Factors influencing the sorption of 3-ethylpyridine to Calcium Montmorillonite
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Pharmaceuticals, which commonly exist as charged organic compounds in the environment, are rapidly increasing in use. Humans have developed new pharmaceuticals to address the opioid epidemic, the coronavirus pandemic, and antibiotic resistant bacteria, most of which include allylic or heterocyclic amines. Use of these pharmaceuticals inevitably results in their introduction to the environment. Determining the environmental fate of these pharmaceuticals is important because the risk of a contaminant is a function of exposure and harm, and we cannot know the extent of exposure until we know how the chemical behaves in the environment.

Soils contain sites of positive and negative charge and can retain oppositely charged chemicals. Quantifying charged chemicals' sorption, defined as the extent to which the chemical is retained on soil, is important in determining a chemical's fate. Sorption can be quantified through the water-soil partitioning coefficient (K_d) which is the concentration of the chemical on soil (C_s) divided by the concentration in the water (C_w) at equilibrium ($K_d = C_s/C_w$).

Predictive models for the sorption of charge compounds are not well developed. Addressing this issue, MacKay and Vasudevan (2012) proposed the use of a probe compound to determine site density and the baseline driving force for sorption and scaling factors to adjust for differences in sorption affinity between the probe compound and the compound of interest. For cationic compounds, cation exchange, where an inorganic cation which occupies a negative site on soil, such as Ca^{2+}, is replaced by a positively charged amine, has been well established as the primary mechanism of sorption. For both heterocyclic and allylic amines, phenyltrimethylammonium (PTMA) has been identified as a good probe because it effectively models this cation exchange mechanism. However, there has been little comprehensive work done on the effect of structure on the sorption of heterocyclic aromatic amines (HAAs), such as pyridine and its derivatives.

Typically, compound sorption (C_s) increases with an increase in concentration in solution (C_w) and K_d can be understood as the slope of this relationship. In most cases, K_d does not change as C_w changes, which leads to a linear sorption isotherm. However, non-linearity in sorption isotherms has been observed for amines. This non-linearity can be concave down (K_d decreases with increasing C_w), concave up (K_d increases with increasing C_w), or both at different C_w ranges. In order to determine the effect of structure on heterocyclic aromatic amines, we must compare K_d's within the linear ranges (K_{dL}) of these chemicals' isotherms.

The sorption isotherms for 3-ethylpyridine (3EP) onto calcium montmorillonite (Ca-MMT) were measured at a soil loading of 0.5g/L with no background ions, 1.0g/L with no background ion, and 0.5g/L with a 5mM Ca^{2+} background ion concentration. Ca-MMT is a common aluminosilicate clay found in soils. It was found that the presence of Ca^{2+} as a background ion greatly decreases K_d and inhibits 3EP sorption, as the K_d's with a background ion are much lower than without a background ion (Fig. 1). Further, a concave up region, where K_d increases with increasing C_w, was observed when fewer than 10-13% of available sites were occupied, and when greater than about 13% of sites were occupied, a concave down region, where K_d decreases with increasing C_w, was observed for all parameters.

In future work, I hope to define a linear isotherm range and conduct sorption experiments to determine scaling factors for the addition of methyl and ethyl groups onto pyridines.
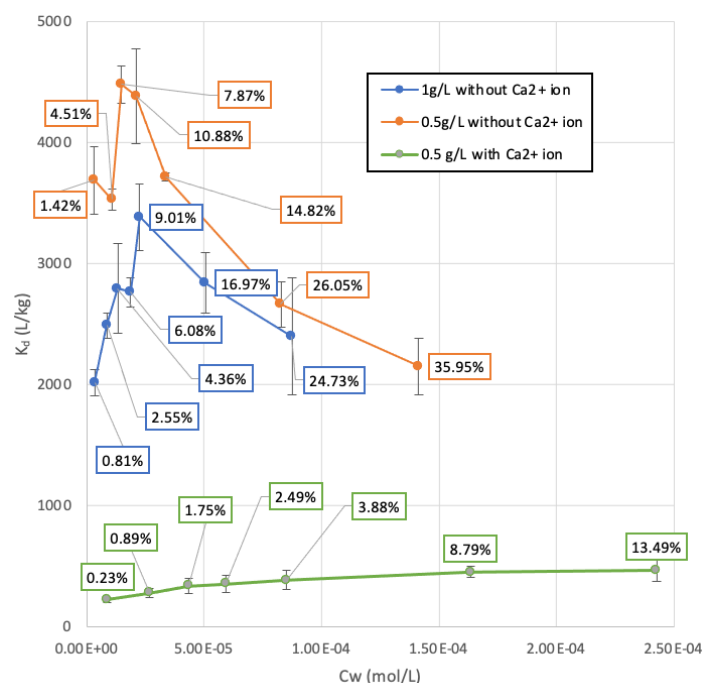
Figure 1: K_d vs. C_w for different parameters, with labels indicating the percent of available sites occupied at each C_w. This can be thought of as a graph of the slope of a C_s vs. C_w graph. The flatter the line here, the more linear the isotherm. Error bards show 95% confidence intervals.