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AN ORIGINAL THERMODYNAMIC ASSESSMENT OF WASTEWATER COMPOSITION IN TANNERY OPERATIONS

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Introduction

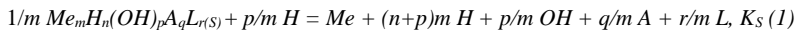
Water quality is essential for human prosperity. However, rapid population growth and intense industrialization lead to the continuous release of various pollutants into water sources. Unsafe water contributes to over 1.2 million deaths annually, while approximately 2 billion people lack access to safe drinking water. Tannery production, characterized by high water consumption, generates significant volumes of wastewater containing chromium, arsenic, heavy metals, organic dyes, sulphides, chlorides, tannins, and solvents. Due to the diverse composition of tannery effluents, a singular method often fails to effectively reduce pollutant levels, resulting in adverse environmental impacts. Speciation of heavy metals within these complex systems further leads to increased environmental and industrial concerns.

A novel thermodynamic methodology has been utilized to analyze intricate chemical equilibria within heterogeneous systems under experimental settings. This approach involves a comprehensive thermodynamic assessment of conditions governing diverse processes in wastewater from tannery production, based on global thermodynamic characteristics. Additionally, a thermodynamic analysis of wastewater chemical composition has been conducted to delineate the speciation of heavy metal ions.

Materials and methods

The analysis of heavy metal speciation in both solid and liquid phases (wastewater), involves the examination of metal species distribution in two-phase systems. To accomplish this, the thermodynamic method developed earlier has been employed. Within this framework, diagrams depicting heterogeneous chemical equilibria are utilized to represent complex equilibria and the distribution of soluble and insoluble species within the studied systems. This method integrates thermodynamic principles with original mass balance constraints that explicitly consider solid phases. The diagrams developed herein, illustrating the variation of global Gibbs energy as a function of pH, $\Delta G(pH)_{Ci}$, facilitate the straightforward identification of solid phase stability areas based on the initial composition of multicomponent systems. In the present study, various minerals with a general formula $Me_mH_n(OH)_pA_qL_r(S)$, representing insoluble heavy metal species, have been

examined. Their solubility is influenced by the dissolution-precipitation equilibrium described below:



The charges of species are omitted for simplicity. In this formula, *A* and *L* represent two inorganic ligands, such as ammonium and phosphate ions in the slightly soluble mixed salt struvite $MgNH_4PO_4 \cdot H_2O(s)$. The general formula also encompasses the formation of minerals such as metal hydroxides $Me(OH)_n(s)$, mixed salts like hydroxyapatite $Ca_5(PO_4)_3OH(s)$, monetite $CaHPO_4(s)$, etc. To compare the total Gibbs energy values for different minerals, equation (1) references one mole of heavy metal *Me*. The total Gibbs energy values (ΔG) for the analyzed processes are derived from the expression:

$$\Delta G = -RT \ln \frac{C_{Me}^r}{C_{Me}^0} - \frac{q}{m} RT \ln \frac{C_A^r}{C_A^0} - \frac{r}{m} RT \ln \frac{C_L^r}{C_L^0} \quad (2)$$

For this equation, the solid phase is stable when the condition $\Delta G > 0$ is met. The value $\Delta G = 0$ corresponds to the initiation of dissolution/precipitation of the solid phase. In these equations, C_i^0 represents the total concentration of the "i" species in the heterogeneous mixture, and C_i^r is its residual concentration in solution, respectively.

Results and conclusions

Our analysis indicates that, under experimental conditions, iron ions exist solely in insoluble forms, whereas other metal ions are present in soluble forms. Using thermodynamic data pertinent to relevant species, the study investigates the thermodynamic stability areas of solid phases and the distribution of soluble and insoluble chemical species concerning solution pH and varying total reagent concentrations in the investigated mixtures. The mobility of metal species is evidently influenced by the characteristics of solid phases and environmental parameters. The thermodynamic examination of complex chemical equilibria within the analyzed mixtures reveals that, due to the extremely low concentrations of the investigated metal ions, except for iron, and minimal concentrations of inorganic ligands, except for sulfate, the formation of solid phases such as hydroxides, neutral, or mixed salts is negligible. Calculation results from the distribution diagram for Fe^{3+} insoluble species indicate that iron phosphate predominates up to pH 6.4. In the pH range of 6.4 to 7.2, both insoluble iron phosphate and hydroxide coexist. Beyond pH 7.2, the solid phase consists solely of iron hydroxide.

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