PARTITION AND SORPTION OF HEAVY METALS TO SOILS

Camelia BEȚIANU, Loredana BRÎNZĂ,
V.L. PAVEL, Maria GAVRILESCU
„Gh. Asachi” Technical University of Iaşi, Faculty of
Chemical Engineering and Environmental Protection
e-mail: betianuc@ch.tuiasi.ro

The fate of toxic metallic cations in the soil environment depends largely on the interactions of these metals with inorganic and organic surfaces. The extent to which a metallic cation interacts with these surfaces determines the concentration of metal in solution and, consequently, the potential for movement into groundwater or uptake by plants. A considerable amount of work has been done to evaluate the adsorption of various heavy metals by soils and soil constituents, such as clays and organic matter fractions.

The objectives of this work were to determine the sorption capacity of four soil categories, in absence and presence of different quantities of the yeast Saccharomyces cerevisiae, during the sorption ability of copper ion. Also, the semi-batch experiments were set in order to find how much time the sorbent is active during copper sorption process.

The mobility of heavy metals in soil was described by the distribution coefficient, K_d, defined as the ratio of metal concentration in the solid phase to that in the liquid phase at equilibrium, determined from the slope of the linear part of the adsorption isotherms.

The results show that there are differences between sorption capacities of various soils, and the sorption process kinetics and dynamics are influenced by the presence of S. cerevisiae, which can act both as biosorbent and as organic matter in soil.

The sorption process kinetics can be described by a pseudo-second order model, indicating that the rate limiting step is a chemical sorption process between copper and soil.

***Keywords**: copper, kinetics, partition coefficient, Saccharomyces cerevisiae, sorption isotherm.*

One of the most important factors influencing the transport and environmental fate of chemicals in soil and sediment is the sorption-desorption process. Emissions of heavy metals to the environment make it relevant to observe the changes in the concentrations and distribution of these elements in soil, to study the regularities and causes of their migration, and to predict the changes in the state of the soil layers [2, 7].

Sorption is used to describe the process by which a chemical moves from one phase and becomes accumulated in another, particularly where the second phase is a solid [1]. There is a considerable amount of literature published regarding the sorption behaviour of heavy metals with soil components [2, 4]. Different soil types can behave in various ways during sorption process, also depending by the presence of other organic components [4].

The metal partition coefficient (K_d; also known as the sorption distribution coefficient) is the ratio of sorbed metal concentration (expressed in mg metal per kg sorbing material) to the dissolved metal concentration (expressed in mg metal per L of solution) at equilibrium (*eq. 1*).

$$K_d = \frac{sorbed\ metal\ concentration\left(mg/kg\right)}{dissolved\ metal\ concentration\left(mg/L\right)} \quad (1)$$

For a particular metal, K_d values in soil are dependent upon various geochemical characteristics of the soil and its porewater. Geochemical parameters that have the greatest influence on the magnitude of K_d include the pH of the system and the nature and concentration of sorbents associated with the soil or surface water.

MATERIALS AND METHODS

1. Sorbent preparation

Soil samples were collected from A_0 and A_1 horizons at four sites in different locations of Iasi. They were *Chernozemus* (A), *Fluvisols* (B), *Podzols* (C) type and o mixture from the first and the third (D) [6]. The soils were air dried and the fraction < 3 mm was used. For all soil samples pH and soil organic matter content (OMC) were determined. Shaking 5 g of air-dry soil with 10 mL of deionized water for 60 min., allowing the solution rest overnight, and then measuring the solution with a pH meter determined the soil pH. Soil samples were heated at 105 °C (3 h) and then at 340 °C (2 h) in order to remove all organic matters content.

2. Cooper solution

A 0.1M $CuS0_4.5H_2O$ solution was prepared as stock solution for sorption experiments and Cu^{2+} ion was determined using a volumetric method [5].

3. Sorption measurements

Sorption was carried out in semi-batch experiments, using 60 g of each soil in three replicates. Three series of experiments were prepared in flasks with perforated bottom: (A, B, C, D) as a witness experiment, (A1, A2, A3, A4), with 2 g of yeast (*S. cerevisiae*), and (A4, B4, C4, D4), with 4 g of yeast, respectively. First, 40 ml solution of the metal was added. At 24 hours intervals samples of solutions were taken and analyzed (respectively at 0, 24, 48, 72, 96, 120, 144, 168 and 192 hours). After the sample was taken, another volume of 40 ml solution was introduced in the flasks. The flasks were maintained at 30ºC under agitation.

RESULTS AND DISCUSSION

1. Sorption dynamics and performance

Sorption process was studied during 192 h. According to literature, sorption can be divided into two main processes: adsorption of the ions on sorbent surface and bioaccumulation within the sorbent pores. Results were expressed as the amount of metal ions adsorbed on dried algae at any time (*q*, mg/g), adsorbed metal ions per gram of seaweed at equilibrium (q_e, mg/g), maximum amount of metal ions the biomass can adsorb (q_{max}, mg/g), initial metal concentration (C_0, mg/L), concentration of metal ions that remain in solution at the equilibrium (C_e, mg/L), and sorption efficiency (*eq. 2*)

$$E\,\% = (1 - C_e/C_0)\ \mathrm{x}100 \quad (2)$$

Biosorption metal uptake (q) was calculated from the sorption system mass balance (*eq. 3*):

$$q = V\,(C_i - C_f)/S \quad (3)$$

where V is the solution volume, S the amount of solids (biomass), and C_i and C_f the initial and final metal concentrations respectively.

The effect of contact time on Cu^{2+} sorption on soil was investigated using the four types of soils with various quantities of yeast, as was presented in the previous part. The results presented in *fig. 1* show that the rate Cu^{2+} ions sorption is generally extremely fast in the first 100 hrs, and then it decreases for the soils A, A2, A4, for that the equilibrium being reached after 120 hours.

The partition coefficient, K_d is dependent on the soil type and the presence of the yeast. *Fig. 2* shows that soil C is retains in the largest degree the metal, followed by D, B and A. Also, in the case of soil C, the presence of yeast improves the metal retention, which is higher if the yeast quantity is increasing. This behaviour is confirmed by the variation of sorption capacity with effluent concentration (*fig. 3*). The soil C proved to be the most efficient for copper sorption, and this capacity is enhanced by the presence of yeast, which can act as a biosorbent as well as an organic compound. Soil A is less efficient for copper sorption and yeast presence does not improve sorption capacity.

Figure 2 also illustrates that the soil type has a more significant influence on copper sorption than the different yeast quantities.

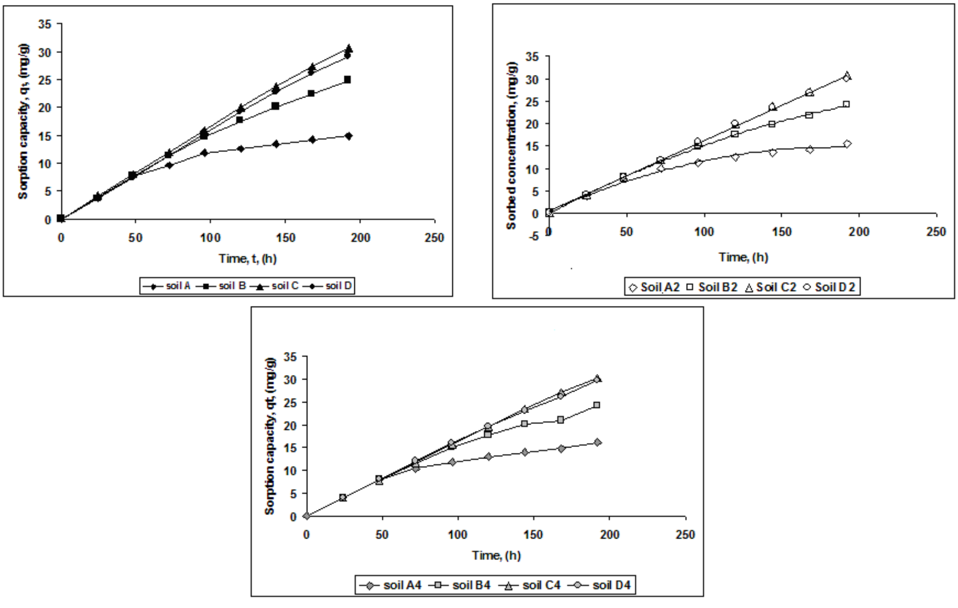

Figure 1. **Sorption dynamics of copper on soils**

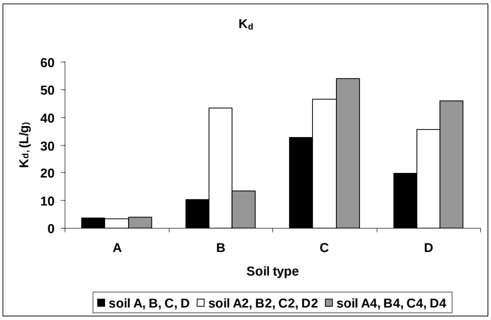

Figure 2. **Partition coefficient of copper on investigated soils**

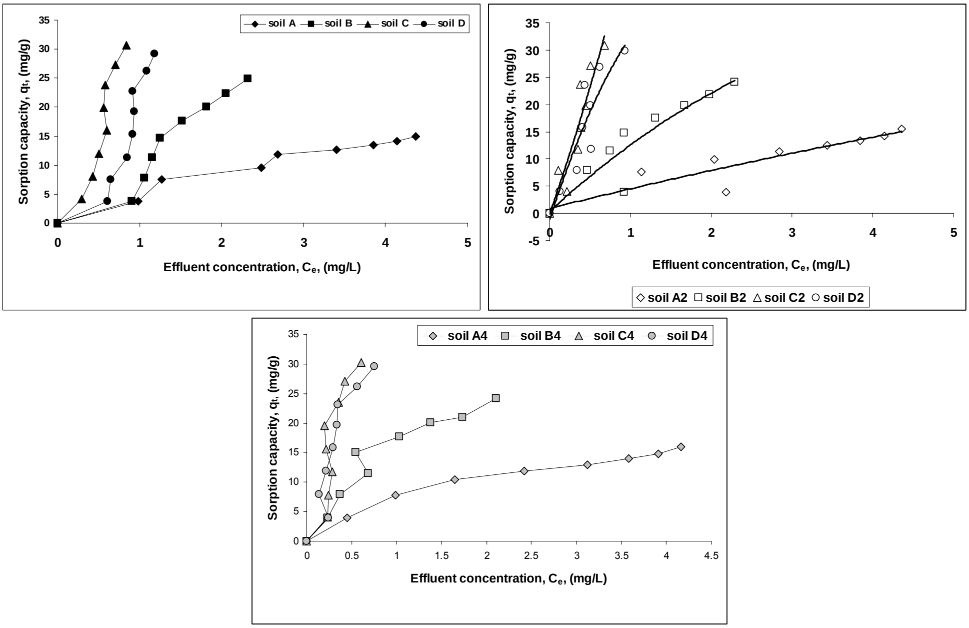

Figure 3 **Sorption capacity of copper on investigated soils as a function on effluent concentration**

2. Sorption kinetics

In order to investigate the mechanism of copper sorption by the soils, and the potential rate-controlling steps, kinetic models have been used to test experimental data. These kinetic models included diffusion, pseudo-first order, and pseudo-second order models [3]. Diffusion and pseudo-first order models only achieved a good fitting for the first hours of experimental data (not shown). The best fit, in the whole data range were found with a pseudo-second order model, indicating that the rate limiting step is a chemical sorption process between copper and soil.

The pseudo-second order kinetic model developed by Ho et al. (2001) is expressed by *eq*. (4):

$$\frac{t}{q_t}=\frac{1}{kq_e^2}+\frac{1}{q_e}t \qquad (4)$$

where: k - the pseudo-second-order rate constant of sorption (g/mg h), $kq_e{}^{2}=h$ is the initial sorption rate (mg/gh), q_t - the amount of copper sorbed at time t(h). The equilibrium sorption capacity, q_e and the pseudo second order rate constant k were experimentally determined from slope and intercept of straight line plots of t/q_t against *t* (*Fig. 4*). Their values are presented in *Table 1.*

Table 1

Parameters of the pseudo-second order kinetic model

Soil	q_e (mg/g)	k (g/(mg.h)). 10^3	R^2
A1	18.248	1.049	0.8807
B1	39.37	0.177	0.5091
C1	54.65	0.093	0.7593
D1	54.95	0.084	0.7144
A2	18.69	0.940	0.8653
B2	38.91	0.168	0.7247
C2	56.18	0.086	0.7322
D2	53.76	0.094	0.7561
A4	19.27	0.960	0.8737
B4	35.71	0.230	0.8907
C4	56.64	0.084	0.7426
D4	52.36	0.100	0.7681

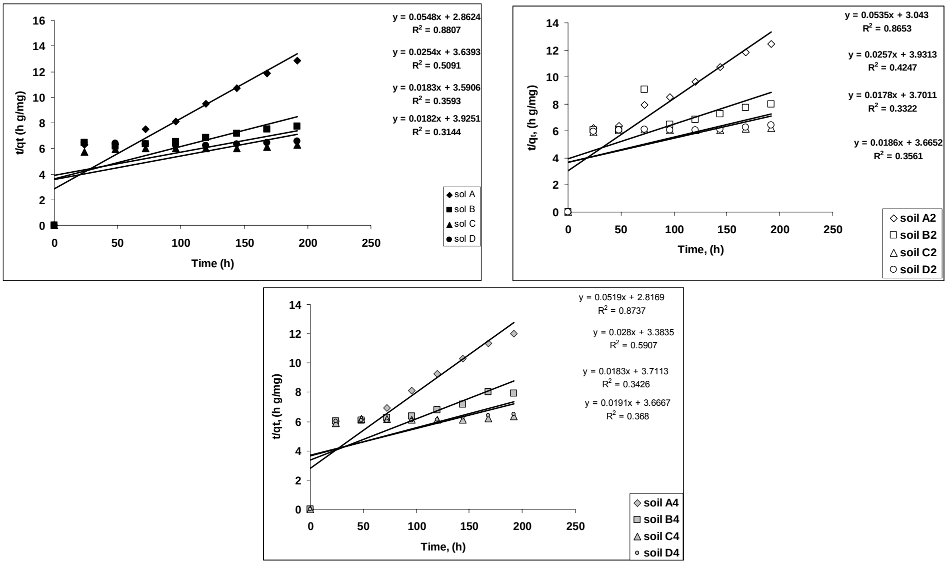

Figure 4 **Graphic determinations of the kinetic parameters of the pseudo-second order kinetic model**

CONCLUSIONS

Release of heavy metals onto the soil as a result of agricultural and industrial activities may pose a serious threat to the environment. This study investigated the kinetics of sorption of heavy metals on the non-humus soil amended with *Saccharomyces cerevisiae.*The sorption ability of various soils was analyzed in a semi-batch system, by addition of certain portions of solution containing copper ions at various time intervals, in order to simulate the rainfalls, which can transport the heavy metals in soils, up to the groundwater level.

From an environmental point of view soil sorption of Cu is a fast process: more than 95% of the sorption takes place within 50 hrs, equilibrium is reached in 120 hrs. The presence of the yeast enhances the sorption process, but the most significant effect upon sorption intensity is exhibited by the soil type. The process kinetics follows the pseudo-second order kinetic model, indicating that the rate limiting step is a chemical sorption process between copper and soil.

Further experiments have to be done in order to investigate the effects of other parameters specific to sorption processes.

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