Removal of arsenic (III) from groundwater by titanium dioxide as adsorbent

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1. Abstract

It is necessary to develop new and economic alternatives for arsenic (As) removal by adsorbents. The aim of this study is to investigate the feasibility of using commercially available titanium dioxide (TiO_2) for arsenite (As(III)) removal from aqueous solutions. Batch experiments were performed to determine the effect of several variables such as adsorbent dosage, contact time, initial arsenite concentration, adsorbent particle size, etc. on the removal of arsenite from water. Results show that the kinetic rate of As(III) adsorption was high in the first 30 minutes and slows thereafter. The maximum achieved removal efficiency of As(III) was 98.8% using an adsorbent dosage of 2.1 g/L in 1.5 hours of contact time. Freundlich isotherm better described the adsorption process, which indicates that the multilayer adsorption should be involved in the process of As(III) removal. Commercial TiO_2 had high adsorption capacity for As(III) removal under natural conditions of pH 8 at room temperature (26±1ºC).

Keywords: Adsorption, water, arsenic, titanium oxide.

2. Introduction

Arsenic is found in low quantities as part of the geological background of several aquifers. However, sometimes these arsenic concentrations are high enough to cause harmful effects in humans. Cases of millions of affected people have been studied and documented in many parts of the world such as Bangladesh (0.25-1600 µg/L), India (50-23800 µg/L), Taiwan (10-1800 µg/L), Mexico (1-160 µg/L), USA (2600 µg/L) (Lillo, 2000). The US Environmental Protection Agency (EPA, 2003) and the World Health Organization (OMS, 2004) established a limit concentration of 10 µg/L total As in water as a recommendable limit. In Mexico, the maximum concentration of total As in water for human consumption is 25 µg/L (NOM-127, 1994). The removal of As (III) through adsorption processes using TiO_2 has been widely documented and has shown to be highly efficient. The objective of this study is to determine adsorption capability of arsenite by TiO_2.

3. Materials and Methods

As(III) stock solution (100 µg/L) was prepared using sodium arsenite ($NaAsO_2$, 100%) (Fisher laboratories). The salt was diluted in water, which comes from underground water wells in Chihuahua City. The total As concentration of this water was 20 µg/L. The adsorbent was provided by Degussa México, S.A.
Different amounts of TiO_2 were mixed with the As(III) solution using jar test equipment. TiO_2 amounts ranged from 0.1 to 2.1 g/L and were constantly agitated at 150 rpm (Maiti et al., 2007) for 3 hours. The influence of stirring on the adsorption processes was determined for 100, 150 and 200 rpm. The solution was precipitated, filtered and digested, and then the As was quantified. The analysis was conducted under room temperature (26±1ºC) and neutral water pH.
The surface area was determined by the Brunauer-Teller (BET) method using Quantachrome Corporation equipment. The absorbent crystal structure was determined using Phillips x-ray diffraction equipment (model X'Pert), and the elemental analysis and particle size was conducted using a Phillips transmission electron microscope (TEM), model CM-200. As concentrations were determined using a GBC atomic absorption spectrophotometer with Hydride generation (model Avanta Sigma).

4. Results and Discussion

4.1 Characterization of adsorbent

The specific surface area was 55.24 m^2/g. It was a non-porous material (isotherm type II) according to the BET isotherm classification (Gregg et al., 1967). The X-Ray diffraction analysis shows that the adsorbent contains 78.9% of anatase and 21.1% of rutilo. The Transmition Electron Microscope (TEM) shows the inorganic composition of the material: Ti (61.4%) and O (38.6%) (Fig. 1a). The micrographs were taken at 38 Kx (Fig.1b) and 6.6 Kx (Fig.1c) magnifications. In both cases, the micrographs show nonporous particles with almost homogeneous sizes (nearly 30 nm).

Element	Unit	Quantity
Ti	%	61.40
O	%	38.60
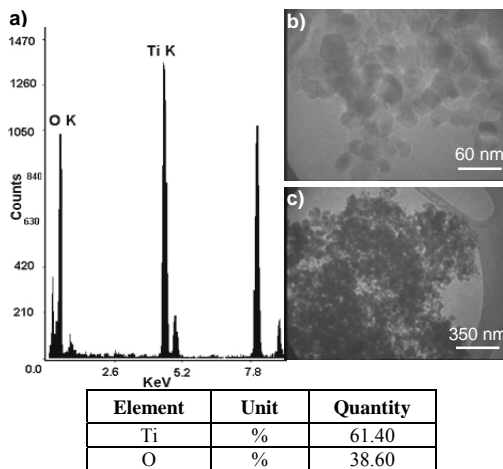
Figure 1: *a) TiO$_2$ EDS (kx 38). b) Micrographs at kx 38 and c) kx 6.6*

4.2 As (III) removal efficiency

Arsenic removal (%) for different retention times and TiO$_2$ are presented in Figure 2. From the figure it is evident that uptake of As(III) by TiO$_2$ increases rapidly in the first 30 minutes and slows thereafter. The initial increase in the adsorption rate may be attributed to the fact that more surface area is available for arsenic uptake. Further increments of adsorbent dose represent minimal increases in removal efficiency due to decrease of the active sites of adsorbate. After one hour the adsorbent is saturated and the system reaches equilibrium. The equilibrium time is independent of adsorbent dose. 98.8% of As(III) was removed during the first 1.5 hours using 2.1 g/L of adsorbent dose. For 1.7 g/L and 36 minutes or 1.5 g/L and 54 minutes, water with concentrations lower than 10 μg/L were also obtained. The As removal efficiency using small amounts of TiO$_2$ (0.1-0.5 g/L) is low (Fig. 2). Similar results are reported by S. Bang (2005).
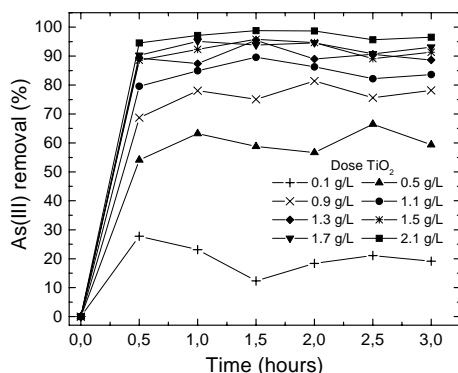
Figure 2: *As(III) removal efficiency (Co: 120 μg/L, pH: 8.0, time: 3 h, agitation: 150 rpm, Temp: 26±1ºC)*

4.3 Effect of stirring speed

The effects of the stirring velocity (rpm) on the arsenic adsorption by TiO$_2$ are presented in Figure 3. It was observed during the experiment that at 200 rpm the removal of arsenic was very low. This is likely the adsorbent-adsorbate interaction was destabilized by the high turbulence. On the other hand, the efficiencies achieved with 100 and 150 rpm are quite similar; however, 100 rpm is not enough to keep 100% of the TiO$_2$ particles in suspension as an homogeneus mixture. The optimum stirring was 105 rpm for obtained water with concentrations lower than 10 μg/L.

Figure 3: *Three-dimensional surface (concentration vs agitation vs time) by Minitab 15 Statistical Software*

4.4 Adsorption isotherms

The four most common models to describe adsorption process are the isotherms of Langmuir, Freundlich, BET and Dubinin Rasdushkevich (DR). Experimental results fit well with the Freundlich equation (Fig.4). It indicates heterogeneity of the surface (stronger and weaker binding sites for adsorption). From DR isotherm analysis the adsorption mechanism can be explained by the physisorption process.

$$\text{Ln } q_e = -0.3346 + 0.4949 \text{ Ln C}$$
$$R^2 = 0.991$$
$$SD = 0.075$$
$$q_e = 0.716 \, C^{0.49}$$
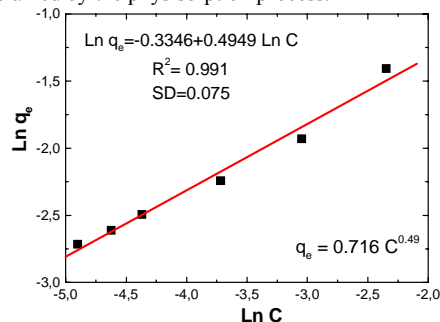
Figure 4: *Freundlich isotherm plot (Co: 120 μg/L, pH: 8.0, dose:0.1 to 1.7 g/L, rpm: 150 and T: 25±2ºC)*

5. Conclusions

This study indicates that the TiO$_2$ is a highly effective adsorbent for the removal of As(III). The characterization showed that the TiO$_2$ is a non-porous material with a surface area 55.24 m^2/g. The conditions for optimum removal (98.8%) were 1.5 hours and 2.1 g/L. For 1.2, 1.3, 1.5, 1.7 g/L adsorbent dose and 1.5, 1.2, 0.9, 0.6 hours of agitation respectively, achieved water quality required by international regulations (<10 μg/L As(III)). The optimum stirring speed was 105 rpm. The experimental results fit well with the Freundlich equation. According to DR isotherm the adsorption mechanism can be explained by physisorption process.

6. References

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