COMPARING STUDY ABOUT THE METHODS TO MEASURE THE COPPER SORPTION CAPACITY OF SOILS

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The cation capacity of soils has a big importance in case of nutrients and toxic elements. The cations retarded during similar processes in the solid phase of soil. It can be very useful to modelling these processes under laboratory circumstances. During these experiments, two main method types could be identified. One of them (batch method) gives information about the equilibrium, until the other (soil column or continuous flow method) gives kinetically approaches and results. The result by the different methods – where was measured the sorption amount of copper on high organic content soils – were compared with each other.

In case of batch technique (applied Langmuir isotherm) the model provides information about: adsorption capacity (A_{max}), affinity of the adsorbent in case of adsorptium (k). If the flow-through model (soil column) was used, the results give information about the adsorption capacity also, and the retardation factor could be calculated from the curve. Based on it, the distribution, which related with the lineralized k value mentioned before, could be calculated too. These distributions can be compared with the gradients of the isotherm (from batch technique, practically the buffer capacity). With this information the sorption isotherms of the different soils could be modelled. Based on the results: the two different methods could be compared withstand the differences in the two measurement methods and terms of circumstances and measurement parameters of them.

Keywords: copper, adsorption, batch, Langmuir, soil

Introduction

Adsorption is one of the most important interfacial phenomenon in the element and material transport systems for the soil. The soil has so many parameters such as pH, organic content, and the compound what have effect to the bounding ability. There exist more methods to examine the sorption attribute of the solid phase. The two most commonly used methods are the batch technique and the soil column method (Bermúdez-Couso et al, 2012). In both methods there could be equilibrium between solid and liquid phase despite the different circumstances. Also exist several models to describe the adsorption. Two models are well known such as the Langmuir and Freundlich isotherms models (Hinz, 2001; Limousin et al., 2007; Foo&Hameed, 2010). However there is a difference among the models. In case of Langmuir model there is a roof for the adsorption capacity calculation which takes into account the limitation for adsorption and calculates with it (Jiang et al., 2005):

$$q = \frac{KcM}{(1 + Kc)}$$

Opposite this the Freundlich isotherm does not take account the loading of the surface (Sparks, 2003). The general form for it:

$$q_e = k_f c_e^n$$

Based on these it was practical to use the Langmuir approach for the calculation. The purpose of examination was to compare the information between the two different adsorption methods (batch and soil column) in terms of the different soils.

Materials and methods

In case of batch technique (applied Langmuir isotherm) the model provides information about: adsorption capacity (A_{max}) and affinity of the adsorbent in case of adsorptium (k). If the flow-through model (soil column) was used the results give information about the adsorption capacity also and the retardation factor could be calculated from the curve parameters. Based on this the distribution which related with the lineralized k value mentioned before could be calculated too. These distributions can be compared with the gradient of the isotherms (from batch method practically the buffer capacity). With these information the sorption isotherms of the different soils could be modelled.

The brown forest soil samples originate from Hungary, Trizs municipal (near the Bükk Mountains). These samples were taken from the "A" soil level (which was mixed with coal) at a control area and three different age (25, 35 and 80 years old) leftover charcoal burner. The determination of soil abilities based on general methods. The density was measured by pycnometer with 10-15 grams of sieved (2 mm sieve) air dry soil samples. For determine the ignition loss the jars were filled up to half and put into furnace on 105 C° and 2-3 hours long. The porosity is the porous volume in the undisturbed soil in percentage. However in this measurement the soil was not undisturbed because 2 mm sieve was applied (Stefanovits et al., 2010).

During the experiment copper solution with different concentration were used on the soil columns (as stationary phase). The outcome results could be found in *Table 2*. The outcome liquid was poured into 100 cm^3 units and the elapsed time was recorded for each one. These concentrations were measured by FAAS (Perkin Elmer, on 324.8 nm wavelength). After the calculations the empiric model was fitted on the results. This takes account the sorption (advective-dispersive transport through porous media) and also the velocity of the liquid through the column:

$$\frac{c_e(L, T')}{c_o} = 1 - \frac{1}{2} \left\{ \text{erfc}\left(\frac{R_d - T'}{2(T'R_d/P_L)^{1/2}} \right) + \exp(P_L)\,\text{erfc}\left(\frac{R_d + T'}{2(T'R_d/P_L)^{1/2}} \right) \right\}$$

where P_L is the column Peclet number, *erfc* is the complementary error function (Shackelford&Glade, 1997; Huysmans&Dassargues, 2004). R retardation factor can be calculated by fitting the model which is connected to the buffer capacity related to adsorbed material (k) if the velocity is constant and the adsorption is linear. The distribution between the solid and liquid phase could be described by this formula:

$$R = 1 + \frac{\rho B}{P}$$

where R is the retardation factor, ρ is the density (g/cm^3), p is porosity (%) and B the buffer capacity.

Used the soil abilities (such as the mass of the samples) and additional measured values (as the adsorption profiles) the breakthrough curves can be drawn. These gives information about the maximum adsorbable amount (A_{max}) or the inflection point (maximum adsorbable capacity). These values could be found in Table 2.

Results and discussion

Based on the *Table 1* values the abilities of the different soils are really similar. The only exception is the different organic carbon content. This difference is really important in case for maximum adsorption amount of the copper.

Table 1: Soil abilities summary table used in the experiment

Soil sample	Density (g/cm^3)	Volume mass (g/cm^3)	Porosity (%)	Ignition loss (%)	pH (KCl)	Organic Carbon content (%)	Dry material content (%)
Control	2,38	1,01	57,65	2,17	4,5	4,1	97,87
80 years	2,24	0,99	55,77	2,06	4,1	6,1	97,98
35 years	2,08	0,92	55,72	3,14	5,5	12,6	96,95
25 years	2,15	0,74	65,60	3,17	4,7	11,8	96,92

Figure 1 shows an adsorption curve. The curve provides information about the start of the adsorption and the breakthrough point. It gives information also the fill up of the soil. The points are the extracts concentration change in case of the elapsed time.
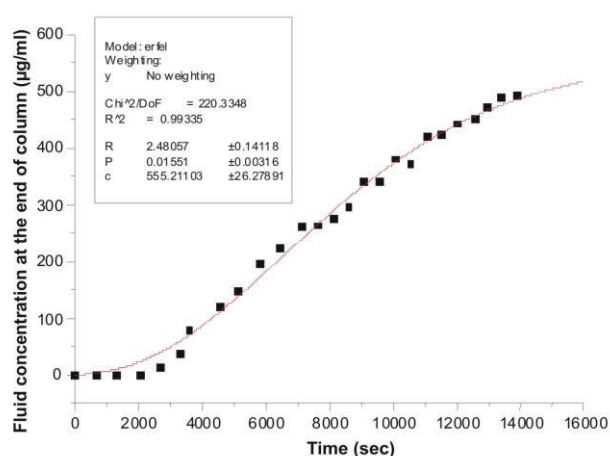

Figure 1: Copper adsorption for 80 years old charcoal-soil system sample
(Applied: 500 mg Cu eluent concentration)

These curves were done for all the experiments. The graphs give the mathematical parameters what could be used to determinate the results in *Table 2*.

Table 2: Calculated maximum adsorbable copper amount for the two different methods

Soil Sample	Retardation factor	Buffer capacity (dm^3/kg)	Eluent concentration (mg Cu/dm^3)	Batch method (Langmuir) A_{max}(mg/kg)	Soil column method A_{max}(mg/kg)
Forest soil (control)	1,96	14,49	500	1716	2459
80 years old charcoal-soil system	2,48	25,35	500	1435	2432
35 years old charcoal-soil system	3,01	41,72	1000	7904	8937
25 years old charcoal-soil system	1,83	20,31	2000	7943	10235

Based on these results the 25 and 35 years old charcoal-soil systems have the highest copper adsorption capacity. Both of the two methods gives bigger amount of bounded materials compared to the control and 80 years old soils. The smaller organic carbon content means lower adsorption according to the values.

Conclusions

As summary can declare that the soil column technique can used for the measurement of metal adsorption in case of different origin soils. The concentration of eluent has big influence on the breakthrough point also on the exhaustive point. However these different concentrations have no effect to the maximum adsorbable amount. The maximum adsorption values from the batch technique could be compared with the calculated results from the soil column method. The results from the soil column method were bigger than the batch technique. It was caused by the different circumstances for the two methods. Also an important point that the difference increased between adsorption maximum of batch and soil methods as the difference raised in the organic carbon content.

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