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Predicting Fe^{3+} dose for As(V) removal at pHs and temperatures commonly encountered in natural waters

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ABSTRACT

Equations describing quantitatively the relation between Fe^{3+} dose and residual arsenic concentration, C_e, at pH values ranging between 6 and 8 and various initial arsenic concentrations, C_o, were established using a natural water spiked with As(V). These equations were used to calculate the specific arsenic removal, q, in μg As removed per mg Fe^{3+} added. In turn, reliable equations relating q and C_e in the range between 2 and 20 μg As/L were derived. The latter equations predicted Fe^{3+} dose, necessary to achieve any selected C_e, when the water's C_o and pH were known, with a satisfactory degree of accuracy (relative standard deviation less than 15%). In addition, comparison of As(V) removal data from full scale water treatment plants to those predicted by the empirical equations presented in this work, corroborated the fact that these equations can serve as a reliable guide for the prediction of Fe^{3+} dose necessary to remove As(V) from drinking water. The process of arsenic removal by using Fe^{3+} as a coagulant was found to be exothermic in character and C_e showed an increase by a factor of about 1.5 for each 10 °C increase in temperature.

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1. Introduction

Arsenic is considered to be a toxic metalloid for humans and since drinking water is a potential source of arsenic, the Maximum Contaminant Level (MCL) was set at 10 μg/L [1]. For this reason, several methods have been developed for the removal of arsenic from drinking water. The most important among them are: (a) coagulation/filtration [2–7], (b) adsorption on titanium dioxide [8], (c) adsorption on activated alumina [9–10], (d) adsorption on iron oxides [11], (e) ion exchange [9,10,12] and (f) reverse osmosis [10]. Under typical pH conditions (6–8), As(V) exists as an anion with $H_2AsO_4^-$ to be the predominant species at pH 6 and $HAsO_4^{2-}$ at pH 8, while As(III) is fully protonated and exists as an uncharged molecule (H_3AsO_3) [13]. All these methods are more effective for the removal of ionic forms of As(V) in comparison to uncharged arsenite acid of As(III). Therefore, a pre-oxidation step, either by a chemical reagent [2] or by bio-oxidation [14], is usually required for effective As(III) removal. Conventional treatment involving coagulation/filtration with alum or ferric chloride was found to be the most cost-effective treatment [9,10], with iron being more effective than aluminum particularly at high pH values [6]. The mechanisms operating in the arsenic removal include adsorption onto the hydrolysis products of Fe^{3+} and Al^{3+} and occlusion in the agglomerates formed. Several studies have been reported for removing arsenic from drinking water by coagulation, most of them using $FeCl_3$ or alum [6,7], whereas some researchers have examined the use of cationic [7] or anionic [4] polymers to enhance coagulant removal, increasing arsenic removal in turn. The effect of some common ions, present in the water, in arsenic removal was also studied [5,15]. The body of evidence from these studies supported the idea that arsenic removal depended on the initial arsenic concentration, coagulant dose and pH of the treatment. However, most of the mentioned studies have focused either on achieving residual arsenic lower than MCL or revealing the mechanism of the process, describing qualitatively the relationship between the parameters affecting arsenic removal.

There are, however, some studies [16] which, at a water treatment plant and using Fe^{3+} as a coagulant, attempted to derive a general quantitative equation relating the amount of sorbed arsenic to the amount of ferric oxyhydroxide present. The equation was based on mass balance interactions of soluble As(V), sorbed or co-precipitated As(V) and of sorption sites on the ferric oxyhydroxide surface. Its simplified form was

$$\text{As sorbed, }\% = \frac{K \times [\text{Fe}]}{1 + K \times [\text{Fe}]} \qquad (1)$$

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where K is a constant and [Fe] is the quantity of ferric oxyhydroxide present in mM.

Eq. (1) is particularly attractive because it can readily predict As(V) removal in any system, if a single constant (K, mM^{-1}) can be established and the quantity of ferric oxyhydroxide present is known. However, this equation was expected to be valid under some limited circumstances, i.e. for given water over a small coagulant dose range and at a constant pH [16] and it is also expected in theory that the constant K should depend on pH and the residual arsenic concentration. In addition, this surface complexation model drastically overemphasizes the competitive effect of sulfate, while no significant decrease of As(V) removal was observed in the presence of sulfate even at a concentration of 10 mM (960 mg/L) [5,15]. Consequently, to the best of our knowledge, no reliable equations have been derived to predict Fe^{3+} dose for effective arsenic removal with respect to pH, initial arsenic concentration and temperature. Temperature may fluctuate either due to the atmospheric conditions or due to the geothermic origin of the water. Therefore, experiments conducted at a wide range of temperature are justified.

In this work arsenic removal from a natural water was studied using Fe^{3+} as a coagulant with the main objective to derive reliable equations which would quantitatively describe the relationship between residual arsenic concentration and the parameters that influence arsenic removal, namely initial arsenic concentration, Fe^{3+} dose, pH and temperature. The practical significance of these equations lies in the fact that they could predict, with a reasonable degree of accuracy, Fe^{3+} dose for the effective arsenic removal of contaminated natural waters at common pH, temperature and initial arsenic concentration.

2. Materials and methods

2.1. Water source

Water samples from underground drinkable natural water were collected during spring and autumn of 2006. The main quality parameters of this water, during the period of the study, affecting arsenic removal were as follows: pH 7.4, conductivity = 580 μS/cm, total dissolved solids = 0.38 g/L, total hardness 270 mg $CaCO_3$/L, dissolved organic carbon = 0.9 mg/L, HCO_3^- = 355 mg/L, SO_4^{2-} = 14 mg/L, Si = 8.4 mg/L, PO_4^{3-} = 0.1 mg/L, As $\leq$ 1.5 μg/L. The choice of this water was predicated by the fact that its physicochemical parameters and the concentration of the anions and cations that influence arsenic removal are typical of natural waters and therefore the results obtained could be applicable to a majority of natural waters. However, considering that 1 mole of ortho-phosphate can formally react with 1 mole of Fe^{3+} to form $FePO_4$ and in practice Fe/P ratios 1.5–2 are needed to precipitate phosphate [17], the predicted Fe^{3+} dose must be increased by $2\times[PO_4^{3-}]$ μM for a phosphate concentration greater than 1 μM. In addition, a moderate increase in predicting Fe^{3+} dose is expected, due to Si-concentrations higher than 10 mg/L at pH > 7.5 [15,17].

2.2. Reagents

A 1000 mg/L As(V) stock solution was prepared from reagent grade $Na_2HAsO_4{\cdot}7H_2O$ (10 mg Fe/kg) dissolved in distilled water. Working standards were freshly prepared by proper dilution of the stock solution. Water samples were spiked with As(V) by adding the appropriate volume of the working arsenic standards to achieve As(V) concentrations of 25, 50, 100, 250, 500 and 1000 μg/L.

A 1000 mg/L Fe^{3+} stock solution (pH 0.7 ± 0.2) was prepared by diluting 8 g of 12.5% (w/w) $FeClSO_4$ and 5 mL reagent grade conc. H_2SO_4 (0.01 mg As/kg and 0.1 mg Fe/kg) in 1 L distilled water. The $FeClSO_4$ was selected as the most cost-effective source of Fe^{3+}. Technical specifications of $FeClSO_4$ were as follows: pH < 1, density 1.52 g/mL, Mg = 0.4%, Cl^- = 7.8%, SO_4^{2-} = 23.1%, As < 0.1 mg/kg, Cd < 0.1 mg/kg, Cr 5 mg/kg, Cu 0.5 mg/kg, Hg 0.01 mg/kg, Pb < 0.1 mg/kg, Sb < 0.1 mg/kg, Se < 0.1 mg/kg, Zn 14 mg/kg. Fe^{3+} doses of 1, 2.5, 5, 7.5 and 10 mg/L were used by applying appropriate aliquots of the stock solution to the water samples. Concentrations of Fe^{3+} in the stock solution and the Fe^{3+} treated samples, were always verified by flame atomic absorption spectrophotometry using a Perkin Elmer instrument, model AAnalyst 800, after acidifying the samples at pH $\leq$ 1 with reagent grade conc. HNO_3 (0.01 mg As/kg and 0.2 mg Fe/kg). The pH of the water samples was initially adjusted either with reagent grade 1N HCl or 1N NaOH, in such a way that the addition of Fe^{3+} dose that followed brought the pH at the selected values, that is, 6, 6.5, 7, 7.5 and 8.

2.3. Procedure

Spiked water samples were kept for 24 h in a thermostatic cabinet, to achieve equilibrium at the selected temperature (6, 20, 35 and 50 °C). This wide range of temperature was selected for the following three reasons: (a) to simulate natural conditions during winter and summer (low temperature range), (b) to simulate conditions of geothermic origin waters (high temperature range) and (c) to calculate the isosteric heat of adsorption. The ferric dose was added to the water sample inside the thermostatic cabinet, rapidly mixed at G value of 90 s^{-1} for 2 min, flocculated at G value of 35 s^{-1} for 30 min and filtered through a 0.45 μm pore-size membrane filter. Initial and residual arsenic concentration was determined by graphite furnace atomic absorption spectrophotometry using a Perkin Elmer instrument, model AAnalyst 800. The detection limit of the method, calculated from 7 replicates of 2–5 μg As(V)/L, was estimated to be 1.5 μg As(V)/L. The conditions for the procedure, particularly flocculation time and filter medium, were adopted after preliminary experiments as described in the next section.

3. Results and discussion

3.1. Establishing the experimental conditions

We implemented a wide range of C_o (50–1000 μg/L), resulting in wide range of C_e values, respectively, to minimize experimental and determination errors on C_e values and to increase in turn the accuracy of the proposed prediction model, since C_e was found to be independent of C_o, as discussed in Section 3.2. Preliminary experiments were conducted, with a spiked sample containing initial arsenic concentration (C_o) equal to 500 μg/L and using a Fe^{3+} dose equal to 2.5 mg/L, at pH 7, to establish the flocculation time at various temperatures and spotlight their influence in arsenic removal (Fig. 1). Since during flocculation, all reactions (adsorption, occlusion and co-precipitation) leading to arsenic removal are completed, the terms “reaction time” and “flocculation” time are used synonymously, throughout the paper. The rapid-mixing time of 2 min was selected in accordance with the literature [3]. The results showed the following:

- At 20 °C temperature, maximum arsenic removal was achieved after a rapid-mixing time of 2 min and the subsequent filtration through a 0.45 μm pore-size membrane filter (Fig. 1). Using this filter, ferric oxyhydroxide particulates were completely removed, as reported by other researchers [5].
- At 6 °C temperature, however, a reaction time of 30 min was necessary for maximum arsenic removal (Fig. 1), obviously due to a decrease of arsenic adsorption rate.

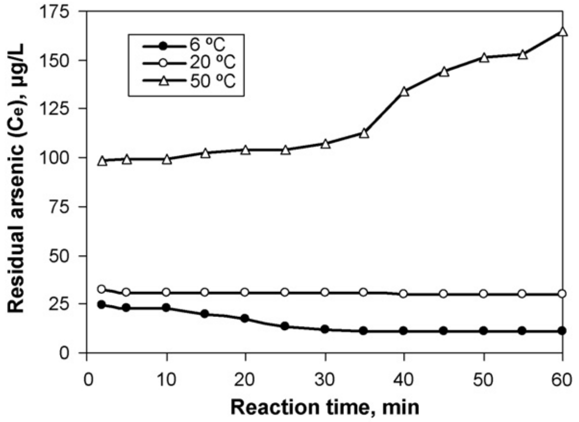

Fig. 1. Residual As concentration (C_e) as a function of reaction time at various temperatures ($C_o = 500\ \mu g/L$, Fe^{3+} dose = 2.5 mg/L and pH 7).

- At 50 °C temperature an increase in C_e was observed compared to the lower temperatures (Fig. 1). This is indicative of the exothermic character of the adsorption, as discussed in detail in Section 3.5. Surface adsorption reactions of oxyanions like arsenate consist both of a chemical component (creation of a stable molecular entity with surface functional groups) and of an electrostatic component (interaction between ions and charged surfaces). In most of the cases, particularly at low surface coverage, these reactions were found to be exothermic [19]. The abrupt increase in C_e after 30 min of reaction time might be due to the decreased stability (aging) of the flocs formed.

In view of the above results and to be on the safe side, a 30 min reaction time was adopted and a 0.45 µm pore-size membrane filter was used in all subsequent experiments.

3.2. *Experimental results and parameters necessary for deriving the predictive equations*

To produce the equations for predicting Fe^{3+} dose, it was necessary, through the primary data, to derive certain quantitative equations and then calculate the specific arsenic removal (q). Plotting C_e versus Fe^{3+} dose (X) for all C_o and pH values used in this study generated hyperbolic curves, whose mathematical general form was

$$C_e = aX^{-b} \tag{2}$$

where a and b constants, on which no physical meaning can be assigned because of the nature of the experimental conditions and the way the variables are plotted.

Representative examples of the relationships between Fe^{3+} dose and C_e are shown in Figs. 2 and 3, along with the corresponding quantitative equations in each case. Three things become apparent from these curves:

- First, for any given C_o, the higher the Fe^{3+} dose the lower the C_e and for a given Fe^{3+} dose, the higher the C_o the higher the C_e observed.
- Second, a decrease in pH resulted in a decrease in C_e, which for example can be seen when the location of the curves and the constant a for $C_o = 250\ \mu g/L$ in Figs. 2 and 3 are compared. This was expected and also reported by other investigators [3,5]. The increase in As(V) removal with a decrease in pH has been reported to be common with various coagulants [18]. This pH dependence of As(V) removal can be justified considering that during coagulation As(V) is removed by sorption onto the surface of ferric oxyhydroxides resulting from metal hydrolysis [18]. These surfaces develop a charge, positive or negative by the dissociation of the surface hydroxyl groups, which corresponds to adsorption or desorption of protons depending on the pH of the solution. Stated in another way, the charge depends on the point of zero charge (pzc) of the solid, which for the majority of the common ferric oxyhydroxides is between 7.2 and 9 depending on the nature of the solid and the technique used to measure it [20,21]. The protonation–deprotonation reactions of surface hydroxyls can be represented by the following equations (≡denotes surface group):

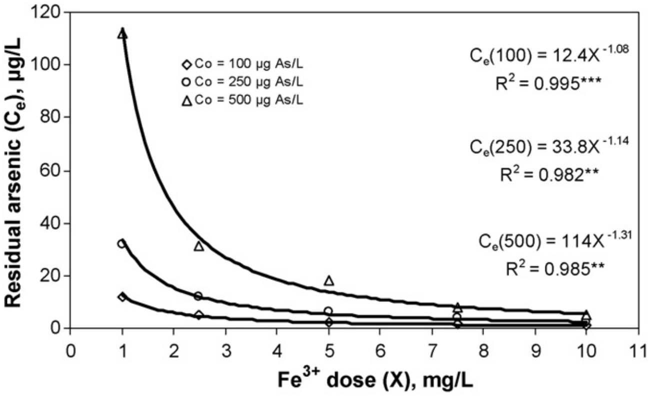

Fig. 2. Representative examples of the relation between Fe^{3+} dose and C_e at 20 °C and at pH 7. **, ***Statistically significant at $p \leq 0.01$ and 0.001, respectively.

$$\equiv \mathrm{FeOH} + \mathrm{H}^+ \rightleftarrows \equiv \mathrm{FeOH_2}^+$$

$$\equiv \mathrm{FeOH} \rightleftarrows \equiv \mathrm{FeO}^- + \mathrm{H}^+$$

Below the pzc of the solid, positive hydroxyl groups ($\equiv \mathrm{FeOH_2}^+$) predominate, whereas above the pzc the negative groups ($\equiv \mathrm{FeO}^-$) become the dominant species.

In view of the above, it seems that arsenate anions ($\mathrm{H_2AsO_4}^-/\mathrm{HAsO_4}^{2-}$) can be removed from solution (sorbed onto the ferric oxyhydroxide surfaces) through their electrostatic binding with positive charged surfaces. But the main mechanism for arsenate sorption is their ability to replace surface hydroxyls and form a stable surface complex on a ferric oxyhydroxide surface. This mechanism is facilitated by the ease with which arsenate ions can approach the surface of the ferric oxyhydroxide. This depends on the surface charge, which in turn explains the dependency of arsenate sorption on the solution

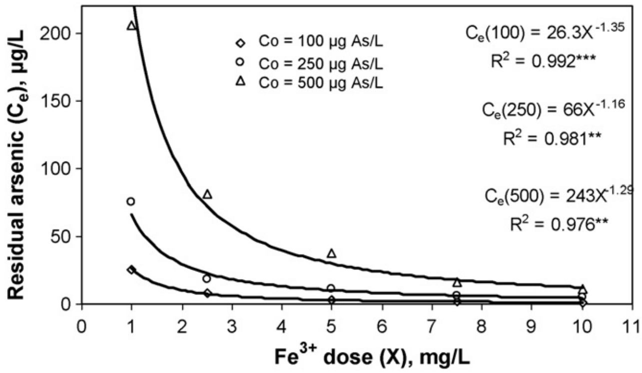

Fig. 3. Representative examples of the relation between Fe^{3+} dose and C_e at 20 °C and at pH 7.5. **, ***Statistically significant at $p \leq 0.01$ and 0.001, respectively.

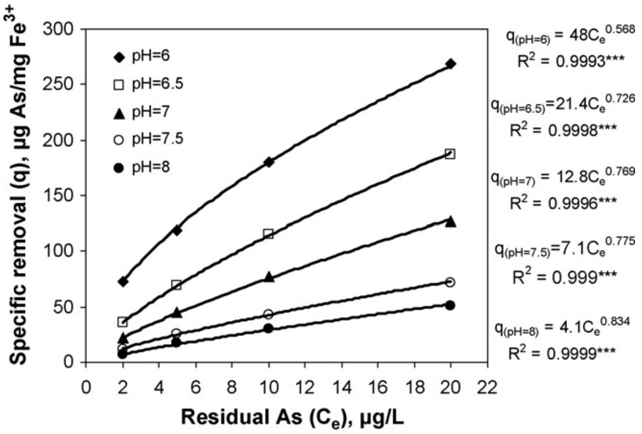

Fig. 4. Specific arsenic removal (q) as a function of C_e at various pH values and at 20 °C. ***Statistically significant at $p \leq 0.001$.

pH. At low pH the fraction of positively charged surface hydroxyl groups ($\equiv FeOH_2^+$) increases, arsenate ion can approach the surface closely, replace hydroxyls and form a stable surface complex. In addition, Lakshmanan et al. [18], reported that, when using a total As(V) concentration of 0.67 μM (in the form of $H_2AsO_4^-$ and $HAsO_4^{2-}$), the concentration of $H_2AsO_4^-$ was significantly increased from 0.02 to 0.5 μM, when the pH dropped from 8.5 to 6.5, resulting in a greater As(V) removal. In contrast by increasing the pH, the fraction of negatively charged ($\equiv FeO^-$) surface groups increases, rendering the surface more negative and the repulsion of arsenate ions stronger, which eventually results in their lesser sorption.

- Third, which is more important and strictly pertinent to the objective of this study, the quantitative equations derived (examples are shown in Figs. 2 and 3) can give reliable and accurate estimates of C_e as a function of Fe^{3+} dose, as judged by the high value of R^2, which is statistically significant at $p \leq 0.01$ and shown in Figs. 2 and 3.

Using Eq. (2), at each specific pH value and C_o, the required Fe^{3+} dose for achieving any value of C_e (μg As/L), and in turn the corresponding value of q (μg As/mg Fe^{3+}), were calculated. To derive a quantitative expression relating q and C_e we plotted q versus C_e. The result was a Freundlich-type ($q = K_F C_e^n$, where $n < 1$) curve shown in Fig. 4. Since the range of C_e with practical significance and interest in drinking water treatment is located between 2 and 20 μg/L, only the values of q for C_e equal to 2, 5, 10, 20 μg/L will be taken into account in the following discussion and an example of these values at pH 7 is shown in Table 1. Due to the high relative standard deviation (RSD) of As(V) determination at the method's detection limit, the calculated q values at C_e = 2 μg As(V)/L presented a RSD between 10 and 15% (Table 1) resulting in a corresponding RSD of Fe^{3+} dose prediction, while at higher C_e values a RSD lower than 10% was observed. Values of q for the other pH values 6, 6.5, 7.5 and 8 were also obtained. The results of all these calculations indicated that the value of q depended only on the value of C_e and was independent of C_o, since at those low C_e concentrations the surface sites are not saturated. These values of q were used for deriving the predictive equations as described in the following section.

Table 1
Calculation of q as a function of C_e at various C_o at pH 7 and 20 °C.

C_e, μg As/L	C_o, μg As/L					Mean	CV%
	50	100	250	500	1000		
	q, μg As/mg Fe						
2	21.5	18.1	20.6	22.4	25.7	22	12.8
5	43	41	45	45	48	44	5.9
10	77	74	82	76	75	77	4.1
20	124	125	137	126	119	126	5.3

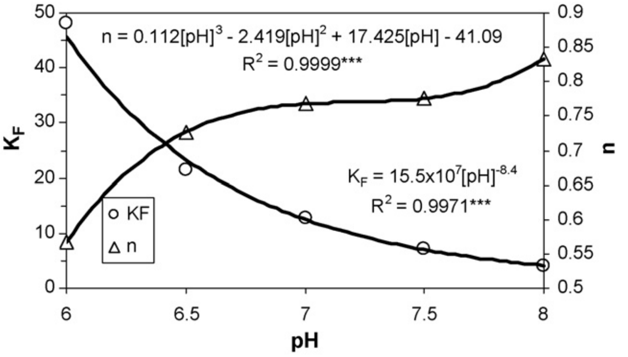

Fig. 5. Plot of K_F and n values of equations of Fig. 4 versus pH (T = 20 °C). ***Statistically significant at $p \leq 0.001$.

3.3. Deriving the predictive equations

To derive the predictive equations we plotted q versus C_e of 2, 5, 10, 20 μg/L. Indeed, the relationship between these two variables was of hyperbolic character ($q = K_F C_e^n$) with a high value of R^2, statistically significant at $p \leq 0.001$ (Fig. 4). The abrupt decrease of n value as the pH decreased from 6.5 to 6 can be attributed either to the increase sorption intensity of $H_2AsO_4^-$ which dominates at this pH range [13], or to the increase of the fraction of the positively charged surface groups ($\equiv FeOH_2^+$) [18,22]. In contrast, the significant increase of n value as the pH increases from 7.5 to 8 can be attributed to the increase of the fraction of the negatively charged surface groups ($\equiv FeO^-$), the stronger repulsion of arsenate ions from the surface and their eventual decreased sorption. The regression equations of Fig. 4 are of practical interest because by using them, the calculation of the required Fe^{3+} dose for arsenic removal from specific water becomes feasible.

Example 1: What is the required Fe^{3+} dose to reduce arsenic to 5 μg/L from a water with pH 6.5, temperature 20 °C and C_o = 42 μg/L? From the second equation of Fig. 4:

$$q_{(\text{pH } 6.5)} = 21.4 C_e^{0.726}$$

and placing C_e = 5 μg/L, q is calculated to be equal to 68.9 μg As/mg Fe^{3+}.

Hence, for the removal of 42-5 = 37 μg As/L, the required Fe^{3+} dose is

$$Fe^{3+}\ \text{dose} = \frac{37\ \mu\text{g As/L}}{68.9\ \mu\text{g As/mg Fe}^{3+}} = 0.54\ \text{mg/L}$$

Similarly, the required Fe^{3+} dose for C_e = 2 μg/L, for the same water, is found to be 1.13 mg/L, which means that if the desirable reduction of C_e is from 5 to 2 μg/L, this would result in an almost 110% increase in Fe^{3+} dose. For the residual arsenic concentrations (C_e) of practical interest, namely 2 and 5 μg/L, it was calculated that by increasing the pH from 6.5 to 7.5, q is decreased by about 2.8 times, meaning an equivalent increase of Fe^{3+} dose.

The question that arises is if Fe^{3+} dose can be calculated at any pH different from the preset pHs shown in Fig. 4. To address this question, K_F and n values of Fig. 4 were plotted versus pH, resulting in relationships with high value of R^2 statistically significant at $p \leq 0.001$ (Fig. 5). Using these relationships of Fig. 5, Freundlich-type equations relating q and C_e for any pH in the range between 6 and 8 can be derived, as explained in example 2.

Example 2: Calculate the relationship between q and C_e at pH 6.8 and temperature 20 °C. From the relationship (3) between K_F and pH (Fig. 5):

$$K_F = 15.5 \times 10^7 [\text{pH}]^{-8.4} \qquad (3)$$

and placing pH 6.8, K_F is calculated to be equal to 15.7 (L/mg).

From the relationship (4) between n and pH (Fig. 5):

$$n = 0.112[\text{pH}]^3 - 2.419[\text{pH}]^2 + 17.425[\text{pH}] - 41.09 \qquad (4)$$

and placing pH 6.8, n is calculated to be equal to 0.762. Consequently, the relationship between q and C_e at pH 6.8 are the following:

$$q_{(\text{pH } 6.8)} = 15.7 C_e^{0.762} \qquad (5)$$

Using this equation, Fe^{3+} dose can be predicted in the same way as in example 1.

3.4. Validity of predictive equations

In an attempt to validate the predictive equations, we obtained arsenic removal data from other researchers' work and compare these actual removal data with our model results.

- At the village Malgara in the municipality of Axios in northern Greece and in a full scale treatment plant, a total C_o = 18 μg As/L (2 μg As(III)/L plus 16 μg As(V)/L) decreased C_e to 2 μg As(V)/L plus 1.4 μg As(III)/L at the coagulation step (pH 7.9, 21 °C), by the addition of 2.3 mg Fe^{3+}/L [23]. The predictive equation at pH 7.9 (see example 2) was: $q_{(\text{pH } 7.9)} = 4.4 C_e^{0.815}$. The predicted q value for C_e = 2 μg As(V)/L, is 7.7 μg As(V)/mg Fe^{3+} and the Fe^{3+} dose [(16–2)/7.7] = 1.8 mg/L. Increasing this Fe^{3+} dose by 3 μM Fe^{3+} for the removal of 1.6 μM phosphate, the predicted dose was calculated to be 2 mg Fe^{3+}/L, which is close (within 15% RSD) to the actual dose of 2.3 mg Fe^{3+}/L.
- At the village Kymina also in the municipality of Axios, and in a full scale treatment plant (100 m^3/h), a total C_o = 44 μg As(V)/L decreased to a C_e of 4 μg (As)/L at the coagulation step (pH 7.7, 21 °C), by the addition of 2.7 mg Fe^{3+}/L. The predictive equation at pH 7.7 was: $q_{(\text{pH } 7.7)} = 5.5 C_e^{0.792}$. The predicted q value for C_e = 4 μg As(V)/L, is 16.5 μg As(V)/mg Fe^{3+} and the Fe^{3+} dose is 2.45 mg/L. Increasing this Fe^{3+} dose by 2 μM Fe^{3+} for the removal of 1.2 μM phosphate, the predicted dose was calculated to be 2.55 mg Fe^{3+}/L, which is very close to the actual dose of 2.7 mg Fe^{3+}/L.
- Chwirka et al. [3] using coagulation/microfiltration process (C/MF) for arsenic removal from drinking water at pH 6.8, found that a C_o = 100 μg/L of a water from the C/MF pilot in Naval Air Station, Fallon Nevada, was reduced to C_e < 2 μg/L after the addition of 15 mg $FeCl_3$/L. This dose is equal to 5.2 mg Fe^{3+}/L and results in a q value of 19.2 μg As/mg Fe^{3+}. A C_e = 1.4 μg/L is predicted from Eq. (5) $q_{(\text{pH } 6.8)} = 15.7 C_e^{0.762}$ when q = 19.2 μg As/mg Fe^{3+}. Additionally, in El Paso, Texas, using 1 mg/L chlorine for arsenic oxidation and 35 mg/L CO_2 to achieve a pH of 6.8, a $FeCl_3$ dose 5 mg/L (q = 14.7 μg As/mg Fe^{3+}) reduced a C_o = 25 μg/L to C_e < 2 μg/L. A C_e = 0.9 μg/L is predicted by Eq. (5).
- McNeil and Edwards [16] in a summary of data from utilities included in their survey 2, reported that at utility K2 a C_o = 9.6 μg As(V)/L was reduced to $C_e \leq 0.1$ μg As(V)/L by adding 0.08 mM Fe^{3+} (q = 2.1 μg As/mg Fe^{3+}) at pH 7.1. From $q_{(\text{pH } 7.1)} = 11 C_e^{0.772} = 2.1$ μg As/mg Fe^{3+}, a C_e = 0.12 μg/L is predicted.
- Lakshmanan et al. [18] reported at pH 7.5 q values of about 22 μg As/mg Fe^{3+} for C_e = 5 μg As(V)/L and 38 μg As/mg Fe^{3+} for C_e = 10 μg As(V)/L. These q values compare closely to the respective values of 24 μg As/mg Fe^{3+} and 42 μg As/mg Fe^{3+} predicted from $q_{(\text{pH } 7.5)} = 7.1 C_e^{0.775}$.

In conclusion, actual removal data proved that the empirical equations presented in this paper can predict efficiently Fe^{3+} dose for As(V) removal for drinking water production. The validity of the prediction equation was verified using waters of different chemical composition.

3.5. Influence of temperature on residual arsenic concentration (C_e)

The experimental results showed that treatment temperature influences C_e significantly. As mentioned in Section 3.1, an increase in temperature was accompanied by a decease in As(V) sorption and the consequent increase in C_e, denoting the exothermic character of the reaction. Adsorption data obtained at different temperatures were used to calculate the isosteric heat of adsorption (ΔH_Γ) at a given adsorption density by means of the Clausius–Clapeyron equation:

$$\Delta H_\Gamma = -R \frac{\ln(C_{e2}/C_{e1})}{(1/T_2) - (1/T_1)} \qquad (6)$$

where R is the universal gas constant; C_{e2} is the equilibrium solution concentration of arsenic at temperature T_2 at a given adsorption density and C_{e1} is the equilibrium solution concentration of arsenic at temperature T_1 at the same adsorption density.

For low surface coverage corresponding to C_e of practical interest in water treatment, namely less than 20 μg As/L, and for temperatures between 6 and 20 °C the isosteric heat of adsorption ranged between −25 and −30 kJ/mol As.

The fact that raising the temperature resulted in lower As(V) sorption, can be explained on the basis of the following:

- A raise in temperature is accompanied by a decrease in Fe^{3+} hydrolysis resulting in lower yields of the ferric oxyhydroxide products [21].
- At low temperature nucleation is retarded and oligomers of low crystallinity and high surface area are formed (e.g. ferrihydrite). Increasing the temperature the rate of crystallization is increased resulting in ferric oxyhydroxides of high structural order (e.g. geothite), that is, of smaller surface area and the consequent lower As(V) sorption.
- Increasing the temperature shifts the pzc of the various ferric oxyhydroxides to lower values [20,22]. Although this fall of the pzc, as the temperature is raised, is not that dramatic [20], it can lead to an increase of the negative surface charge of the adsorbent and the consequent decrease in As(V) sorption.

The quantitative relationship between C_e (μg As/L) and temperature (°C), at a constant Fe^{3+} dose of 2.5 mg/L, was described by a logarithmic equation of the general form:

$$\ln C_e = a_T + b_T T \qquad (7)$$

where again a_T and b_T are constants.

Similar equations, at Fe^{3+} dose 2.5 mg/L, were derived for all pH values and C_o, a representative example of which is shown in Fig. 6. It is worth noting that the slope of Eq. (7) (constant b_T), for all pH values and C_o, was nearly constant and equal to 0.039 ± 0.002. The practical significance of Eq. (7) is that the value of C_e at any water temperature, within the range of temperature tested, can be predicted as it is shown in the following example.

Example 3: Find C_e when the temperature of the water of example 1 is increased to 30 °C.

Applying Eq. (7) for 20 and 30 °C:

$$\ln C_{e(20)} = a_T + 0.039 \times 20$$

$$\ln C_{e(30)} = a_T + 0.039 \times 30$$

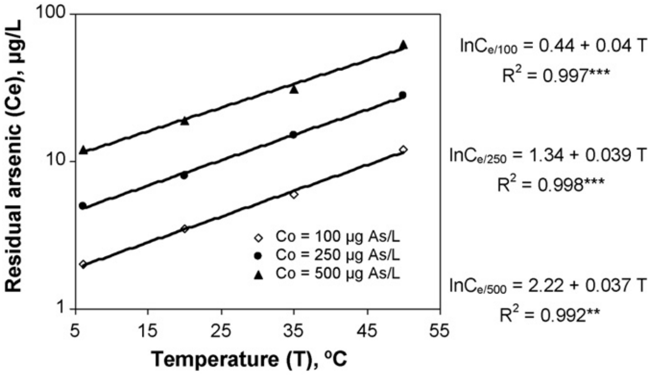

Fig. 6. Influence of temperature on C_e at pH 6.5 (Fe^{3+} dose 2.5 mg/L). **, ***Statistically significant at $p \leq 0.01$ and 0.001, respectively.

and subtracting the two equations and placing the value of $C_{e(20)}$ equal to 5 μg/L, we obtain:

$$\ln 5 - \ln C_{e(30)} = 0.039 \times 20 - 0.039 \times 30$$

which gives the value of C_e at 30 °C equal to 7.4 μg/L. This means an increase of residual arsenic concentration of about 1.48 times (7.4/5) for a 10 °C increase of water temperature. Similar calculations at various other temperatures also showed that C_e increases by a factor of about 1.5 for each 10 °C increase in temperature.

4. Conclusions

The relationship between specific arsenic removal (q) and residual arsenic concentration (C_e), in the range between 2 and 20 μg/L, was described by a hyperbolic curve ($q = K_F C_e^n$) with a high value of R^2, statistically significant at $p \leq 0.001$ and therefore it served to predict, with a RSD ≤ 15%, the Fe^{3+} dose necessary to achieve any selected C_e:

- at a pH range between 6 and 8 and
- at an initial arsenic concentration (C_o) up to 1000 μg/L.

Furthermore, reliable equations were derived for calculating q at any pH in the range between 6 and 8. By means of these equations Fe^{3+} dose could be predicted at any pH value of the water. Actual removal data obtained from other researchers validated the proposed prediction equations. A complementary result of this work was that the treatment temperature was found to be logarithmically related to C_e providing predictive equations for calculating C_e at the range of temperatures studied in this work. Generally, C_e showed an increase by a factor of 1.5 for each 10 °C of temperature increase.

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