Arsenic Removal from Aqueous Solutions using a Binary Mixed Oxide

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In the most cases the drinking water has been identified as one of the major sources of arsenic exposure by the general population. A variety of treatment processes has been studied for arsenic removal from water. One of the most used methods is the adsorption. The most efficient adsorbent materials are those with iron content considering the affinity of arsenic species towards iron compounds. In the present paper the As (III) adsorption performance of a binary mixed oxide Fe_2O_3*-*SiO_2 *was investigated. The sorption process is best described by the pseudo-second-order kinetics. The theoretically predicted equilibrium adsorption capacity was close to the experimentally determined value (80.6 μg/g). Modeling of the equilibrium data with Freundlich and Langmuir isotherms lead to a better correlation coefficient in the case of Langmuir model. The value of the calculated maximum adsorption capacity is close to the experimental value (340 μg/g). The dimensional separation factor used to predict the essential characteristics of Langmuir isotherm indicates favorable adsorption in the studied concentration range (100-700 μg As(III) / L). The studied binary mixed oxide develops promising adsorbent properties concerning the arsenic (III) removal from aqueous medium.*

Keywords: arsenic removal, binary mixed oxide, sorption kinetics, sorption equilibrium

Depending on the sources the drinking water contains many trace contaminants, both cationic and anionic [1]. Among common inorganic pollutants, arsenic species has been largely studied because of its potential harmfulness to human health [2]. The symptoms of chronic poisoning on human beings are numerous: skin cancer, liver, lung, kidney, and bladder cancer as well as conjunctivitis, hyperkeratosis, and in severe cases gangrene in the limbs and malignant neoplasm [3-5]. Therefore the arsenic species maximum permissible limit in drinking water according to World Health Organization (WHO) is 10 μg/L [6-9]. In conclusion there is a real need for development of removal methods for inorganic arsenic from drinking water and under ground water [6, 10, 11].

Varoius methods are proposed to reduce arsenic level in natural waters, including redox processes, precipitation, co-precipitation, adsorption, electrolysis, cementation, solvent extraction, ion-exchange, flotation, and biological processing [12-15]. According to the literature data [1-5] the adsorption is one of the most used methods for arsenic removal from water. Various types of adsorbents have been developed by researchers for the removal of arsenic from water, such as: coconut husk carbon, MnO_2 coated sand, basic yttrium carbonate, several iron compounds or iron containing wastes, activated alumina, carbon from fly ash, granular titanium dioxide and hybrid polymeric sorbents [5-10]. Among all these sorbents the iron salts based sorbents were found to be the most efficient in arsenic removal from drinking water, due to its strong affinity for dissolved arsenic. Arsenic species give interactions with iron compounds at each sorption site of the solids and so they are effectively removed from solution [2-6, 13-17].

The purpose of the present paper was to evaluate a binary mixed oxide Fe_2O_3-SiO_2 as potential As (III) adsorbent. We focused on this mixture because iron oxide is responsible for arsenic removal and the presence of silicon oxide leads to a higher surface area, so we expect to obtain a high adsorption capacity.

Experimental part

Obtaining of binary mixed oxide

The sorbent from a binary mixed oxide was obtained from a mixture of iron oxalate and SiO_2 which was introduced as Ultrasil VN3 (Degussa). SiO_2 has been wet homogenized with iron oxalate = 1:1 in a porcelain dish and dried at 110°C. The resulting mixture has been grinded and then annealed in an electric oven at 550°C in an porcelain crucible for the decomposition of iron oxalate to Fe_2O_3 [18]. The components dosage for the mixture has been made in such a way to have a sorbent Fe_2O_3 / SiO_2 1 :1. The BET surface area of the obtained sample has been determined by nitrogen adsorption-desorption using a MICROMERITICS ASAP 2020 INSTRUMENT and the surface area has been compared with those of the simple oxides.

Sorption performance

The influence of different physico-chemical parameters (contact time and initial concentration of arsenic species in liquid phase) upon the arsenic species adsorption onto binary mixed oxide was investigated. In order to establish the adsorption performance the experiments were carried out with 0.1 g of binary mixed oxide in 100 mL solution having the concentration of 100 μg/L in $AsCl_3$. In the first instance the effect of contact time was studied. The samples were stirred using a glass rod (stirring speed 200 rpm) at different contact times (15, 30, 45, 60, 90, 120 and 150 min). Similar batch experiments were performed to study the influence of the initial As (III) concentration (100, 200, 300, 400, 500, 600 and 700 μg/L). After stirring, the samples were centrifuged at 1200 rpm for 30 min using a ROTINA 420 centrifuge. The arsenic residual concentration in the resulting solutions was determined through atomic absorption spectrometry with hydride generation, using a spectrophotometer VARIAN SpectrAA 110 VGA 77, at 193.7 nm. As (III) species was selectively reduced to arsenic hydride H_3As with natrium boronhydride $NaBH_4$ (0.6% w/v) solution in NaOH buffer (0.5% w/v).

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The adsorption performance expressed as the amount of As (III) adsorbed per gram of sorbent q_e (µg/g), is calculated from experimental data using the following equation [3, 7, 16, 17, 19]:

$$q_e = (C_o - C_e)\frac{v}{m} \qquad (1)$$

where:

C_o - initial concentration of arsenic in solution, µg/L;

C_e - equilibrium concentration of arsenic in solution, µg/L;

v - volume of solution, L;

m - amount of adsorbent, g.

During adsorption experiments the initial *p*H of the solutions was kept between 6.7 and 7, which is the most common pH value found in the natural waters. The *p*H of the solutions was measured using a multi parameter instrument WTW Multi 197i. The experiments were performed at the ambient temperature (20 ± 1°C).

Results and discussion

Sorbent properties

The BET specific surface area of the binary mixed oxide is 78.01 m^2/g, which is higher than the surface area of Fe_2O_3 (14.57 m^2/g) and smaller than the surface area of SiO_2 (144.04 m^2/g). One may notice that the addition of Ultrasil powders to Fe_2O_3 sample leads to the increase of the Fe_2O_3 surface area. This was the reasons for the choice of this mixture as potential arsenic adsorbent [18].

Effect of contact time and kinetic studies

In order to determine the time necessary to reach the equilibrium it was studied the effect of stirring time on the adsorption capacity of the binary mixed oxide in the process of As (III) species removal from water. The results presented in figure 1 show that the equilibrium was reached after 90 min, when more than 90% of arsenic was adsorbed.

In order to express the kinetics of arsenic adsorption onto binary mixed oxide the results were analyzed using the below presented models.

The pseudo-first-order kinetic model based on the solid capacity, proposed by Lagergren can be used to determine the rate constant for the adsorption process. Its integrated form [3, 7, 16, 17, 20] is expressed by equation (2):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

where:

q_t and q_e represent the amounts of the arsenic adsorbed on the binary mixed oxide at time t and at equilibrium time, respectively, µg/g;

k_1 - the specific adsorption rate constant, min^{-1}.

The pseudo-first-order rate constant (k_1) and the equilibrium adsorption capacity (q_e) are determined from the linear plot of ln(q_e-q_t) versus t (fig. 2).

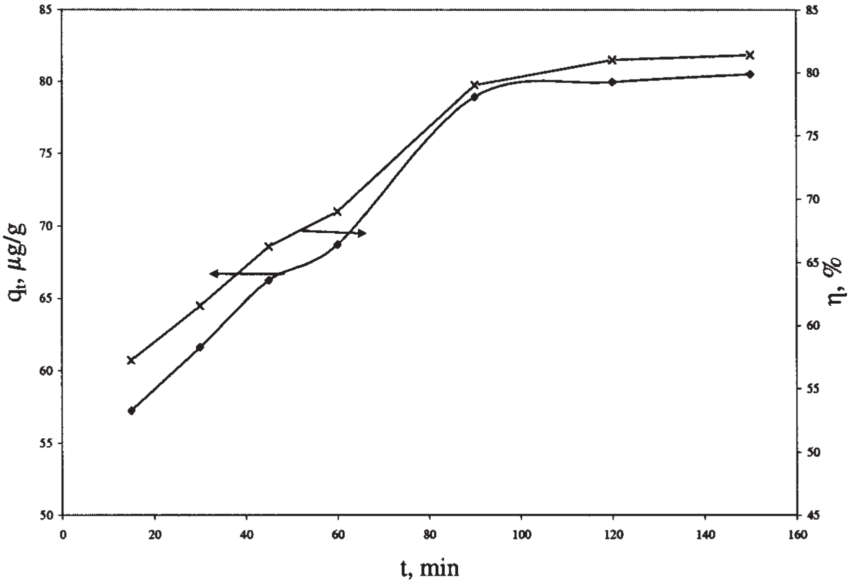

Fig. 1. Effect of stirring time on arsenic adsorption capacity of Fe_2O_3-SiO_2

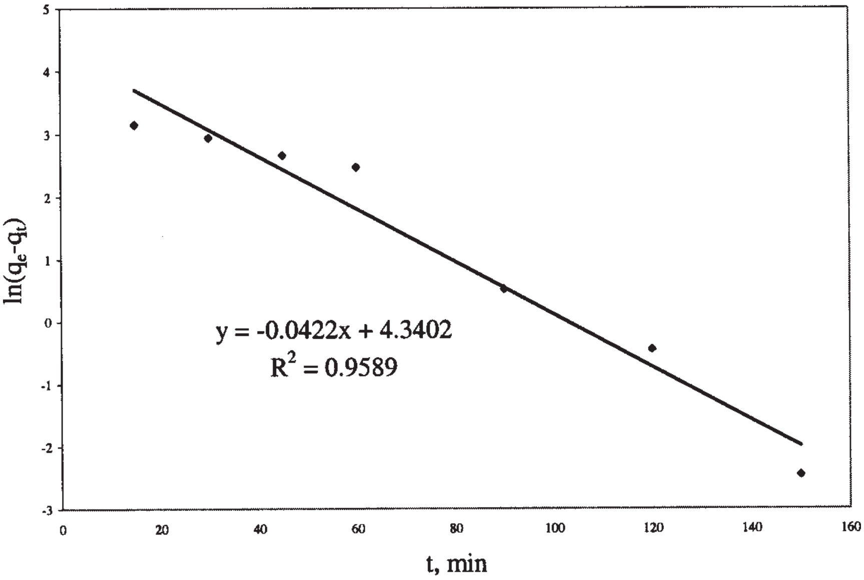

Fig. 2. Pseudo-first-order kinetic plot

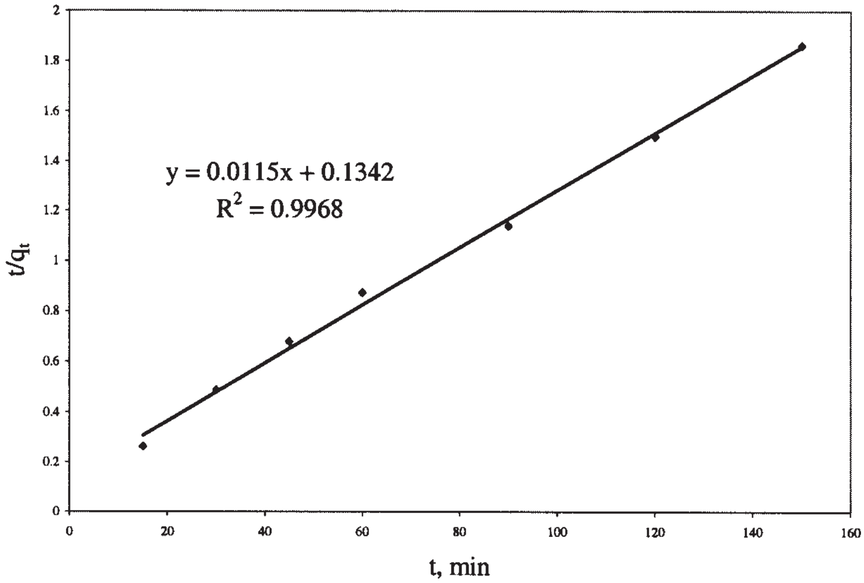

Fig. 3. Pseudo-second-order kinetic plot

Table 1
KINETIC PARAMETERS FOR As(III) SORPTION ONTO BINARY MIXED OXIDE

q_e, exp, μg/g	Pseudo-first-order model			Pseudo-second-order model		
	q_e, kinetic plot, μg/g	k_1, min^{-1}	R^2	q_e, kinetic plot, μg/g	k_2 $min^{-1}(\mu g/g)^{-1}$	R^2
80.6	76.7	0.0422	0.9589	86.95	$9.85 \cdot 10^{-4}$	0.9968

The linear form of the pseudo-second-order rate expression of Ho and McKay, based on the solid phase sorption [3, 7, 16, 17, 21], is given by equation (3):

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (3)$$

where:

$h = k_{s2} \cdot q_e^2$; k_2 is the pseudo-second-order constant, $min^{-1}(\mu g/g)^{-1}$.

Other terms have their usual meanings. A plot of t/q_t versus t should yield a straight line. From the intercept and slope (fig. 3) are calculated the second-order rate constant (k_2) and the equilibrium adsorption capacity (q_e).

The values of the constants, together with the regression coefficients (R^2) obtained in both cases are summarized in table 1.

The experimental data do not fit the kinetic isotherm of the pseudo-first-order model because the obtained correlation coefficient is not close to 1 and there is a difference between the q_e value experimentally obtained and the value directly obtained from the kinetic plot. In the case of the pseudo-second order model, the theoretically predicted equilibrium adsorption capacity is close to the experimentally determined value. Alongside the correlation coefficient closer to 1, this indicates that the kinetics of As (III) species removal through adsorption on binary mixed oxide Fe_2O_3-SiO_2 is well explained and approximated by the pseudo-second-order kinetic model.

Effect of initial concentration and equilibrium study

The adsorption isotherm of As (III) is presented in figure 4. At arsenic species equilibrium concentrations higher than 200μg/L the value of adsorption capacity remains practically the same. The experimentally determined maximum adsorption capacity of the binary mixed oxide is 340 μg/g.

Several models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently used models [3, 5, 7, 9, 16, 17]. In this work, both models were used to describe the relationship between the amount of As (III) ions adsorbed by binary mixed oxide and its equilibrium concentration in solution batch contact time over 90 min as it results from figure 1.

The linear form of the Freundlich isotherm equation can be written as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (4)$$

and the linear form of the Langmuir isotherm as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (5)$$

where:

q_e is the amount of arsenic adsorbed per gram of sorbent, μg/g;

C_e is the equilibrium concentration of arsenic, μg/L;

K_F and 1/n are characteristic constants that can be related to the relative adsorption capacity of the adsorbent and the intensity of adsorption, respectively;

q_m is a measure of monolayer adsorption capacity [μg/g] and K_L is a constant related to the free energy of adsorption.

The curves and parameters, as well as the correlation coefficients (R^2), for As (III) species removal through adsorption onto binary mixed oxide are presented in figures 5 and 6 and table 2.

The Freundlich plot has a very low correlation coefficient; this suggests a restriction on the use of

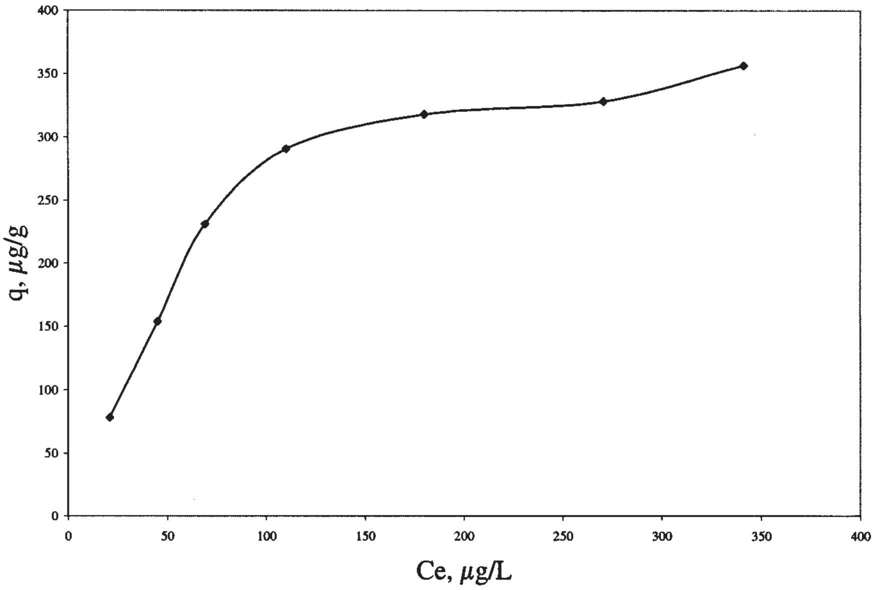

Fig. 4. Adsorption isotherm of As(III) on the binary mixed oxide

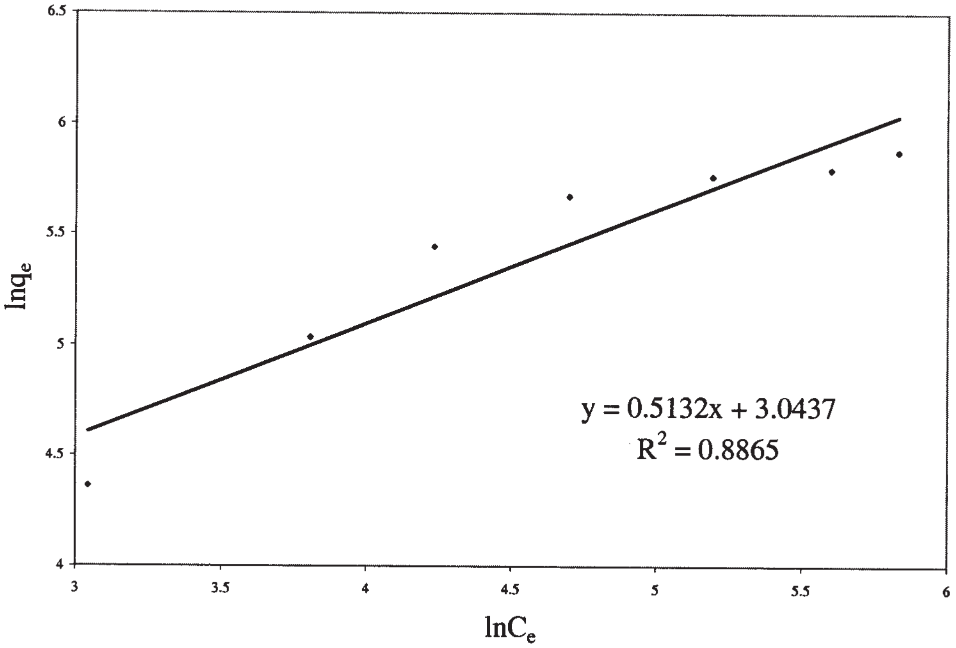

Fig. 5. Freundlich plot of As(III) adsorption on Fe_2O_3-SiO_2

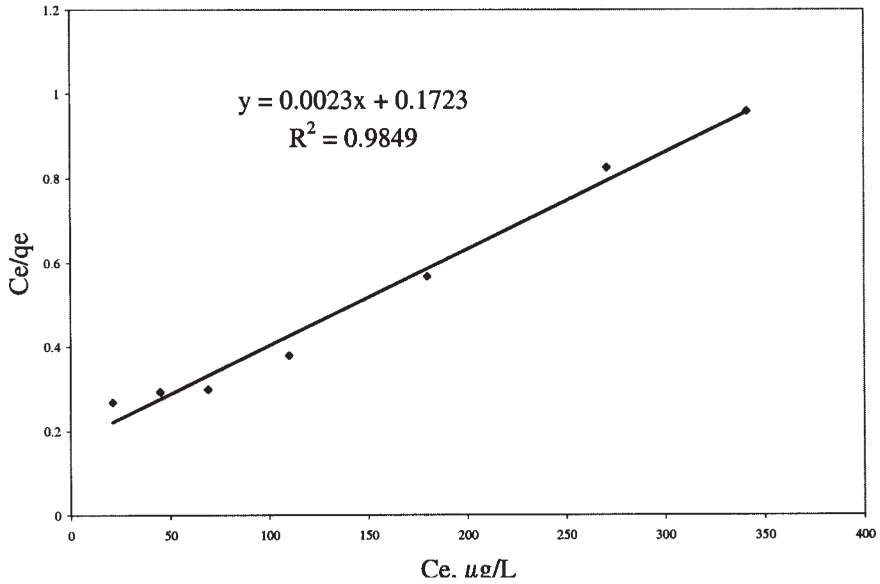

Fig. 6. Langmuir plot of As(III) adsorption Fe_2O_3-SiO_2

Freundlich isotherms. The value of $1/n < 1$, which provides information about surface heterogeneity and surface affinity for the solute, indicates a favorable sorption of As (III) species and a very high affinity of the binary mixed oxide for As (III) due to the iron presence in the oxide.

The Langmuir model effectively describes the sorption data with a correlation coefficient of 0.9849. Thus the isotherm follows the sorption process in the entire studied concentration range. Furthermore, the values for the

Table 2
ISOTHERM PARAMETERS FOR As(III) ADSORPTION ON Fe_2O_3-SiO_2

Freundlich isotherm			Langmuir isotherm		
K_F, μg/g	1/n	R^2	K_L, L/μg	$q_{m\ calc}$, μg/g	R^2
20.98	0.5132	0.8865	0.0133	434.78	0.9849

calculated (from the Langmuir plot) and experimental maximum adsorption capacity are very close.

The dimensional constant, called separation factor (R_L), is used to describe the essential characteristics of Langmuir isotherm ($R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; and $R_L = 0$, irreversible):

$$R_L = \frac{1}{1 + K_L C_o} \qquad (6)$$

In fact, the separation factor is a measure of the used adsorbent capacity. R_L values were calculated for the studied concentration range and found to be $0 < R_L < 1$, showing favorable adsorption.

Conclusions

The sorption performance of a synthetic binary mixed oxide Fe_2O_3-SiO_2 for the As (III) species removal from water was evaluated. This material was chosen as potential adsorbent for arsenic removal because it was observed that the addition of the SiO_2 to the Fe_2O_3 samples leads to the increase of Fe_2O_3 active surface area.

The effect of contact time on As (III) sorption on the binary mixed oxide revealed that the equilibrium is reached in 90 min , with a typical adsorption performance of about 90%. The adsorption process followed a pseudo-second-order kinetics and the theoretically predicted equilibrium adsorption capacity was close to the experimentally determined value (80.6 mg/g).

Equilibrium adsorption data were modeled using Freundlich and Langmuir adsorption isotherms, and it was observed that the Langmuir model effectively describes the sorption data. The value of the calculated maximum adsorption capacity is close to the experimental value (340 μg/g). The dimensional separation factor used to predict the essential characteristics of Langmuir isotherm indicates favorable adsorption in the studied concentration range (100-700 μg As (III) /L).

The studied binary mixed oxide develops promising adsorbent properties concerning the arsenic (III) removal from aqueous medium.

Acknowledgements: The authors gratefully acknowledge the financial support provided by the UEFISCSU, under grant no. 694/19.01.2009, Code 927, "Integrated concept about depollution of waters with arsenic content, through adsorption on oxide materials, followed by immobilization of the resulted waste in crystalline matrices".

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Manuscript received: 19.05.2010