Toxicity and biosorption responses to arsenite (As[III]) were examined in a 96-h exposure study using Scenedesmus quadricauda, one of the most popular green algae distributed in freshwaters in China. Results indicated that the pH-dependent distribution of two arsenite species (H2AsO3(-) and H3AsO3) played an important role in biosorption and toxicity. The undissociated H3AsO3 was more toxic than its monoanionic H2AsO3(-) through comparison of algal cell numbers, chlorophyll-a contents, and algal ultrastructural changes observed with transmission electron microscopy. An effective biosorption of 89.0mgg(-1) at 100mgL(-1) As[III] was found in the treatments with an initial pH of 9.3 and 25.2µgg(-1) at 0.03mgL(-1) As[III] at an initial pH of 8.2 as a result of the predominant species of H2AsO3(-) under the ambient pH and Eh conditions. Our results imply that S. quadricauda may provide a new means for the removal of toxic arsenite species present in contaminated surface water.