oxide to the slag (see also [12]). Formation of the Fe–Si complexes on the surface of the ICPG system may be responsible for the tight bonding of the As to the ICPG media.

It is also of interest to understand the possible role of Al in the formation of As(III) and As(V) adsorption complexes forming at the $\gamma\text{-Al}_2\text{O}_3$ /water interface [36,37]. Recently it has been shown that the adsorption capacity of iron oxide impregnated onto activated alumina (IOIAA) is significantly higher than the published values for iron oxide-coated sand and ferrihydrite [38]. However, the mechanism of the As adsorption in the IOIAA media has not been studied.

The results of the filter test indicate that the ICPG media are highly effective at removing arsenic from water at normal pH. One of the possible explanations for this high efficiency is related to the material structure and high porosity of the granules that make the ICPG a highly adsorptive media. A comparison of the SEM images (Fig. 1) of the granule surfaces before and after use as a filter media indicates that reaction or adsorption could occur not only on the grain surface but also spreads to the surface of the open pores in each grain. Although the internal pores may not be coated with iron and may not adsorb As, we believe that water does penetrate inside the pores. The flow of the drinking water through internal pores may not reduce the As concentration but it would help remove small microscopic particles from the water. This could explain why the ICPG filter effluent is generally very clean. Moreover, The Toxicity Characteristic Leaching Procedure (TCLP) test carried by Shaw Environmental, Inc. (Cincinnati, Ohio) shows that no As was leached (less than 0.5 $\mu\text{g/L}$) from the media. Therefore, the ICPG media may be used simultaneously for general water purification and for As removal from drinking water.

Our results are consistent with the filter test conducted by Shaw Environmental Inc. (Ohio, USA). Under EPA Contract, Shaw Environmental Inc. carried out an independent assessment on the ICPG that was selected as one of the 15 finalists in the 'Grainger Challenge' sponsored by the National Academy of Engineering [22]. The report states that "the resulting water quality was found to be excellent in that it is clear, colorless, and with most parameters (e.g., pH) unchanged", concluding that "ICPG consistently removed arsenic from test water to below 50 $\mu\text{g/L}$ design level" (NAE Final Report, 2006).

5. Conclusions

A new media, ICPG, has been developed for As removal from drinking water. Several advantages of the ICPG media such as (a) its granular structure, (b) its ability to absorb As using of Fe(0) coated on the granules surface; (c) the inexpensive preparation process for the media from clay material make ICPG media a highly effective media for removing arsenic at normal pH. Column filtration tests demonstrated that within the stability region (flow rate lower than 15 L/h, EBCT >3 min), the concentration of As in the effluent was always lower than 50 $\mu\text{g/L}$. The 2-week system ability test showed that the media consistently removed arsenic from test water to below the 5 $\mu\text{g/L}$ level. The average removal efficiencies for total arsenic, As(III), and As(V) removal for 2-week test period were 98%, 97%, and 99%, respectively, at an average flow rate of 4.1 L/h at EBCT of 17 min and normal pH. Fitting the experimental data to Freundlich and Langmuir isotherms at normal pH showed that the Freundlich constants of the ICPG are very close to those of the ferric

hydroxide, nanoscale zero-valent iron and much higher than those of nanocrystalline titanium dioxide. Parameter $1/n$ for the ICPG is smaller than 0.55, indicating a favorable adsorption process [1]. The maximum adsorption capacity (q_e) of the ICPG from the Langmuir isotherm is very close to that of nanoscale zero-valent iron indicating that zero-valent iron is involved in the process of the As removing from the water. The results of the TCLP analysis revealed that the media is non-hazardous, as shown by the ND (non-detectable) result for arsenic.

It is shown that the IGPC used as the media in water filtration procedures maintains the water quality with respect to other cations, and that the scavenged arsenic is tightly bonded to the media during the adsorption process, and as a result very little arsenic flashes out from the exhausted media. We believe that the test results reported here indicate that the new ICPG media fulfills the critical requirements of a column adsorbent for arsenic removal listed in the introduction. Therefore, the new ICPG media could promise a system for arsenic removal from drinking water in the developing countries.

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