

# EXTRACTION OF METALS FROM AQUEOUS SOLUTIONS USING TI-BASED NANOSTRUCTURES: A REVIEW

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## Abstract

Titanium-based nanostructures due to their special physicochemical properties are receiving a great deal of interest for the application in several fields. Among these applications, the Ti-based nanostructures are finding their value as “green adsorbents” or ion exchange for metals present in aqueous solutions arising from various environments. The present paper reviewed the applications of these amazing materials in the removal of metals from heavy.

The precursor used to prepare various form of titanium-based nanostructure is  $\text{TiO}_2$ . The first description of how titanate nanotubes were obtained by hydrothermal process in alkaline media dated back 1998. In the process, anatase powders were chemically treated with 5-10 M NaOH solutions during 20 h at  $110^\circ\text{C}$ , the as obtained nanotubes presented a specific surface as high as near  $400 \text{ m}^2/\text{g}^2$  [1]. This type of treatment was constantly repeated in all the literature consulted in this work.

Different titanate-based nanostructures can be isolated by variation of the sodium hydroxide concentration and the reaction time, some of them are nanoparticles, nanosheets, nanotubes, nanowires and nanoribbons.

Titanate nanotubes were used for the removal of copper (II) from aqueous solutions [2]. The adsorption capacity of the nanotubes depends of the amount of  $\text{Na}^+$  in the nanotube, since if this presence is not very low (i.e. higher than 7.2 % wt.), the nanotubes are good adsorbents of copper (II) with a maximum capacity of near 1.9 mmol/g at a pH value 5.

Titanate fibers with  $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$  (i.e.  $x = 2$ ) were investigated as adsorbents for copper (II) [3]. The results concluded that the nanofibers with the higher sodium content are the most effective adsorbents for copper (II) being this adsorption greater as the pH of the solution is increased, reaching a maximum of 99% at pH of 4, when the solution of 100 mg/L metal were tested.

As (V) is mainly adsorbed at acidic pHs values, As (III) is best removed from aqueous solutions at pH around 7 using these nanoadsorbents [4]. The temperature in which nanotubes are formed influences the arsenic uptake as results in Table 1 shown, is far greater than that obtained by the use of titanium oxide powders. The maximum capacity of As (III) and (V) obtained by the Langmuir model is 0.8 mmol/g and 2.8 mmol/g respectively.

It is described the adsorption of lead (II) using titanate nanotubes [5]. The high lead loadings onto de nanotubes, as much as near 1.0 mmol Pb(II)/g adsorbent, can be achieved at pH values of 5-6. The adsorption decrease with the decrease of the pH values.

Three types of titanate adsorbents were investigated to remove Pb (II) from aqueous solutions, nanotubes, nanowires and amorphous nanoparticles [6]. In the three cases, the metal adsorption fitted to the Langmuir model. The adsorption order for the metal is found to be: nanotubes>nanoparticles>nanowires with capacities of near 0.7, 0.5 and 0.4 mmol/g for equilibrium lead concentration of near 1 g/L, respectively

Various divalent cations were used to determine the adsorption properties of sodium titanate nanotubes [7]. The adsorption order, found at pH 3 and ionic strength of 0.1 is  $\text{Pb} > \text{Cd} > \text{Cu} > \text{Zn} > \text{Ca} > \text{Sr} > \text{Ni}$ . This adsorption capacity can be linker with the hard and soft acids and bases theory. The nanotubes showed higher affinity for softer acids, so the nanotubes investigated in this work can be considered soft bases.

Ti nanoflowers has large specific surface area and their performance in the removal of heavy metals were thus investigated, the metals investigated were lead (II) and mixed aqueous solutions of cadmium (II), zinc (II) and nickel (II) [8]. Experimental results showed that removal order found for these nanocompounds is  $\text{Cd (II)} > \text{Zn (II)} > \text{Ni (II)}$  with maximum adsorption capacities of 0.7, 0.4 and 0.3

mmol/g, respectively, for a metal (each) equilibrium concentration around 0.17, 0.10 and 0.09 g/L. The performance of these adsorbents with respect to the metals removal is compared against those of titanate nanotubes or nanowires, for each metal, the adsorption capacity follows the next order: nanoflowers>nanotubes>nanowires. With respect to lead (II) adsorption using nanoflowers, adsorption equilibrium is reached within less than 10 min of contact of the aqueous solution and the adsorbent, this quick adsorption is related to the structural characteristics of titanate nanoflowers.

The adsorption power of titanate nanotubes on multi-elemental solutions was investigated in systems containing Pb (II), Cu (II), Cr (III) and Cd (II) [9]. From adsorption experiments carried out at an aqueous pH value of 5, the adsorption order and maximum metal loading was: Pb (II) (2.6 mmol/g)>Cd (II) (2.1 mmol/g)>Cu (II) (1.9 mmol/g)>Cr (III) (1.4 mmol/g), whereas the corresponding metals equilibrium concentration are: 0.50, 0.10, 0.13 and 0.14 g/L, respectively.

In the adsorption of Pb(II), Cd(II) and Cr (III) by titanate nanotubes [10], it was found that the pH of the aqueous solutions is the key factor for metal adsorption, whereas the presence of humic acid in this solution also influenced favorably the metal adsorption, due to the formation of metal-humic acid complexes, which evidently alter the adsorption capacity of the nanotubes. In the case of the pH, the metals adsorption is enhanced as the pH of the aqueous solution increases from 2 to 6, and follows the order lead (II)>cadmium (II)>chromium (III), however at the highest pH value, chromium is adsorbed preferably to cadmium. The presence of humic acid favored metal adsorption at concentration of the acid in the solution below 1 mg/L and above 5 mg/L, whereas between these two limiting values the metals adsorption decay.

The various tested Ti-based nanostructures certainly presented good properties as adsorbents of metals from aqueous solutions of various sources; however their application in this environmental field is not fully investigated. Very little information is currently in our hands related with the performance of these nanostructures when used in a continuous operation. The future for these nanoadsorbents in this field seemed to be promising and worth to be investigated

## References

- [1] Kasuga, T., Hiramatsu M., Hoson A., Sekino T. and Niihara K., *Langmuir*, **14**, (1998), 3160
- [2] Liu S.S., Lee C.K., Chen H.C., Wang C.C. and Juang L.C., *Chemical Engineering Journal*, **147**, (2009), 188.
- [3] Li N., Zhang L., Chen Y., Tian Y. and Wang H., *Journal of Hazardous Materials*, **189**, (2011), 265.
- [4] Niu H.Y., Wang J.M., Shi Y.L., Cai Y.Q. and Wei F.S., *Microporous and Mesoporous Materials*, **122**, (2009), 28.
- [5] Chen Y.C., Lo S.L and Kuo J., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **361**, (2010), 126.
- [6] Huang J., Cao Y., Deng Z. and Tong H., *Journal of Solid State Chemistry*, **184**, (2011), 712.
- [7] Du A.J., Sun D.D. and Leckie J.O., *Journal of Hazardous Materials*, **187**, (2011), 96.
- [8] Huang J., Cao Y., Liu Z., Deng Z., Tang F. and Wang W., *Chemical Engineering Journal*, **180**, (2012), 75.
- [9] Liu W., Wang T., Borthwick A.G.L., Wang Y., Yin X., Li X., and Ni J., *Science of the Total Environment*, **171**, (2013), 456-457.
- [10] Wang T., Liu W., Xiong L., Xu N. and Ni J., *Chemical Engineering Journal*, **366**, (2013), 215-216.

## Tables

Table 1. As(III) and (V) adsorption using various titanate nanotubes.

Temperature of formation	As(III), mmol/g	As(V), mmol/g
110° C	0.08	0.08
180° C	0.11	0.13

Time: 300 min. The adsorption using the pristine titanium oxide powder is 0.02 mmol/g and 0.03 mmol/g for arsenic (III) and (V), respectively.