

Hydrothermal Alteration of Diatomite for Removal of Aqueous Cu^{2+} , Pb^{2+} , and Zn^{2+}

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Natural unconsolidated diatomite was hydrothermally treated with a strong alkaline solution (1 M KOH) containing 22 mM of Al at 100 and 125 °C and for up to 64 d to obtain high-value material for cation removal from aqueous solution. At reaction times of 2 and 1 d, respectively, the zeolite merlinoite is formed by building bundle-like aggregates. However already at 0.25 d coupled dissolution and precipitation yield in an intermediate amorphous potassium-rich aluminosilica phase, most conspicuous as 20 to 2000 nm-sized spherules. TEM-SAED and -EDX analyses confirm its amorphous character and indicate a chemical composition from 45 to 66 wt-% of SiO_2 , 22 to 41 wt-% of Al_2O_3 and 5 to 17 wt-% of K_2O . Although zeolitization of diatoms has already been conducted (e.g. Du et al., 2011) such an intermediate phase has not yet been observed.

Cation ion removal capacities of the reaction products versus unaltered diatomite were studied by using a synthetic Cu^{2+} , Pb^{2+} and Zn^{2+} solution (each 500 μM ; pH 5) and a mine drainage solution from a carbonate-hosted lead-zinc deposit (0.48 μM of Pb^{2+} , 17 μM of Zn^{2+} ; pH 8) at 25°C. All alteration products display significantly higher cation removal capacities compared to the unaltered diatomite. Interestingly the presence of the intermediate phase results in highest cation removal capacities up to 99.9 % without a significant cation selectivity (bulk specific surface area: 30 - 40 m^2g^{-1}). Selectivity for cation removal in the order of $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ is stimulated by the occurrence of merlinoite (bulk specific surface area: 15 - 20 m^2g^{-1}), where removal capacities are low compared to alteration products with dominance of the intermediate phase. Selectivity behaviour can be explained by competing ion exchange of merlinoite. In contrast more efficient, but non-selective cation removal is obtained by less intensely altered diatomite with high specific surface areas which contains the intermediate phase. Thus bio-opal in terms of frequently occurring diatomite can be immediately and efficiently transformed to a highly active composite material for cation removal from aqueous solution. Tailoring issues are referred to the formation of intermediate phases versus zeolites and the apparent hierarchical micro- to nanostructures.

Reference:

Du, Y.; Shi, S.; Dai, H. (2011): Water-bathing synthesis of high-surface-area from diatomite. *Particuology*. 9 (2). 174 – 178.