The potential of porous diatom silica shells as a naturally abundant low-cost sorbent for the removal of arsenic in aqueous solutions was investigated in a batch study. The objective of this work was to chemically modify the silica shells of a diatom *Melosira sp*. with bifunctional (thiol and amino) groups to effectively remove arsenic in its toxic As(III) form (arsenite) predominant in the aquatic environment. Sorption experiments with this novel sorbent were conducted under varying conditions of pH, time, dosage, and As(III) concentration. A maximum adsorption capacity of 10.99 mg g^{-1} was achieved within 26 h for a solution containing 12 mg L^{-1} As(III) at pH 4 and sorbent dosage of 2 g L^{-1}. The functionalized diatom silica shells had a surface morphological change which was accompanied by increased pore size at the expense of reduced specific surface area and total pore volume. As(III) adsorption was best fitted with the Langmuir-Freundlich model, and the adsorption kinetic data using pore surface diffusion model showed that both the external (film) and internal (intraparticle) diffusion can be rate-determining for As(III) adsorption. Fourier transform infrared spectroscopy (FTIR) indicated that the thiol and amino groups potentially responsible for As(III) adsorption were grafted on the surface of diatom silica shells. X-ray photoelectron spectroscopy (XPS) further verified that this unique sorbent proceeded via a chemisorption mechanism through the exchange between oxygen-containing groups of neutral As(III) and thiol groups, and through the surface complexation between As(III) and protonated nitrogen and hydroxyl groups. Results indicate that this functionalized bioadsorbent with a high As(III) adsorption capacity holds promise for the treatment of As(III) containing wastewater.