Evaluation of the removal capacity for antimony(V) by illite via adsorption

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INTRODUCTION

Antimony (Sb) is a potentially toxic element, being considered a priority pollutant. It is emitted to the environment by natural (weathering of rocks and volcanic activities) and anthropogenic (mining/metallurgical activities, energy production from fossil fuels, pigment production, ceramic/glass manufacture, shooting practices, road traffic, and waste incineration and disposal) sources. These latter are the main responsible for environmental pollution by Sb (Tang et al., 2023). Particularly, the exploitation of Sb ore deposits is regarded as its primary anthropogenic source (Guo et al., 2014). Stibnite (Sb_2S_3) is the main profitable ore of Sb. This mineral readily dissolves under atmospheric conditions, releasing Sb. Different stibnite weathering products can attenuate its spread into the environment, with Sb oxides, iron antimonates, and calcium antimonates being its most efficient sinks. Additionally, iron (oxyhydr)oxides and iron (oxy)hydroxy sulfates commonly present in mine scenarios also importantly scavenge this element. Recently, it has been indicated that clays can also play a significant role in the immobilization of Sb in polluted clayey soils and wastes (Drahota et al., 2023). Of clay minerals, illite is the most abundant in Earth's upper crustal environments and particularly is also one of the most found clays in soils (Warr, 2022), predominating in soils of arid and high-latitude regions (Ito & Wagai, 2017). Illite is a dioctahedral, potassium-deficient mica-like mineral having a non-expandable 10-Å c-spacing. This clay has a variable charge due to edge sites and un-completed bonds of approximately 5 meq/100 g, contributing considerable to its cation exchange capacity (Meunier & Velde, 2004). These variable charge positions can also act as adsorption sites for anionic species such as $[Sb(OH)_6]^-$, which is the soluble form of Sb(V) under a wide pH range. The main objective of this work was to establish the removal capacity for Sb(V) by illite via adsorption to assess its potential contribution to sequester Sb in areas impacted by mining activities.

MATERIALS AND METHODS

An illite sample from Ariño (Teruel, Spain), supplied by the MYTA, SA Company (SAMCA Group), was employed in this study. This mineral sample was characterized to determine its mineralogical composition, specific surface area (SSA), and cation exchange capacity (CEC). The mineralogical composition was determined by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer, the SSA was analyzed by the single point method using a Micromeritics Flow Sorb II 2300 analyzer, and the CEC was determined by the ammonium acetate method. Batch adsorption studies to establish the adsorption isotherms of Sb(V) on the illite sample were performed in polypropylene flasks (50 mL) by subjecting an illite sample dose of 10 g/L to an interaction period of 48 h with Sb(V) solutions of different concentration (1-35 mg/L) adjusted to pH 8. These adsorption studies were performed in absence and presence of ammonium sulfate (0.5 M). The interaction period was carried out on a rotary shaker in a thermostatic chamber set at 22 °C. After the interaction period, the adsorbent was separated using a centrifugation step (4000 rpm) over 10 min and Sb was analyzed in the obtained supernatants by inductively coupled plasma-atomic emission spectrometry using a Varian 720-ES instrument.

RESULTS AND DISCUSSION

As determined by XRD, the illite sample was composed of illite, quartz, chlorite, plagioclase, and K-feldspar. Its SSA and CEC showed values of 40 m^2/g and 20.2 meq/100 g, respectively. The adsorption isotherms obtained for the removal of Sb(V) by the illite sample are shown in Fig. 1.
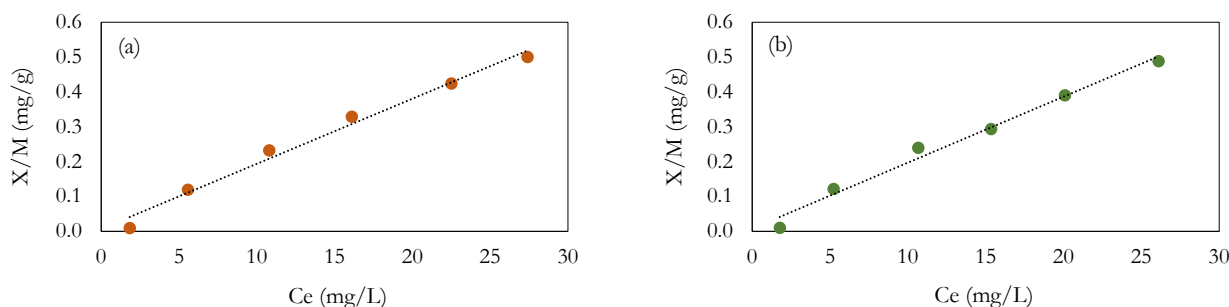
Fig 1. *Adsorption isotherms for the removal of Sb(V) by illite: (a) absence of sulfate and (b) presence of sulfate.*

According to the classification of Giles et al. (1960), the isotherms for the adsorption of Sb(V) on the illite sample at the studied Sb(V) concentration range are C-type (constant partitioning). A lineal partitioning was produced between the equilibrium concentrations (Ce) of Sb(V) in solution and the Sb(V) amounts (X/M) removed by the illite sample in both absence and presence of sulfate [R^2 = 0.9856 (p < 0.001) and R^2 = 0.9850 (p < 0.001), respectively]. This isotherm type is characteristic of substances removed at relatively quite low levels. The distribution coefficient (Kd) [Kd = (X/M)/Ce] for both isotherms showed a value of 0.019 L/g. The maximum adsorption capacity attained by the illite sample at the studied Sb(V) concentration range exhibited values of 0.500 mg/g in absence of sulfate and 0.489 mg/g in presence of sulfate. Similar Sb(V) adsorption capacities were found in both circumstances. Therefore, sulfate seems not to compete effectively with Sb(V) for adsorption sites on illite, indicating that this clay could tightly bind Sb(V). Accordingly, illite may successfully sequester Sb(V) in mining areas impacted by the weathering of sulfidic mine wastes, where sulfate is a ubiquitous anion. Sulfate has been found to be mostly removed on variable charge minerals such as aluminum oxides by the formation of outer-sphere complexes (Wijnja & Schulthess, 2000), whereas Sb(V) is mostly adsorbed on these phases and on clays such as kaolinite by the formation of inner-sphere complexes (Ilgen & Trainor, 2012). The different binding strength found in the adsorption of sulfate and Sb(V) on these phases makes Sb(V) outcompetes for their variable charge sites.

ACKNOWLEDGMENTS

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