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ORIGINAL PAPER

Bulgarian natural diatomites: modification and characterization

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Natural Bulgarian diatomite modified by oxidation with sulfuric acid and H_2O_2 or by coating with manganese oxide was characterized considering its chemical composition, surface area, pore volume, and structure. Modified diatomites displayed larger surface area and pore volumes in comparison with untreated natural diatomite, which favored their sorption behavior. Sorption properties of diatomites towards Fe^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Pd^{2+}, Ca^{2+}, and Mg^{2+} were investigated and their sorption capacities were determined. Sorption properties of manganese oxide-modified diatomite were superior to those of diatomite modified by oxidation. Owing to its high sorption capacity towards Co^{2+}, Ni^{2+}, Pb^{2+}, Cr^{3+}, Fe^{2+}, Cu^{2+}, and Cd^{2+}, the manganese oxide-modified diatomite is a promising low-cost sorbent for selective removal of milligram amounts of these toxic metal ions from contaminated water.

Keywords: natural diatomites, modification, adsorption, toxic metal ions

Introduction

In recent years, contamination of ground and surface water with heavy metals has become a major concern. Heavy metal ions like Fe^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Tl^{+}, Mn^{2+}, Cr^{3+}, Ni^{2+}, and Co^{2+} are not biodegradable and they tend to accumulate in living organisms causing various diseases and disorders (Bailey et al., 1999). In literature, many treatment processes for the removal of heavy metal ions from waters and wastewaters have been proposed, e.g., chemical precipitation, membrane filtration, ion exchange, coagulation, adsorption, etc. Adsorption is considered to be a particularly competitive and effective process for the removal of trace quantities of heavy metal ions from different kinds of water. Interest in using low-cost materials for adsorption of heavy metal ions has increased. Generally, solid materials with microporous structure can be used as adsorbents, e.g., activated carbon, clays, iron oxides, synthetic and natural zeolites, molecular sieves, etc. The most important properties of an adsorbent are its surface area and structure. Activated carbons are, however, not suitable to be used in large scale due to their high production and regeneration costs. Alternative low-cost materials like clays and activated peats have been tested as potential sorbents for the removal of heavy metal pollutants from water (Babel & Kurniawan, 2003; Bhattacharyya & Gupta, 2008; Puanngam & Unob, 2008; Boevski et al., 2011).

Acid activation of a clay mineral is a common chemical modification approach enhancing its adsorption capacity and providing it with properties suitable for the desired applications (Kooli & Jones, 1997). Acid activators including sulfuric acid, phosphoric acid, hydrochloric acid, nitric acid, and acetic acid were used to modify diatomites for the removal of organic residues and to chemically create finer pores (Tsai et al., 2004).

Due to its high surface charge, hydrous manganese dioxide effectively scavenges metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} from aqueous solutions (Tripathy et al., 2006). Moore and Reid (1973) showed that MnO_2-impregnated acrylic fibers effectively remove radium from natural waters. Sagara et

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