



## REVERSE IRON ORE FLOTATION ADSORPTION MECHANISM UNVAILED BY MOLECULAR DYNAMICS

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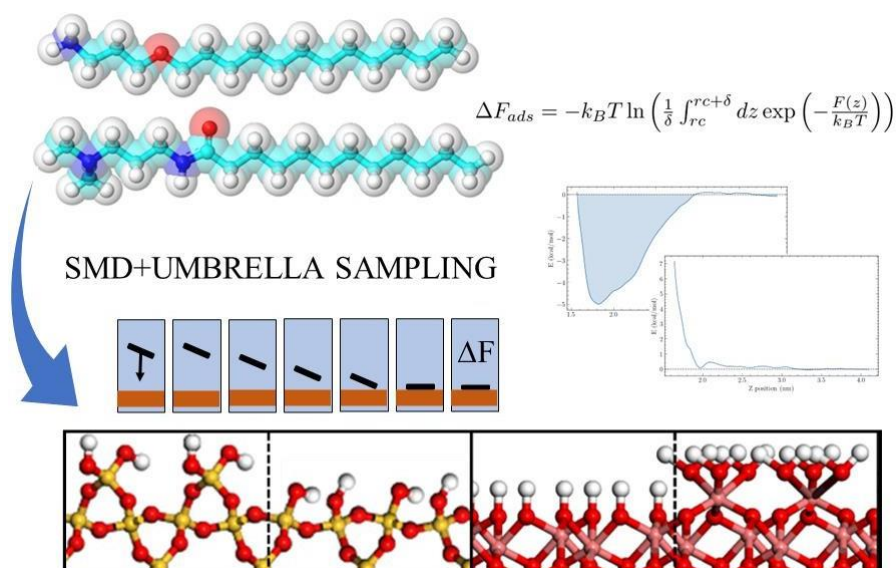
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### GRAPHICAL ABSTRACT



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One common approach for concentrating iron ores by flotation is the reverse flotation of quartz using cationic collectors. The polar head of the collector and the mineral surface interact electrostatically to drive the adsorption mechanism that drives the gangue's cationic flotation. Depressants are still needed to hinder the iron-containing minerals flotation, for example, polysaccharides are used in processes involving quartz and hematite to attain selectivity. Fatty amines were the first developed and applied collectors, and with the passing of time, etheramines and other variants were tested and proved to be more efficient. Reverse cationic flotation has not shown little appreciable progress since it was first used in iron ore facilities. Thus, designing new collectors with high adsorption energy with gangue minerals and weak



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interactions with iron-containing minerals is an important goal of the mineral industry. In this work, we compute adsorption free energies (FE) between some mineral surfaces with etheramine and a proposed collector (amidoamine) using Molecular Dynamics (MD) techniques. The changes in selectivity were discussed then. Four structures, namely amidoamine (N-[3-(dimethylamino)propyl]dodecanamide), etheramine (3-dodecoxypropan-1-amine), and their protonated counterparts, were modeled with OPLS-FF. The behavior of mineral surfaces, including Hematite, Quartz, Gibbsite, and both terminations of Kaolinite (siloxanes and aluminols), was described using Clay-FF. The entire system was solvated with SPC/E water. Using Packmol, we constructed a system consisting of 1 mineral-1 collector, solvated with water. Subsequently, Steered Molecular Dynamics (SMD) simulation was employed to vary the distance between the surface and collector. The positions were then obtained for use in the Umbrella Sampling (US) simulation windows (set of points along the coordinate  $z$ ). Near the surface the windows were more closely spaced ( $0.2 \text{ \AA}$ ) and far from it the spacing was increased to  $0.5 \text{ \AA}$ . We used the Weighted Histogram Analysis Method (WHAM) to obtain free energy profiles (PMFs).

The determination of adsorption FE involves the difference between the energies associated with the bonded and non-bonded states. These energies are tied to the equilibrium constant of the adsorption processes. Using Statistical mechanics, researches reports connections between the PMFs from MD simulations and the free energy. The standard method for computing FE typically involves aligning non-bonded energies in the PMF with 0. Subsequently we applied a Boltzmann distribution-weighted integral, considering only the negative values of the PMF.

This choice allows for a more complete assessment of the sampling achieved through the US. After obtaining the energy values, we identified two distinct groups. The first group displayed low or negligible adsorption-favorable energy and included Hematite, Goethite, Gibbsite, and Aluminol surfaces of Kaolinite, the energies were more significant when ionized etheramine was applied. Conversely, Quartz and Siloxane surfaces of Kaolinite exhibited favorable adsorption energies. It's important to note that Gibbsite and Aluminol surfaces of Kaolinite are part of the gangue, and their low adsorption values contribute to decreasing the iron concentration in the final product. Various mechanisms drive adsorption, with surface chemistry exerting a significant influence on many of them, water structuring stands out among them. In the low energetic group, a notable observation was a substantial barrier in the PMFs. This barrier is linked to adsorbed water on the surface, hindering effective collector interactions.

A notable finding is the fine contrast in the interactions of protonated etheramine and amidoamine within the low energetic group. While both exhibit enhanced interactions due to charges, etheramine demonstrates higher favorability. In summary, we could access the FE through MD. The affinity of amine-based collectors with quartz and siloxane from kaolinite mirrors the behavior observed in reverse iron ore flotation. Upon comparing the two proposed collectors, it becomes evident that amidoamine could be a more efficient reagent. Some experimental data, already published, align with the theoretical results.

Keywords: Adsorption Free Energies, Iron Ore Flotation, Molecular Dynamics Simulation