Removal of Hg(II) by natural zeolite

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Natural zeolite will be more widely considered for roles in environmental clean-up processes-especially those involving radioisotopes and heavy metals (Dyer, 1995). The limited data are also available for mercury ion exchange with the clinoptilolite in terms of equilibrium isotherms and kinetics using radiochemical analysis with 203Hg and 22Na as a radiotracer. (Misaelides et.al., 1994).

Modified natural zeolite with sodium produced a cation exchangeable material which has been tested for the ability to remove Hg(II) from aqueous solution with nitric acid using a flow injection mercury system (FIMS 400). The amounts of adsorption depend mostly on contact time, acid concentration of aqueous solution and initial mercury concentration, mixed cation of mercury and its subgroup elements. The study of the kinetics of mercury uptake revealed that all sorbents exhibit a fast rate of sorption. The highest sorption capacities were observed for the sodium forms (TSA-Na, TEC-Na, TUS-Na) and were up to 5 timer higher than for the natural zeolite (TSA, TEC, TUS).

The maximum sorption capacity toward mercury is determined as 0,09286 µg/g at an initial concentration of 10µg/L for TSA-Na. The sorption of Hg (II) has an ion-exchange nature and consists of three stages, i.e., the adsorption on the surface of microcrystals, the inversion stage, and the ion exchange in the interior of the microcrystal. Sorption capacity decreases with the increase of mercury concentration. The presence of other metal ions such as Cd(II), Cu(II), Ni(II) and Zn(II) increases Hg(II) uptake capacity. Finally, sorption for Hg(II) was investigated in batch systems to evaluate the short-term stability of the sorption properties.

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Pyrrhotite oxidation in weakly acidic solutions

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The kinetics and mechanism of pyrrhotite (for simplicity noted FeS) oxidation by dissolved oxygen was investigated in weakly acidic solutions as a function of pH (2.75 to 3.45) and temperature (25 to 45°C). The changes in Eh, pH and total dissolved iron were monitored to quantify the reaction progress. Additionally, Fourier transform infrared spectroscopy (FTIR) was used to characterize the oxidation products of FeS.

The experimental results demonstrate the importance of temperature and initial pH for the FeS oxidative dissolution. The amounts of dissolved iron (n_{Fe}) and removed H^+ (n_H) increase with temperature and initial $[H^+]$. The activation energy of FeS oxidative dissolution is 41.6 ± 10.7 kJ mol^{-1} at initial pH=3.00 suggesting that the kinetic regime is controlled by a mix of diffusion and surface reaction (De Guidici *et al.*, 2005). It was found that the reaction order of oxidative dissolution of FeS is 1.03 ± 0.02 (25°C) with respect to initial $[H^+]$.

FTIR spectroscopy indicated the presence of several sulfur species (S^0, S_n^{2-}, $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-}) and ferric hydroxides or oxyhydroxide ($Fe(OH)_3$ and goethite) on residual FeS surface.

It is important to note that the experimental ratios of n_H over n_{Fe} (n_H:n_{Fe}) observed at 25°C decrease over a first period of time (0-4 h) of FeS oxidative dissolution from 7.97 down to 2.01. Afterwards, the n_H:n_{Fe} ratio becomes lower than 2 and remains roughly constant (4-72 h). At higher temperatures (35 and 45°C) and pH 3.00, $n_H:n_{Fe} < 2$ and is quasi-invariant over the reaction time.

The experimental observations suggest a mechanism based on the protonation of FeS surface (Chirita and Descostes, 2006) followed by oxidation of FeS by dissolved oxygen to produce Fe^{2+}, S^0 and S_n^{2-}. Fe^{2+} is unstable in oxidative conditions (Descostes *et al.*, 2002) and transforms into $Fe(OH)_{3(s)}$ and goethite after approximately 30 h of reaction.

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