## Depiction of the adsorption of Copper and Cadmium with Langmuir and Freundlich isotherms

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The solubility and bioavailability of heavy metals are directly dependent on soil characteristics (Krishnamurti et al., 1999), such as pH, redox potential, clay minerals, soil organic matter and calcium carbonate content (McLean & Bledsoe, 1992; Rieuwerts et al., 1998). The adsorption of metals is known to be directly proportional to the pH of the soil (Rieuwerts et al., 1998). The higher the pH of the soil, the higher the retention of heavy metal cations on the soil surface (Sposito, 2008; McBride, 1994; Sparks, 1995). However, not only the characteristics of the soil play a catalytic role in the adsorption process, but also the nature of the metals involved and the competitiveness between them are determining factors (Antoniadis et al., 2007). The isotherms that were used for the adsorption of heavy metals on solid surfaces, were Langmuir and Freundlich.

The Langmuir model has been used successfully to describe the adsorption behavior of many systems, such as the adsorption of non-polar gases on activated carbon and zeolites (Chang et al., 2020). In cases of low temperatures and high pressures, it may be insufficient to describe isothermal adsorption of pure pressure components (Benard & Chahine, 1997). The Freundlich isotherm is applied to adsorption processes occurring on heterogeneous surfaces (Ayawei et al., 2015a). This model determines the heterogeneity of the surface and the exponential distribution of active sites and their energies (Ayawei et al., 2015b).

In order for the adsorption method to be conducted, was essential to prepare a sufficient amount, at least 10L, of dilute salt solution so as to be used as a background electrolyte. For this purpose, 1.47 g of solid  $CaCl_2 \cdot 2H_2O$  was dissolved in 700 mL of deionized  $H_2O$  in a 1000 mL beaker, the contents of which were then added to a 1000 mL volumetric flask, which was made up to the mark with deionized  $H_2O$ . In this way a solution of 0.01 M CaCl<sub>2</sub> was prepared. Then, were prepared the solutions of specific concentrations of both copper and cadmium.

The purpose of this assignment was, to study the adsorption of Copper (Cu) and Cadmium (Cd) in both acidic and alkaline soil pH with Langmuir and Freundlich isotherms. Both isotherms described the adsorption of each metal satisfactorily, with a slight predominance of Langmuir isotherm, since  $R^2$  in all cases was close to the unit.

In figures 1 & 2 the adsorption of Cu and Cd using Langmuir isotherm in both alkaline and acidic soil sample, are presented.

In addition, the nonlinear equations for each metal in both soil samples, were determined through the diagrams of Langmuir and Freundlich isotherm.

The adsorption of copper was performed on two soil samples with different pH, with the first sample being alkaline and the second acidic. In Figure 1, in the alkaline soil sample, the trend line is linear, while the value of a and b, as proved by the equation of the line, is equal to 0.0074 and 0.0014 respectively. From these values it appears that  $K_L$  is equal to 0.1892 and qmax to 714.29. Similarly, in the acidic soil sample, the trend line is linear, while the value of a and b, as proved by the equation of the line, is equal to 0.0182 and 0.0019 respectively. From these values it appears that  $K_L$  is equal to 0.1044 and qmax to 526.32. Finally, with the value of  $R^2$  being high in both cases, it is concluded that the adsorption of copper was very successful with the Langmuir method.

The adsorption of cadmium was performed on two soil samples with different pH, with the first sample being alkaline and the second acidic. In Figure 2, in the alkaline soil sample, the trend line is linear, while the value of a and b, as proved by the equation of the line, is equal to 0.0072 and 0.0013 respectively. From these values it appears that  $K_L$  is equal to 0.1806 and qmax to 769.23. Similarly, in the acidic soil sample, the trend line is linear, while the value of a and b, as proved by the equation of the line, is equal to 0.0182 and 0.0015 respectively. From these values it appears that  $K_L$  is equal to 0.0824 and qmax to 666.67. Finally, with the value of  $R^2$  being high in both cases, it is concluded that the adsorption of cadmium was very successful with the Langmuir method.

Therefore, the soil with both alkaline and acidic pH had the ability to adsorb a larger amount of cadmium (qmax) than copper (Cd>Cu).

Based on the K<sub>F</sub> values of the Freundlich equation, the soil with the alkaline pH adsorbed almost equal amount of cadmium and copper, while in the acidic soil sample the adsorption of metals followed the same sequence with the largest amount corresponding to cadmium (Cd>Cu).



Figure 1: Adsorption of Cu using Langmuir isotherm in alkaline and acidic soil sample, respectively.



Figure 2: Adsorption of Cd using Langmuir isotherm in alkaline and acidic soil sample, respectively.

From the above data it is concluded that, despite the fact that Copper adsorbed with the highest energy, its adsorption was minimal compared to Cadmium in acidic and alkaline soil sample, according to the  $K_L$  values.

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