Synthesis and characterization of imogolite from cement kiln dust: Potential use as arsenite adsorbent

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Imogolite (Imo) belongs to the family of the nanotubular metal oxides which are considered to be essential for nanotechnology as a building block with potential application in molecular separation, molecular storage, as functional filler and in catalysis (Gelli et al. 2018). The Imo synthesis use natural sources containing Si of high purity such as sodium silicate and tetraethyl orthosilicate. In 2013, husk fly ash (SiO2 > 96%) was successfully utilized for Imo synthesis (Hongo et al 2013). However, research about the synthesis of Imo from residues with low content of SiO2 has not been performed, up to date, which implies a challenge, given the chemical restrictions that characterize the Imo (Arancibia-Miranda et al 2013). Industrial residues are highly available and low-cost sources of silica (Yan et al 2016). Their reuse allows interesting applications in adsorption and catalytic processes with a higher valorization degree. The reuse of cement kiln dust (CKD) comprises up to a 67% in developed countries such as USA (Kunal and Siddique, 2012), where as in Chile 100% of CKD is disposed. Therefore, significant efforts could be invested in finding meaningful reuses for Chilean industry. In special for the Chilean mining industry, which present difficulties to meet environmental regulation regarding arsenic in effluents.

In the present study, it is proposed the synthesis and characterization of imogolite from CKD (Imo-CKD) and their potential application as adsorbent for arsenite. Moreover, results from characterization and arsenite adsorption with Imo-CKD were compared with the characterization and arsenite adsorption of imogolite synthesized from tetraethyl orthosilicate (Imo). Chemical characterization of CKD was performed after a method proposed by Querol et al (1995). The major elements were determined by means of inductively coupled plasma atomic emission spectrometry (ICP-AES). Mineralogical characterization of CKD and imogolite samples was performed by means of X-ray diffractometer (Bruker, D8 Advance model). The morphology of CKD was observed by a scanning electron microscope (SEM-EDX, JEOL6400), whereas imogolite samples were observed, with a Zeiss EM 910 transmission electron microscope. FT-IR spectrum of CKD and imogolites was obtained by using an infrared spectrometer Bruker Tensor 27 with Fourier transformation. The AsO33− adsorption experiments were carried out at initial pH of 7.0 using NaCl as support electrolyte and 20 mg of imogolite samples at 300 rpm. The kinetic experiment was performed at 298 K, whereas the isotherm experiments were performed at 298, 300 and 315 K. After filtration and centrifugation, the concentration of AsO33− in solution was determined by means of ICP-AES. For the kinetic experiments, data were fitted to pseudo-first order and –second order (PSO) kinetic models. In case of sorption isotherms, experimental data was analyzed by the Langmuir, Freundlich and Langmuir-Freundlich models.

The results of the chemical characterization indicate a varied chemical composition of CKD with a silica content about 12%, which is also detected by XRD and SEM-EDX. It was detected a high content of Ca and K in CKD (~ 47%) that could be undesirable for the synthesis of Imo-CKD. Several authors have observed that they cause the inhibition or distortion in the geometry of the different precursory structures of the imogolite, due to the changes in the dissociation of the =Si-OH groups, retarding the one-dimensional growth of the nanotube and also favoring the increase of by-products such as allophane, (Abidin et al 2007; McBride et al 1984). XRD patterns of imogolites show characteristics of short-range order para-crystalline materials. In both imogolites is detected broad diffraction peaks occurred predominantly as a consequence of its bundled structure. The XRD pattern for Imo indicates four diffraction bands centered in 21.0, 12.0, 3.4 y 2.2 Å, characteristic signals associated to this nanotube (Zanzotttera et al 2012). Similar diffraction bands are detected in Imo-CKD but with lower intensity; phenomenon provoked by the presence of by-products. Similar behavior for both imogolites was observed in FT-IR. In Figure 1 are shown TEM images from imogolites. Both images show nanotubes highly condensed with the typical nanotubes form of a spiderweb-like structure. The large of nanotubes for Imo-CKD overcome 500 nm whereas for Imo were around 200 nm. It is also detected the presence of amorphous particles mainly attributed to allophane particles.

The adsorption of arsenite onto Imo and Imo-CKD was fast, reaching an equilibrium time between 12 and 20 min, respectively. Experimental data were analyzed with PFO and PSO kinetic models. The best fit corresponded to PSO model with a value of $r^2 > 0.99$, suggesting chemisorption. Imo-CKD showed a slightly higher removal capacity of AsO33− possible associated with the presence of by-products, while the adsorption rate of AsO33−was higher using Imo, phenomena that could be attributed to the homogeneity of surface sites =Al-OH.
Both imogolites presented isotherm sorption curves of type L (Figure 2) which indicates a good affinity between the substrate and the analyte. The experimental data showed the best fit with the Langmuir-Freundlich model with $r^2 > 0.990$, suggesting that the adsorption of arsenite occurs as a multi-layer phenomenon in systems with more homogeneous sites, associated mainly to the predominance of functional groups of the aluminum type in the external surface of the imogolite samples. Furthermore, it was observed that the parameter of Imo-CKD was significantly higher than for Imo, which could be associated with the presence of byproducts like allophane that contributes to a greater diversity of adsorption sites. The heterogeneity index ($m$) of Langmuir-Freundlich model for both samples was < 1, indicating that the materials have predominantly homogeneous sites.

References

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