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Water Purification To Remove As(V) by Electropulse Treatment of an Active Metallic Charge

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Abstract—Power expenditure for water purification to remove arsenic(V) was determined. The processes and kinetics of purification in an electric-discharge reactor with a metallic (aluminum or iron) charge were investigated. The purification mechanisms based on the adsorption of arsenic(V) on a fresh surface of hydroxides formed through dispersion and subsequent oxidation of a charged metal were suggested. Rate equations corresponding to the experimental data and to these mechanisms were given.

One of problems accompanying many commercial processes, especially those in the metallurgical industry, is effective removal of arsenic and other toxic elements from wastewater. Methods for arsenic removal from wastewater can be combined in two groups: those with and without reagents. The second group includes galvanocoagulation, electrocoagulation, and electropulse water purification.

The reagent methods are mainly based on coprecipitation with calcium phosphate [1] and carbonate [2] or on precipitation of arsenic(V) in the form of iron arsenates [3]. These simple and reliable methods have an essential drawback: they permanently use expendable materials, which complicates the scheme of water purification.

As the same time, no-reagent methods are free of this disadvantage.

The galvanocoagulation method [4] is based on the use of short-circuited iron–carbon galvanic cells. The galvanic processes yield iron hydroxides, which adsorb arsenate ions. As well as reagent methods, this method does not consume reagents and electric energy from the outside; however, its drawbacks consist in a low rate of the purification process and necessity for a permanent stirring of the solution to oxidize As(III) to As(V) by hydrogen peroxide or by air bubbling.

In the electrocoagulation method, the electrodes dissolve on passing a current and impurities are bound with a precipitate of the forming metal hydroxide. This no reagent method is readily controlled. The process is characterized by consumption of electric energy per unit mass or one mole of the dissolved electrode. According to the data of different authors [5, 6], the energy expenditure is 20–40 kW h kg^{-1} of a coagulant. The electrodes are passivated during the electrolysis, which requires their periodic replacement. Furthermore, this method is characterized by low purification rates.

Recently electropulse water purification has gained a wide recognition. Water purification by these methods is characterized by a very high rate and efficiency. The energy consumption depends on the type of discharge and mode of its application. Data on the energy consumption for water purification (per unit volume) to remove various organic impurities by electric discharges (ED) in the mode of an electric breakdown of a liquid were reported in the review [7]. Depending on the nature of an admixture and on purification conditions, 10–100 J cm^{-3} (2.8–28 kW h m^{-3}) are consumed. The purification of solutions containing cobalt and strontium ions required 3×10^3–2×10^4 J cm^{-3} (0.84×10^3–0.56×10^4 kW h m^{-3}).

Pulsed nanosecond barrier discharges have been applied to purification of drinking water to remove admixtures. They demonstrated a high efficiency: the energy consumption was as low as 0.2–0.04 kW h m^{-3} [8].

We have shown previously [9, 10] that a highly efficient electroerosion occurs upon pulsed action of

Concentrations of As(III) and As(V) in model solutions after an ED treatment in a reactor with aluminum and iron charge ($c_{\text{in[As(V)]}} = 300$, $c_{\text{in[As(III)]}} = 380$ mg l^{-1})

Run no.	Charge	Solution	Concentration after treatment, mg l^{-1}	
			As(V)	As(III)
1	Al	As(III)	28	52
2		As(V)	15	0
3	Fe	As(III)	0	0
4		As(V)	0	0

electric current on an iron charge: in this case, the energy consumption for transfer of iron to a suspension is 0.067–0.142 kW h mol^{-1}.

The aim of this study was to determine the energy consumption in the electropulse water purification to remove arsenic compounds with the use of a chemically active metallic charge and to analyze the chemical mechanism of this method.

EXPERIMENTAL

The experimental installation consisted of a container with 200 g of metallic shavings (iron and aluminum) used as a reactive charge. The electrodes were lowered into the charge, and 950 ml of a solution under study was poured in. The electrodes were connected to a double-circuit source of pulsed currents, with the following characteristics: pulse duration τ_p = 10 μs, pulse repetition rate 100 Hz, voltage $U = 500$–1000 V, and current of the first half-period of a pulse, I = 250–400 A.

Solutions of As(III) and As(V) salts of various concentrations in distilled water were used. We used GSO (State Standard Sample) 7264–96 to prepare As(III) solutions and analytically pure NaH_2AsO_4, for As(V).

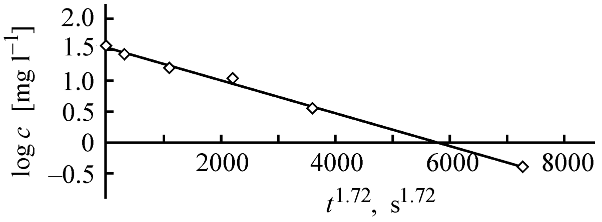

Fig. 1. Concentration of arsenic(V) ions, *c*, vs. the processing time *t*.

The concentration of As(III) was determined by inversion voltammetry with an STA-l instrument. The concentration of As(V) was found photometrically, in the form of arsenic-molybdenum blue [11] and also with the use of a QUICK As test-system (colorimetry on a sensitized paper by Gutzeit's technique) [12].

AsH_3 was qualitatively detected in the atmosphere over the surface of a solution treated with ED, using the QUICK As test-system at a sensitivity of 0.5 μg l^{-1}.

To compare the efficiencies of the aluminum and iron charges in water purification to remove arsenic compounds, we took equal volumes of solutions, with As(III) and As(V) concentrations of 380 and 300 mg l^{-1}, respectively, and treated them for 1.5 min with ED in the systems with iron and aluminum charges. Then the solutions were filtered ("blue-tape" filter) and the contents of both forms of arsenic were determined (see table).

It can be seen from the table that the efficiency of water purification with the iron charge is higher than that with the aluminum charge. Furthermore, As(III) is partially oxidized to As(V) in the case of an aluminum charge and incomplete water purification. In what follows, we studied in more detail the system with the iron charge, because it shows more promise for water purification to remove arsenic compounds.

To study the kinetics of arsenic(V) removal in an electric-discharge reactor with the iron charge, we carried out experiments on the kinetics of As(V) absorption. The concentration of the starting solution was 36.25 mg l^{-1}. In the course of the ED treatment, we sampled the filtrate at certain time intervals and determined its As(V) content:

t, s	$c_{\text{As(V)}}$, mg l^{-1}	t, s	$c_{\text{As(V)}}$, mg l^{-1}
0	36.25	120	3.958
30	27.395	180	0.521
60	16.18	240	0.208
90	11.31		

Processing of the experimental data demonstrated (Fig. 1) that the removal of arsenic(V) (mg s^{-1}) from water is described by equation(I).

$$\log c_{\text{As(V)}} = -0.0002 \log t^{1.72} + 1.5258, \qquad \text{(I)}$$

The erosion of electrodes is described [10] by equation (II).

$$\log c_{\text{Fe}} = 0.72 \log t + 1.1331. \qquad \text{(II)}$$

To study As(III) and As(V) adsorption on a solid erosion product after the ED treatment, we used As(III) and As(V) solutions with the arsenic concentration of 51.92 and 38.01 mg l^{-1}, respectively. A solution was treated within 30 s in a reactor with an iron charge. The As(III) and As(V) contents of the treated solution (filtrate) were determined at certain time intervals. The results of the analyses are given in Fig. 2 in the coordinates: purification degree [$\alpha = (c_{in} - c)/c_{in}$]–logarithm of time.

It can be seen from Fig. 2 that, in both cases, the purification by ED is characterized by a very high rate and takes less than 30 s. Further, the concentrations of both As(III) and As(V) decrease insignificantly via the presumed adsorption.

In the course of the kinetic experiments, we made attempts to determine arsenic in the form of AsH_3 in the atmosphere over a solution with a charge. For this purpose, we tightly sealed a vessel with a polyethylene film and placed in it a strip of the QUICK test-system. The sensitivity of the test was 0.5 μg l^{-1}. At this sensitivity, the color of the strip remained unchanged upon complete purification of a solution with an As(V) concentration of 37 mg l^{-1}.

Mechanisms of water purification to remove admixtures of arsenic compounds. As(V) is present in water as $H_2AsO_4^-$ ions at pH 3–6 and as $HAsO_4^{2-}$ at pH 8–11; As(III) forms mainly H_3AsO_3 molecules at pH < 10 [13, 14]. As(III) and As(V) can be removed from water by an ED treatment through a reaction with iron(III) ions in solution and the subsequent precipitation of arsenates, e.g., by schemes (1) and (2).

$$Fe^{3+} + H_2AsO_4^- \rightarrow FeAsO_4\downarrow + 2H^+, \quad (1)$$

$$Fe^{3+} + H_3AsO_3 \rightarrow FeAsO_3\downarrow + 3H^+. \quad (2)$$

Such a scheme suggests that there is a functional relationship between the purification rate and the concentration of iron(III) ions in solution. As there is no relationship of this kind, these processes can be regarded as hardly probable.

A preliminary oxidation of As(III) by products of ED in water (OH, O_3, and H_2O_2) is also possible:

$$H_3AsO_3 + OH^- \rightarrow H_2AsO_4^- + 2H^+ \text{ etc.} \quad (3)$$

In the absence of oxygen or under oxygen-deficient conditions, oxidized arsenic can be also reduced to elementary arsenic or even to arsine by iron or atomic hydrogen [15]:

$$H_2AsO_4^- + Fe_H \text{ (or H)} + H_2O \rightarrow As\downarrow(AsH_3\uparrow) + Fe(OH)_2\downarrow + OH^-, \quad (4)$$

$$H_3AsO_3 + Fe_H \text{ (or H)} \rightarrow As\downarrow(AsH_3\uparrow) + (H_2O) + Fe(OH)_2\downarrow. \quad (5)$$

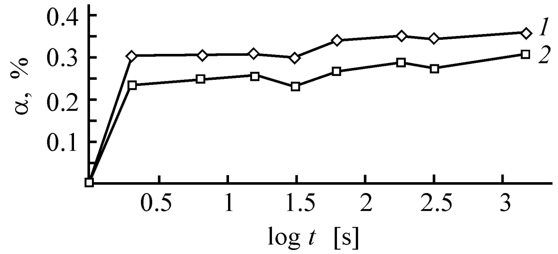

Fig. 2. Degree of extraction, α, of (*1*) As(III) and (*2*) As(V) from water (*1*) with the iron charge and (*2*) after the ED is switched off. (*t*) Treatment time.

The forming As^0 can be precipitated together with iron hydroxides, with arsine evolved as a gas. The possibility that this mechanism may be operative is supported by the data in Fig. 2: the degree of purification to remove As(III) is higher than that for As(V).

Our experiments did not confirm formation of arsine in water purification, i.e., reactions (4) and (5) yielding arsine do not take place. Furthermore, there are publications [15, 16] in which no elementary arsenic was detected on the surface of iron oxide and metal adsorbents by spectroscopic methods.

Therefore, the third mechanism is more probable, in which arsenic-containing ions are adsorbed on iron hydroxides (oxyhydroxides), e.g.,

$$=Fe(OH)_{solid} + H_2AsO^-_{4\,solution} \rightarrow (=Fe)_3AsO_{4\,solid} + H_2O + OH^-_{solution}, \quad (6)$$

$$=Fe(OH)_{solid} + H_3AsO^-_{3\,solution} \rightarrow (=Fe)_3AsO_{3\,solid} + H_2O. \quad (7)$$

Also possible is attachment of $H_2AsO_4^-$ anions to the surface [14].

We can assume that, under the action of ED, iron nanoparticles are removed from irregularities on the charge surface (“spikes”) into solution, and dispersed particles of iron and a part of the metal in the resulting craters are partly or totally oxidized from the surface to give particles of Fe(II) hydroxides, which are rapidly oxidized further by dissolved oxygen. The resulting Fe(III) oxyhydroxide is the most efficient As(V) absorbent; as a result, the rate of its absorption is proportional to the total amount of corroded iron.

This method is rather efficient when ordinary iron-containing adsorbents are used [13]. In our case, its possibility is confirmed by the existence and type of functional *c–t* relationships for formation of iron hydroxide and water purification to remove arsenic (Figs. 1 and 2): the absolute values of the exponents in these dependences differ by exactly unity. According to these data, the adsorption kinetics can be described as follows. The rate of absorption of arsenic compounds by the erosion product is given by

$$\mathrm{d}c_1/\mathrm{d}t = -k_i s c_{\mathrm{Fe}} c_1, \qquad \text{(III)}$$

Here c_1 is the concentration of the As impurity in water; s, specific surface area of the erosion product; and k_i, constant that accounts for the electric discharge characteristics and rate constants of chemical reactions.

As shown previously [10]:

$$c_{\mathrm{Fe}} = (1 + m)kt^{1/(1+m)} = k_1 t^{1/(1+m)} = k_1 t^{v}, \qquad \text{(IV)}$$

where $m = 1/3$ is the erosion index, which gives $v = 0.75$.

On substituting c_{Fe} into (III) and integrating, we obtain

$$\log c_i = \log c_{i,0} - \frac{k_1 k_i s}{2.3(1+v)} t^{\frac{m+2}{m+1}} = \log c_{i,0} - k_3 t^{1+v}, \qquad \text{(V)}$$

where $c_{i,0}$ is the initial concentration of arsenic.

The experimental values $v = 0.72$ and $1 + v = 1.72$ are related to each other in complete correspondence with theoretical expressions (IV) and (V), being close to the theoretical value $v = 0.75$. Thus, the rate of the impurity absorption is proportional to the amount of dispersed metal.

It can be seen from Fig. 2 that the absorption proceeds very fast when the discharge is switched on, and nearly ceases when it is off. This means that absorption processes under ED conditions differ from the ordinary adsorption.

In this context, it is of interest to compare the experimental data on water purification to remove admixtures of arsenic compounds with the data on their adsorption on commercial adsorbents. Published data on the As(III) and As(V) adsorption on various adsorbents [17–19] are diverse, with the adsorption capacity for the most effective of them, $Fe(OH)_3$ and FeOOH, varying from 1 up to 250 mg g^{-1}. Such a wide scatter of the data is due to the dependence of the adsorption on numerous factors: dispersity and porosity of an adsorbent, adsorbate concentration, solution pH, adsorption duration, and stirring or the flow velocity of a solution relative to a layer. In the case of a complete (stoichiometric) reaction of iron oxyhydroxide with As(V), the capacity for As(V) would be 708 mg g^{-1}. Presumably, such a capacity is possible for a colloid solution of the hydroxide, but cannot be reached in the experiment because of the diffusion hindrances. Furthermore, practical use of colloids and suspensions presents serious difficulties associated with the necessity for separation of the dispersed phase from water.

The calculated capacity of an adsorbent monolayer for arsenic(V) is 0.004 mmol m^{-2} [14], i.e., 30 mg g^{-1} at a specific surface area of 100 m^2 g^{-1}.

For the process occurring under an electric discharge, the adsorption values were 96.1 and 156.7 mg g^{-1} for As(III) and As(V), respectively, at the specific surface area of the forming iron oxides equal to 105 m^2 g^{-1}. It is also important to note that these values were obtained under dynamic conditions within a very short time, which was considerably shorter than that required to obtain isotherms in [17, 18]. The capacity of the adsorbent in this case is 0.012 and 0.02 mmol m^2 for As(III) and As(V), respectively.

Thus, we see that the capacity in the electroerosion process approximately corresponds to the adsorption of three monolayers of As(III) and five monolayers of As(V). In all probability, this excess corresponds to a larger specific surface area at the instant of formation of a new phase, rater than to a multilayer adsorption (as it might be assumed). This specific surface area seems to be much larger than 105 m^2 g^{-1} at the beginning of the process, and then decreases to this value because of the cohesion and recrystallization of primary particles. If we assume that the surface is completely covered with arsenate ions, the specific surface area at the instant of adsorption will be 500 m^2 g^{-1} at the monolayer capacity of 0.004 mmol m^{-2} and As(V) adsorption of 156.7 mg g^{-1}. Such a surface area is physically well expected and corresponds to a size of FeO(OH) primary particles equal to 12 nm.

To gain insight into the purification mechanism, it is important to take into account the fact that the adsorption on a commercial adsorbent is limited by the diffusion of the adsorbate into micropores [18]. The capacity of the adsorbent formed in the ED purification exceeds by an order of magnitude that reached on commercial adsorbents (at a comparable sorption duration) and is close to the values corresponding to a complete monolayer on their surface. This indicates that, as expected, there is no diffusion hindrance in micro- and mesopores in adsorption at the instant when the adsorbent is produced, which ensures a higher rate and capacity.

CONCLUSIONS

(1) A study of the possibility of water purification to remove As(III) and As(V) by electric discharges with the use of an iron or aluminum charge demonstrated that the efficiency of the iron charge exceeds that of the aluminum charge. It was found in a study of the kinetics of arsenic(V) sorption that water is mostly purified during the electric discharge. The rate of water purification is proportional to the amount of dispersed iron; the subsequent adsorption on the erosion products is insignificant. The purification efficiency was 0.43 mol(As atoms) $(\mathrm{kW\,h})^{-1}$.

(2) Three possible mechanisms of water purification were considered. The results obtained in this study and published data made it possible to give preference to the mechanism in which an electric discharge acts upon the metal of the charge to form micro- and nanoparticles. Further, these particles are oxidized together with a part of the metal in the forming crater. At the instant when the oxides and hydroxides are formed, they sorb admixtures at a high rate, so that the adsorbent surface is completely filled.

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