

## TiO<sub>2</sub> AS ADVANCED MATERIALS FOR AS ADSORPTION

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### ABSTRACT

*Heavy metals are the major pollutants released from all kind of industries. Arsenic (As) indicates its extreme toxicity even at very low concentrations. It was a reason to use ICP-OES (optical emission spectrometry with inductively coupled plasma) as satisfactory sensitive method for detecting of low As concentrations. In this paper is presented comparison of sorption As<sup>+3</sup> and As<sup>+5</sup> on synthetic sorbent TiO<sub>2</sub> with different contents of iron (1%, 10% and 20% Fe) based on Freundlich's adsorption isotherms. Synthesized TiO<sub>2</sub> doped by Fe was able to increase the adsorption, which proved to be suitable for absorption of As. Results show that TiO<sub>2</sub> with 20% Fe is the most suitable for sorption As<sup>+3</sup> and As<sup>+5</sup>.*

**Keywords:** Freundlich's isotherms, arsenic, TiO<sub>2</sub> sorbent.

### 1. INTRODUCTION

Environmental pollution is one of the major problems, which could originate by several ways such as continuous discharging of the large variety of toxic inorganic and organic chemicals into the environment. This causes severe water, air and soil pollutions. Heavy metals are the major pollutants released from all kind of industries. Because of its toxicity, As in waters is an global problem. Consumption of waters which were polluted by As (in concentration over 0,01mg/L) in long period, cause different kinds of cancer (cancer of skin, lung, kidney, bladder...). By aim to separate As from waters, as only verified method is used adsorption by using of different types of sorbents. Large number of commercially available low-cost sorbents for As sorption is tested. Some sorbent which can be used for As sorption are: activated charcoal, red mud, slag, ash, clay, sand, zeolite, many oxides (of manganese, iron, titanium...), marine sediments, phosphates, bio-sorbents, etc... As for titanium, many laboratory tests were conducted, by aim to determine adsorption capacity for sorption of arsenic; some of these experiments were selected and presented in this paper. Nanocrystalline TiO<sub>2</sub> has the ability to remove arsenate and arsenic and photo catalytic oxidation of As<sup>+3</sup> to As<sup>+5</sup>. TiO<sub>2</sub> has proven to be a good sorbent for the sorption of As<sup>+5</sup> at pH <8 and the maximum removal of As<sup>+3</sup> occurred at pH about 7.5. Adsorption capacity of nanocrystalline TiO<sub>2</sub> for As<sup>+3</sup> and As<sup>+5</sup> was significantly higher compared to the TiO<sub>2</sub> (Degussa P25) and granular iron-oxide. [1, 2]. The adsorption of As(V) and As(III) at the surface sites an iron oxide is mostly ligand exchange which involves the release of <sup>-</sup>OH<sub>2</sub> and/or <sup>-</sup>OH [3]. Both sorption mechanisms are strongly dependent on pH, but while the affinity for As(V) decreases as pH increases, the affinity for As(III) usually remains relatively constant over the typical drinking water pH range of 6.5– 8.5. [4,5]. Jezeque and Chu investigated the use of TiO<sub>2</sub> for

removing  $As^{+5}$  from the water. The adsorption isotherms were performed at pH=3 and pH=7. It was concluded that the adsorption follows the Langmuir's model. Furthermore, the addition of phosphate reduced arsenate adsorption [6].

This paper presents the results of the synthesized  $TiO_2$  doped with iron in order to increase its adsorption power. The results show that  $TiO_2$  with addition of Fe, based on Freundlich's adsorption isotherm, is a good sorbent for the sorption of  $As^{+3}$  and  $As^{+5}$ .

## 2. EXPERIMENTAL

Standard As solution was prepared with concentration of 1g/L. Series of diluted solutions was prepared in next concentrations: 400, 600, 800, 1000 and 2000 ppb for  $As^{+3}$  and 800, 1000, 1500, 2000, 2500 and 3000 ppb for  $As^{+5}$ . For dilution was used distilled water. The diluted standard solutions of As, which were transferred to polyurethane bottle of 100 ml, was added 50 mg of sorbent (titanium dioxide doped with 1%, 10% and 20% Fe). Each concentration of As was done in triplicate. Samples were shaken on shaker in 1h. After completion of shaking, solutions of different concentrations were transferred into plastic cuvettes of 50 mL and centrifuged. After centrifugation, clear solutions were separated from the sediment, and transferred into 50 mL polyurethane bottles. In each bottle was added 100  $\mu$ L of concentrated nitric acid. Thus prepared samples were tested on ICP-OES (optical emission spectrometry with inductively coupled plasma), applied was hydride technique.

## 3. RESULTS AND DISCUSSION

In Figures 1, 2 and 3 are represented by the Freundlich isotherm for  $As^{+3}$  on  $TiO_2$  sorbent with 1 %, 10 % and 20% Fe. Shaking time was 1 h.

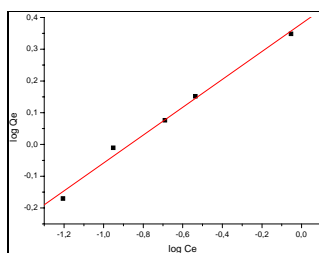


Figure 1. Freundlich's isotherm for  $As^{+3}$  on  $TiO_2$  sorbent with 1 % Fe, while shaking 1h

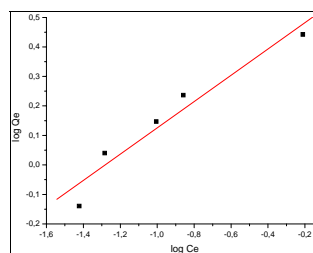


Figure 2. Freundlich's isotherm for  $As^{+3}$  on  $TiO_2$  sorbent with 10% Fe, while shaking 1h.

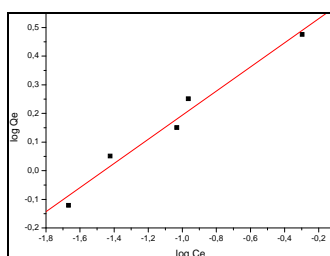


Figure 3. Freundlich's isotherm for  $As^{+3}$  on  $TiO_2$  sorbent with 20% Fe, while shaking 1h.

Data obtained by testing on ICP-OES which are then processed using the software program Origin 6.1 are presented in tables 1. and 2.

Table 1. The values of Freundlich's constants for the sorption of  $As^{+3}$  on sorbent  $TiO_2$  with 1%, 10% and 20% Fe

	Freundlich's adsorption capacity, $K$ (mg/g)	Freundlich's intensity of adsorption $n$	Freundlich's coefficient of correlation $r$
$As^{+3}$ , $TiO_2$ with 1 % Fe, Shaking 1h	2.4003	2.2808	0.9955
$As^{+3}$ , $TiO_2$ with 10 % Fe, Shaking 1h	3.7269	2.2431	0.9686
$As^{+3}$ , $TiO_2$ with 20% Fe, Shaking 1h	4.1207	2.3743	0.9866

By Freundlich's model is noticed that the adsorption capacity ( $K$ ) increases in the series:  $TiO_2$  with 1% Fe, then  $TiO_2$  with 10% Fe and at the end of  $TiO_2$  with 20% Fe. The highest value of the Freundlich's adsorption capacity ( $K$ ) is obtained for  $TiO_2$  sorbent with 20% Fe, which means that last one was the best sorbent for the sorption of  $As^{+3}$ .

In Figures 4, 5 and 6 are represented by the Freundlich isotherm for  $As^{+5}$  on  $TiO_2$  sorbent with 1 %, 10 % and 20% Fe. Shaking time was 1 h.

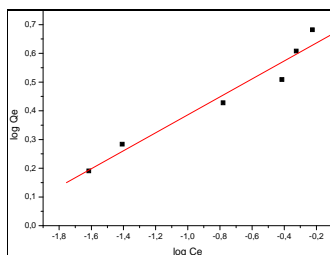


Figure 4. Freundlich's isotherm for  $As^{+5}$  on  $TiO_2$  sorbent with 1 % Fe, while shaking 1h.

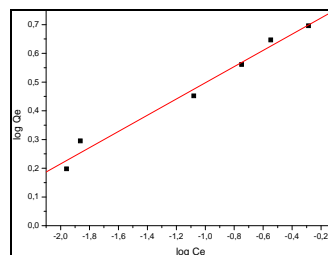


Figure 5. Freundlich's isotherm for  $As^{+5}$  on  $TiO_2$  sorbent with 10% Fe, while shaking 1h.

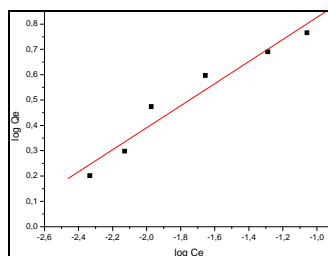


Figure 6. Freundlich's isotherm for  $As^{+5}$  on  $TiO_2$  sorbent with 1 % Fe, while shaking 1h.

Table 2. The values of Freundlich's constants for the sorption of  $As^{+5}$  on sorbent  $TiO_2$  with 1%, 10% and 20% Fe

	Freundlich's adsorption capacity, <b>K</b> (mg/g)	Freundlich's intensity of adsorption <b>n</b>	Freundlich's coefficient of correlation <b>R</b>
$As^{+5}$ , $TiO_2$ sa 1 % Fe, mućkanje 1h	4.9976	3.1991	0.9774
$As^{+5}$ , $TiO_2$ sa 10 % Fe, mućkanje 1h	6.0250	3.5426	0.9909
$As^{+5}$ , $TiO_2$ sa 20% Fe, mućkanje 1h	18.2545	2.2976	0.9734

By Freundlich's model is noticed that the adsorption capacity (K) increases in the series:  $TiO_2$  with 1% Fe, then  $TiO_2$  with 10% Fe and at the end  $TiO_2$  with 20% Fe. The highest value of the Freundlich's adsorption capacity (K) is obtained for  $TiO_2$  sorbent with 20% Fe, so this was the best sorbent for the sorption of  $As^{+5}$ .

#### 4. CONCLUSIONS

The synthesized  $TiO_2$  sorbents were proved as suitable for the sorption of As. In these tests most suitable synthesized sorbents for the sorption of  $As^{+3}$  and  $As^{+5}$ , was  $TiO_2$  with the addition of 20% Fe. By Freundlich's model is noticed that the adsorption capacity (K) increases with increasing concentration of Fe.

#### 5. REFERENCE

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