SORPTION OF As, Ge, Ga FROM THE SOLUTION USING MECHANICALLY ACTIVATED RUTILE

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In order to create an efficient sorbent for the hydrometallurgical extraction of gallium, germanium from the poor raw materials and for the arsenic removal from the technological solutions a modification of commercially available titanium oxide and its sorption properties studies were performed. The mechanical activation in the high-energy planetary mill and ultrasonication of the aqueous suspension were used for modification of the TiO_2. Particle size analysis of modified material performed by dynamic light scattering indicated the presence of particles of nanometer range. According to X-ray diffraction, the proportion of nanoscale fraction is significant. It was found that the mechanical activation and subsequent ultrasonic treatment of TiO_2 increases sorption of gallium, germanium and arsenic (III, V), from 10-40 % to 96-97 % at the optimum pH values of the solution.

Introduction

Titanium dioxide – a popular sorption material, characterized the low cost, environmental safety and chemical stability. It is used for sorption of radionuclides, organic substances, various cations and anions, for purification of fluids from them and also for determining of their contents [1–4].

There are several crystallographic modifications of titanium dioxide. Only rutile is thermodynamically stable among all modifications, but it has the lowest sorption properties, it was found that the sorption capacity increases in a series of rutile <anatase <amorphous TiO_2 [1]. Sorption active modifications of titanium dioxide (anatase, amorphous TiO_2) are obtained by chemical methods, such as hydrolysis of inorganic salts or organic derivatives of titanium. The high sorption degree of germanium and gallium (over 96%) was obtained on the nanoscale anatase [5]. Anatase and amorphous TiO_2 and materials based on titanium oxide, have also found wide application as sorbents for extracting Group V elements of the periodic system (phosphorus, arsenic, antimony and bismuth) from solution [3, 6–8].

The aim of this work is investigation of sorption of germanium, gallium, arsenic (V), arsenic (III) with the most stable modification of titanium dioxide – rutile after its mechanical activation. Studies about the effect of the such modification of rutile on its sorption ability to these elements had not been conducted before.

Results and discussion

Rutile modification was performed by mechanical activation followed by ultrasonic treatment of its aqueous suspension. Ultrasonic treatment promotes disaggregate of the agglomerates, mechanical activation causes grinding of powder oxide particles and increases its surface area and modifies the surface properties, promotes the growth of crystal defects.
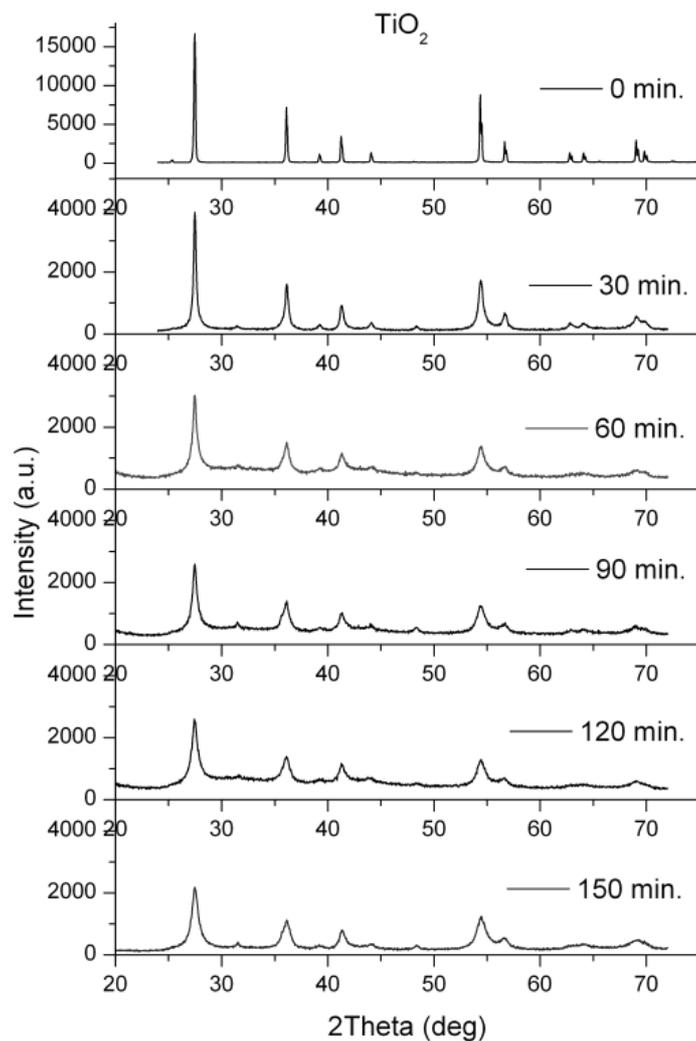
Mechanical activation of TiO_2 (qualification – special purity grade, 100% rutile) was carried out in a high-energy planetary ball mill Pulverisette 7 PremiumLine with a headset from tungsten carbide (diameter balls – 10 mm, the primary disk rotation speed – 800 rpm). Duration of mechanical activation - 150 min. Mode of grinding is dry, beakers cools in air every 15 min.

X-ray examination of TiO_2 samples was carried out on a Shimadzu XRD-7000 diffractometer in Cu Ka-radiation using certified silicon powder as an internal standard. Measurement conditions: I = 30 mA, V = 40 kV, the angle range from 25° to 85° in 2Θ, a step size of 0.03° and a step scan of 3 s. It was found that during of mechanical activation crystalline modification - α - TiO_2 (rutile structure) was not changed (Fig. 1).

The mean size of coherent scattering regions (CSR) of the samples was calculated using Scherrer's formula. Fig. 2 shows that the intensive milling takes place in the first 60 min. of grinding. The average size CSR is reduced from $\approx$220 nm to $\approx$24 nm. Over the next 90 min, size CSR is reduced slightly – to $\approx$15 nm.

Using dynamic light scattering method, it was confirmed that the size of the particles formed during the mechanical activation TiO_2 is almost identical to the size of the crystallites, measured by X-ray diffraction. For measurements 0.2 g TiO_2 after 150 min of mechanical activation was dispersed in 75 ml of a 0.2% solution of anionic surfactant - sodium dodecyl sulfate - in an ultrasonic bath PSB-2835-05 (ultrasonic frequency is 35 kHz). After that obtained suspension was filtered through the Green Ribbon filter paper moistened to remove of indestructible agglomerates. The results of three consecutive measurements of particle diameter on analyzer Zetasizer Nano S90 are presented in Fig. 3 - a maximum of particle size distribution is $\approx$14 nm.

Sorption of Ge, Ga, As from the aqueous solutions were carried out in static mode. A solution of the elements was prepared (all reagents were of analytical grade and purchased – GeO_2, metallic gallium with purity of 99.99 wt. %, $Na_3AsO_4 \cdot 12H_2O$, As_2O_3), then 50 mg/100 mg (Ge, Ga/As) of the rutile were placed (per 25 ml (Ge, Ga) or 100 ml (As) solution, unless otherwise specified) – initial TiO_2 (calcined at 700°C) or after mechanical activation. The required pH of solution was adjusted by addition of NaOH

Fig. 1. X-ray diffraction patterns of TiO$_2$ after different time of mechanical activation
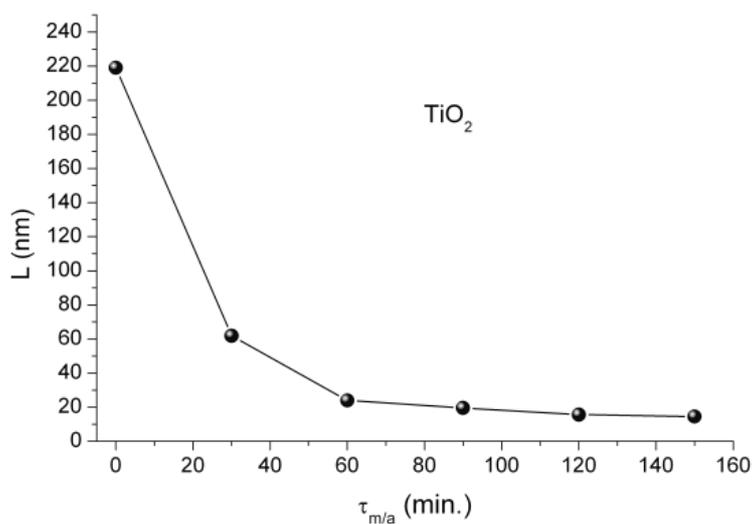
Fig. 2. The dependence of average size CSR TiO$_2$ vs the duration of mechanical activation
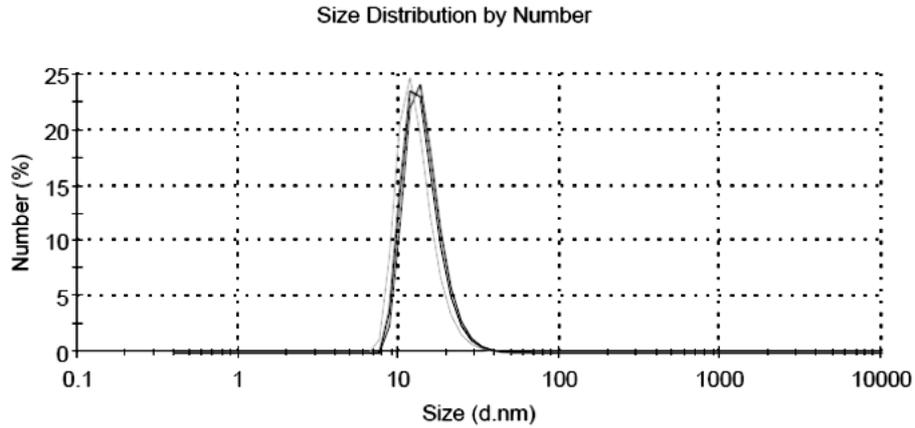
Fig. 3. The results of dynamic light scattering measurements of TiO_2 particle size, mechanically activated 150 min. The aqueous suspension was stabilized by sodium dodecyl sulfate (0.2 wt.%)

and HCl solutions by using ionomer. Sorption without ultrasonic treatment was performed for one day, using - for 30 min. After sorption the sorbent was separated by centrifuging for 15 min at 8000 rpm.

The aim element content in solution before and after sorption was measured by atomic emission spectrometer «Optima 2100 DV» («Perkin Elmer»). The recovery sorption degree (R) was calculated on following equation:

$$R = \frac{C_0 - C_e}{C_0} \cdot 100\%,$$

where C_0 and C_e (mol/l) are the initial and equilibrium concentrations of Ge, Ga, As in solution, respectively.

The following operational parameters were employing: RF power – 1300 W; Ar gas flow rate– 15 l/min; gas flow rates for auxiliary – 0.20 l/min; gas flow rates for nebulizer – 0.80 l/min; pump flow rate – 1.5 ml/min; observation optics – radial; delay time – 45 sec. Spectral analytical lines: Ge I 265.118 nm, Ga I 417.206 nm, As I 193.696 nm.

The effect of pH on the recovery degree of Ga, Ge is shown on Fig. 4 and As (V), As (III) on Fig. 5. The gap in the center of dependencies for gallium in Fig. 4 (b) due to the formation of gallium hydroxide precipitate at this pH range.

It was found that the maximum sorption degree of germanium (R about 97%) is achieved at pH 4-9 with modified TiO_2, and gallium (R about 96%) at pH = 3-4. Thus, it is shown that mechanically activated rutile in the experimental conditions are not inferior to the recovery de-

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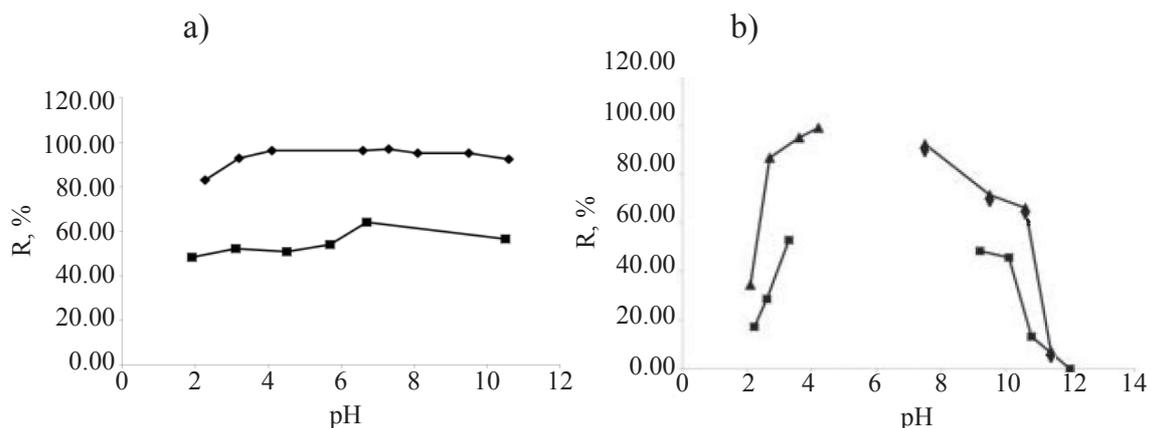
Fig. 4. Effects of pH on the sorption germanium (a), gallium (b) on sorbents:
■ – initial TiO$_2$ with ultrasonic treatment, ♦ - mechanically activated TiO$_2$ with ultrasonic treatment;
C(Ga)=C(Ge)=5 mg/l
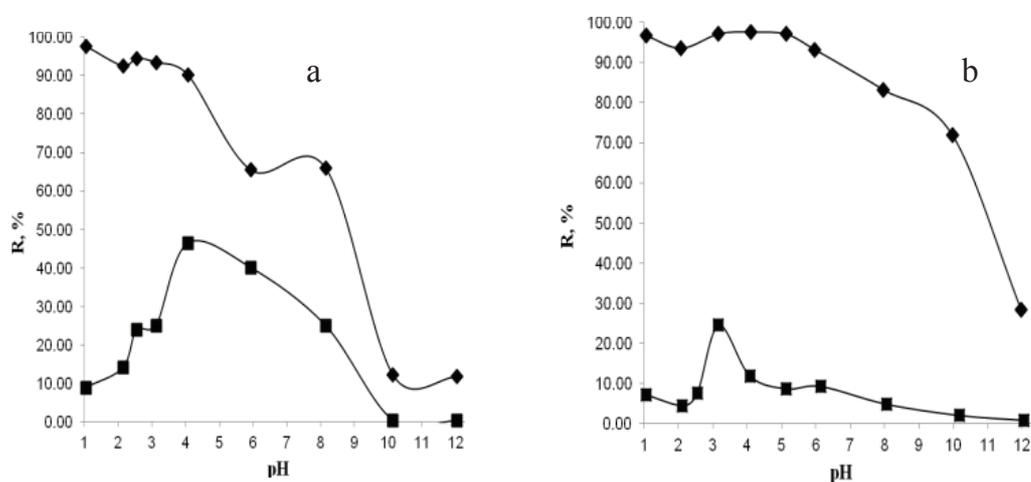
Fig. 5. Effects of pH on the sorption As (V) (a), As (III) (b) on sorbents:
■ – initial TiO$_2$ with ultrasonic treatment, ♦ – mechanically activated TiO$_2$ with ultrasonic treatment;
C(As)=10 mg/l

gree of germanium and gallium sorption on nanoscale anatase (in [5] the maximum recovery degree of sorption was determined for germanium and gallium on the anatase with particle size 10-15 nm 96.6% and 96.3%, respectively).

As for arsenic, the maximum sorption degree of As (V) is achieved in acidic medium at pH 1–3 with modified TiO$_2$, and As (III) at pH 1–5 (R about 97 %).

Thus, mechanical activation followed by ultrasonic treatment of rutile led to increasing the degree of sorption in several times. It is due particularly to a decrease in particle size and increase in the surface of sorbent.

In the optimum sorption pH range the isotherm of germanium, gallium, arsenic (see. Figs. 6 and 7) were obtained. The Langmuir model and Freundlich model are often used to describe equilibrium sorption isotherms (see. Table 2) [9-10]. In a series of 25 ml /100 ml (Ge, Ga/As) flasks aliquot volumes of the elements solutions corresponding to different concentrations (from 10 mg/l to 250 – 300 mg/l) were placed, pH was adjusted to the optimum value, 0.05 g/0.1 g (Ge, Ga/As) of sorbent was added and amounts of sorbed element per unit weight were determined.

The Langmuir model assumes that the adsorbed layer is one molecule in thickness. The Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite
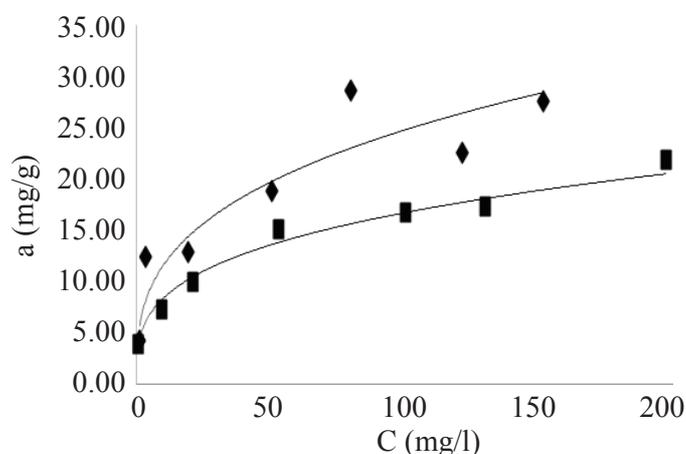
Fig. 6. Isotherm of sorption on mechanical activated TiO_2:
♦ – Ge, pH=6.9-7.6, ■ – Ga, pH=3.1-3.4, after ultrasonic treatment
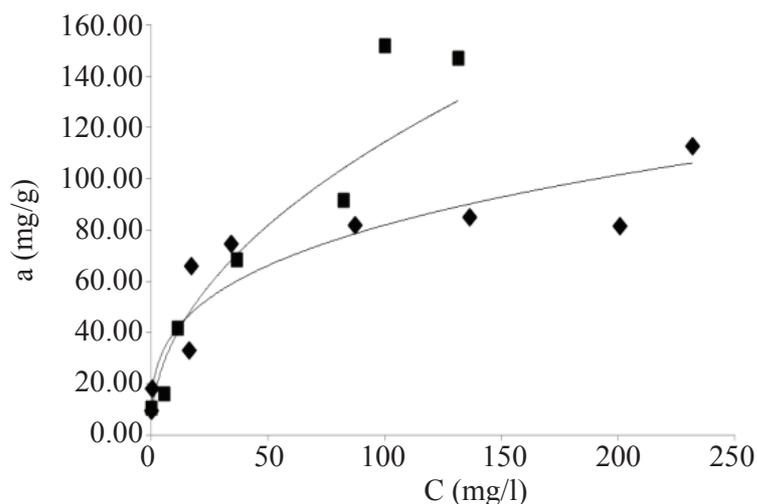
Fig.7. Isotherm of As sorption on mechanical activated TiO_2,
♦ – As (V), pH=1, ■ – As (III), pH=4, after ultrasonic treatment

capacity for the sorbate. The Langmuir equation can be represented by the expression

$$\frac{C_e}{a_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e,$$

where a_e is the solid-phase sorbate concentration at equilibrium (mmol/g), C_e is the aqueous phase sorbate concentration at equilibrium (mmol/l), K_L and a_L (l/mmol) are the Langmuir isotherm constants. A plot of C_e/a_e versus C_e gives a straight line of slope a_L/K_L and intercept $1/K_L$, where K_L/a_L gives the theoretical monolayer saturation capacity.

Freundlich model assumes that there is a continuous variation of absorption energy, since first there is the filling of the most active centers of sorption, then the surface is continuously filled up until not busy centers with the lowest energy. A linear form of the Freundlich expression can be represented as

$$\ln a_e = \ln K_F + \frac{1}{n} \ln C_e,$$

where a_e is the solid-phase sorbate concentration at equilibrium (mmol/g), C_e is the liquid-phase sorbate concentration at equilibrium (mmol/l), K_F is the Freundlich constant (l)$^{1/n}$(mmol)$^{1-1/n}$, and $1/n$ is the heterogeneity factor. A plot of $\ln a_e$ versus $\ln C_e$ enables the constant K_F and the exponent $1/n$ to be determined.

Table 1 demonstrates that for mechanically activated TiO_2 after the ultrasonic treatment experimental data for Ga and As (III) closely follow the Freundlich model of sorption, and for Ge, As (V) the Langmuir model (the correlation coefficients were high). Comparing the characteristics of TiO_2 of different modifications the maximum sorption capacity is even higher than the values obtained for the sorption of germanium at nanoscale anatase (in [5]) – 27.5 mg/g vs 19.68 mg/g, and for the sorption of gallium (in [11]) – 21.8 mg/g vs 8.28 mg/g. As for arsenic obtained in the present work sorption capacity (> 100 mg/g) is higher than the values obtained for the sorption of As at TiO_2 with different crystal morphology (in general 2 – 40 mg/g for 1 g/l of anatase, amorphous TiO_2, anatase and rutile mix and others) [6].

The affinity of As (III) to TiO_2 is higher than for As (V) as indicated by a parameter K_F in Freundlich isotherm equation, which is a quantitative measure of the affinity of sorbate to the sorbent surface. Also sorption capacity for As (III) is higher than for As (V).

Table 1
Langmuir and Freundlich constants for sorption of Ge, Ga, As on modified TiO_2

The Langmuir model				
Analyte	K_L, l/g	a_L, l/mmol	a_m, mg/g (sorption capacity)	R
Ge	2.23	5.81	27.5	0.957
Ga	1.05	3.45	21.8	0.967
As (III)	4.33	1.8	147	0.802
As (V)	7.07	5.25	113	0.948
The Freundlich model				
Analyte	K_F, $(l)^{1/n}(mmol)^{1-1/n}$	$1/n$	n	R
Ge	0.31	0.33	3.02	0.865
Ga	0.21	0.30	3.32	0.983
As (III)	1.62	0.48	2.07	0.919
As (V)	1.00	0.31	3.23	0.939

Conclusion

A result of investigations it was found that the mechanical activation in combination with ultrasonic treatment radically changes the sorption properties of rutile, which promotes an increasing the degree of sorption compared to the original rutile in several times. It was found for modified TiO_2 that the maximum sorption degree of germanium is achieved at pH 4-9, gallium at pH = 3-4, arsenic (III) at pH = 4, arsenic (V) at pH = 1. Obtained sorption isotherms of elements from aqueous solutions are adequately described by the Langmuir (Ge, As (V)) and the Freundlich equations (Ga, As(III)). Sorption capacity value of mechanically activated rutile respect to arsenic, gallium and germanium exceeds the capacity values of anatase and amorphous titanium oxide found in the literature.

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