SIMULATION OF SBO ABSORPTION

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ABSTRACT – This contribution is part of an international research project on prospecting uses for soluble bio-organic substances (SBO) isolated from urban biomasses. SBO have been found to be very similar to humic substance in terms of chemical structure and physical-chemical properties. SBO have been tested as surfactants, detergents and adsorbents. In the present work, mathematical models for the adsorption of N_2 at 77K and crystal violet at 298K in SBO-magnetite systems (with different amount of SBO functionalizing magnetite nanoparticles) are developed. The models were fitted to experimental data. The N_2 adsorption isotherms are of type 4 (following the IUPAC classification). Initially, the linear form of BET equation was used. Later, the number of multilayers was estimated as well. It is about 81 for concentrations of 0.5 mg/L of SBO and 95 layers for 0.05 mg of SBO. In the study of the adsorption of crystal violet in SBO-magnetite particles, the data were divided in four groups. Each group was analyzed individually and the Langmuir and Freundelinch equations were fitted for each. Finally, a model to represent global adsorption kinetic was proposed for fitting the experimental data.

1. INTRODUCTION

This contribution is part of the European mobility project entitled "EnvironBOS - Isolation, Characterization and screening of environmental applications of Bio-Organic substances obtained from urban biomasses". The project relates to the use of substances deriving from biomasses and it consists of an international cooperation among Universities from Spain, Italy, Brazil and Argentina, inside the UE FP7 Marie-Curie action (International Research Staff Exchange) framework**.**

SBO means soluble bio-organic substances. These substances can be obtained from the alkaline hydrolysis of the organic fraction of urban wastes, aged either aerobically or anaerobically, followed by an ultrafiltration step in order to separate different fractions basing on their dimension (Montoneri *et al.*, 2008). The SBO have been tested as surfactants, detergents, in the soil washing, as emulsifiers, foaming agents, textile auxiliary, photosensitizers and adsorbents.

In the present work, it is presented a mathematical study concerning adsorption processes. The work comprehends three parts: 1- Study of N_2 adsorption at 77K on SBO-magnetite systems; 2- study

of crystal violet adsorption at 298K on SBO-magnetite systems; and 3- elaboration of adsorption kinetics relative to crystal violet.

2. FUNDAMENTALS

2.1 Modeling, simulation and parameter estimation

The modeling and simulation process is composed by the same steps of science development, and they are: - preliminary ideas; 1st model; planning of experiments; experiences; evaluation; interpretation; revised ideas and 2nd model. This is the conceptual progress presented by Aris (1994). In the present work this procedure was used: first of all a very simple model was considered, even it did not fit very well the experimental data; secondly, a more detailed model was applied in order to improve the fitting of the experimental data.

The parameter estimation is the step to adjust the mathematical model - and its parameters - to experimental data. Firstly, one assumes a mathematical model. Then, the comparison between the model estimation and the experimental data generates differences, which are the errors. The minimization of these errors can point out the parameters which may represent the experimental data. Here, maximum likelihood estimation was performed. The function that was minimized is the likelihood function.

2.2 N_2 adsorption at 77K in SBO-magnetite systems

In general, the adsorption is studied through heterogeneous kinetics, some of which are well known and commonly used for materials characterization. Brunauer *et al.* (in Hill, 1977) proposed five types of adsorption isotherms: 1- type 1: is characterized by a monotonic approach to a limiting amount of adsorption, 2- type 2: it is a typical example of physical adsorption, and can be occur capillary and pore condensation; 3- type 3: it has a monotonic approach but there is not a final limit value, i.e., no saturation; 3- type 3: it is very similar to type 2, but presents a limit value; 5- type 5: it is very similar to type 3, but presents a limit value as well.

The type 1 can be modeled by using the Langmuir approach and the relative equation is:

$$v = \frac{v_m K P_A}{1 + K P_A} \qquad (1)$$

where v_m is the volume of the monolayer, P_A is the partial pressure of specie A and K is a equilibium constant.

The Equation 1 was obtained assuming some physical hypotheses. Other equations can be used. For instance, the Freundlich equation

$$Q_e = K_F C_e^n \qquad (2)$$

and BET model:

$$\frac{x}{v(1-x)} = \frac{1}{v_m c} + \left(\frac{c-1}{v_m c}\right)x \tag{3}$$

where c is a constant, x is the relative pressure equal to P/P_A.

However, the Equation 3 cannot model multilayer. Hill (1977) presents an equation that may estimates the number of layers (n):

$$v = \frac{v_m c\, x[1-(n+1)x^n + n\, x^{n+1}]}{(1-x)[1+(c+1)x - c\, x^{n+1}]} \tag{4}$$

2.3 N_2 adsorption in SBO–magnetite systems

The adsorption isotherms of N_2 in SBO-magnetite systems were obtained (Magnacca, 2014) for three different material compositions: 0.5, 0.1 and 0.05 mg of SBO. The isotherms are of type 4 (see Figure 1), and the hysteresis loop points out to condensation into the pores (Hill, 1977).

2.4 Crystal violet adsorption in SBO-magnetite systems

Two groups of experiments with crystal violet are studied here. The first one is the adsorption of crystal violet in SBO-magnetite systems (Magnacca, 2014). The second one is the kinetic of the adsorption of crystal violet with SBO-magnetite systems. Several concentrations of CV and SBO were used in both cases.

3. METHOD

The modeling and simulation were done by estimating parameters. In the N_2 adsorption in SBO-magnetite systems, the volume of monolayer (v_m) and C were estimated by using Eq. 3. Then, the number of layers was estimated by using program ESTIMA, which minimizes the likelihood functio. To study the adsorption of crystal violet on the same systems, the data were divided in four groups. Each group was analyzed individually, and Langmuir and Freundlich equations were used.

Finally, a mechanistic model useful for describing the kinetic of the adsorption was proposed here. Crystal violet forms two intermediate species (CV-SBO I and CV-SBO II) when in contact with SBO molecules in homogeneous phase (Gomis *et al.*, 2013), which are:

$$CV + SBO \underset{k_2}{\overset{k_1}{\leftrightarrow}} Complex\,1$$

$$Complex\,1 + CV \xrightarrow{k_3} Complex\,2$$

Assuming that the reactions are elementary and can be applied also to the heterogeneous SBO-magnetite systems, the mathematical model is generated and it is composed by four ordinary differential equations with initial value problem (ODE-IVP).

$$\frac{d\,CV}{dt} = -k_1\,CV\;\;SBO + k_2\,Complex1 - k_3\,CV\,Complex1$$

$$\frac{d\,SBO}{dt} - k_1\,CV\;\;SBO + k_2\,Complex1$$

$$\frac{d\,Complex1}{dt} = k_1\,CV\;\;SBO_2\,Complex1 - k_3\,CV\,Complex1$$

$$\frac{d\,Complex2}{dt} = k_3\,CV\,Complex1$$

For t=0, CV=CV_0, where CV_0 is the initial concentration of crystal violet, SBO=SBO_0, where SBO_0 is the initial concentration of SBO, whereas the concentration of complex 1 and complex 2 are both equal to 0.

The system was solved by using a BDF method with variable order, DASSL (Brenan *et al.*, 1989). The last step is the parameter estimation. Here, the tool ESTIMA was used, which find parameters by maximizing the likelihood function (PINTO, 1993). This is the weighted quadratic difference between experimental and simulated values. The parameters estimated here were the kinetic constants k_1, k_2 e k_3.

4. DISCUSSION AND RESULTS

4.1 BET

Firstly, the linear form of BET equation was used. The correlations obtained are higher than 0.999 (see Table 1) for all the materials studied, indicating a good simulation of the data. The surface area was calculated by fitting linear regression model using Excel tool. The fitted values are reported in Table 1 together with experimental ones (Magnacca, 2014).

Table 1- Results of linear regression using BET equation and experimental data (*) (Magnacca, 2014).

Samples	C	v_m	correl	S(m^2)	S (m^2)*
0.5	123.06	7.867	0.99986	34.2	34
0.1	155.82	12.47	0.99989	54.2	55
0.01	173.58	14.22	0.99992	61.6	63

4.3 Multilayers

The number of the multilayer was calculated by Equation 4. This model is non-linear and a non-linear regression fitting was carried out. The ESTIMA program was employed, and the likelihood function was minimized. The results for three adsorptions curves cab be seen in Figures 1(a), (b) and (c). The algorithm used here permits to estimate the number n of the layers. It is about 95 for 0.05 mg of SBO, between 61 and 84 for 0.1 mg of SBO, and about 81 for 0.5 mg of SBO.

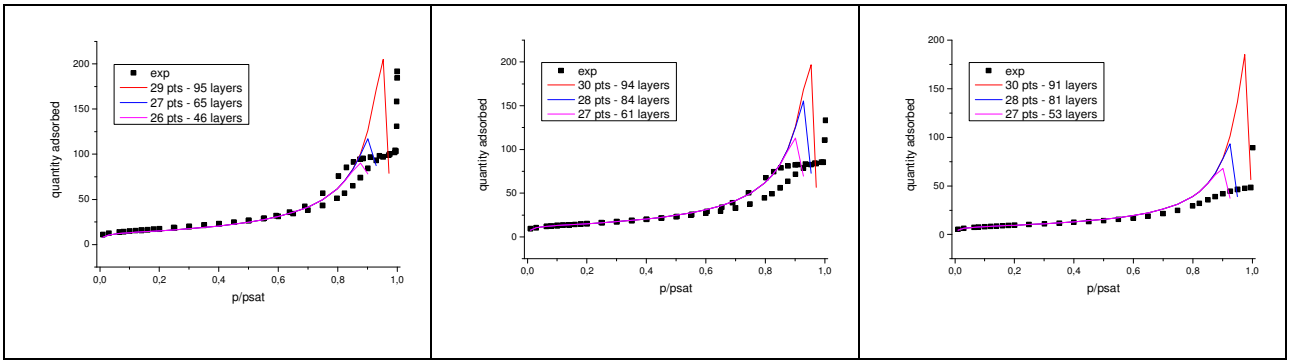

Figure 1 – N_2 adsorbed volumes (cm³/g at STP) *versus* relative pressure in SBO-magnetite systems (a) SBO=0.05 mg; (b) SBO=0.1 mg; (c) SBO=0.5 mg.

4.4 Crystal violet interaction with SBO-magnetite systems: adsorption models

The data were divided in four data groups as reported in Figure 2. The isotherms are of type 1 and Langmuir and Freundlich equations were applied.

The experimental data are fitted by the linearized Langmuir equation - see correlations in the Table 2, not by Freundlich equation. The Excel tool was sufficient to perform these elaborations - see correlations in the Table 3.

Table 2 - Results of Langmuir equation linear regression

Data group	K_L	a_L	correl
150 I	28,670	31,426	0.99993
150 II	38,054	41,990	0.99984
150 III	55,111	61,095	0.99999
1000	4050	3970	0.98785

The values obtained by non-linear regression, calculated by ESTIMA program are reported in Table 4. The parameters obtained in the two cases (linear and non-linear calculations) are quite different whereas the graphics are very similar, which may point out to a singular response surface. The estimation to non-linear Freundlich equation did not reach convergence, whereas Langmuir equation represents almost well each group.

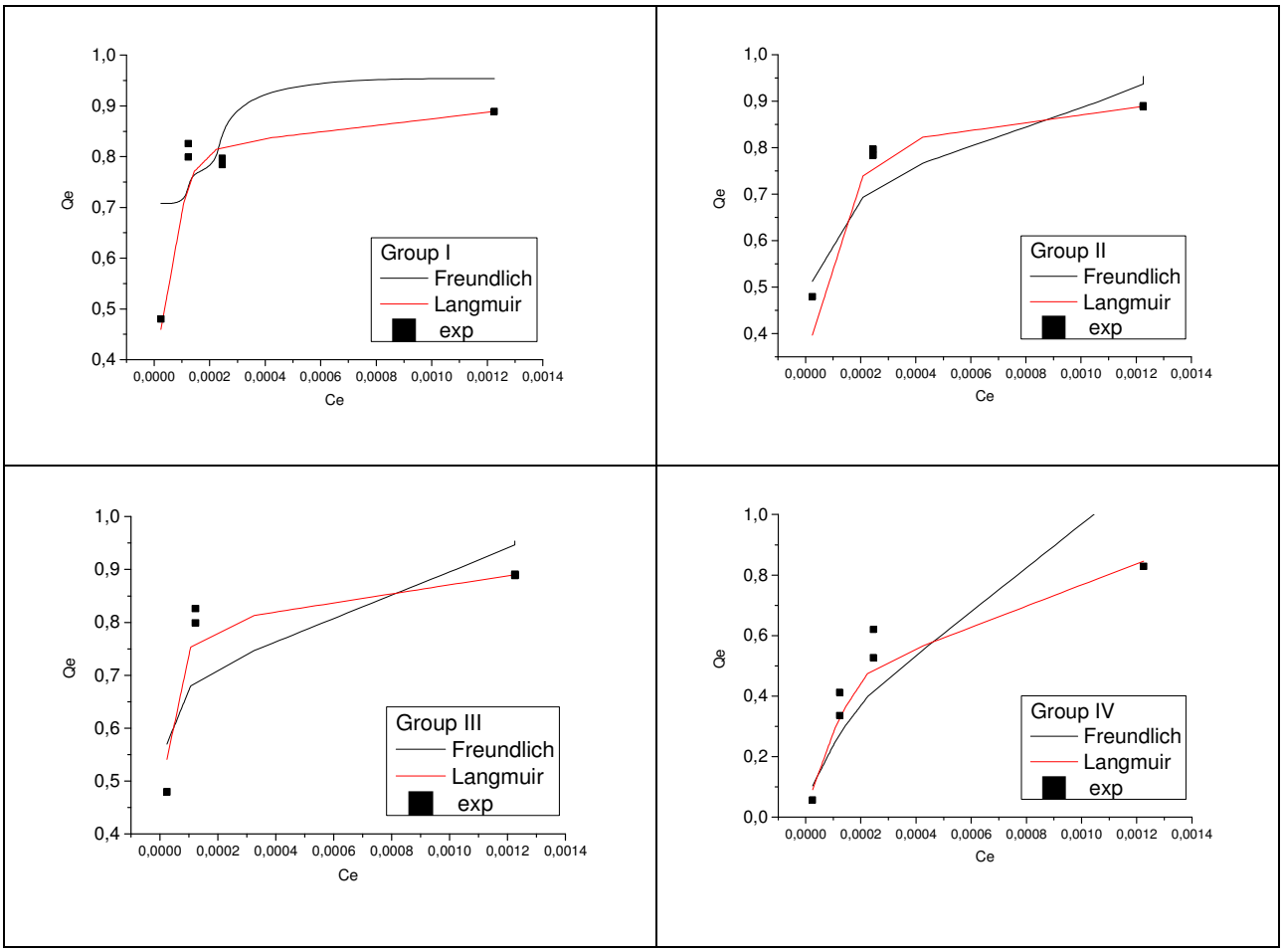

Figure 2 - Experimental data and simulated adsorption isotherms: (a) 150 I, (b) 150 II, (c) 150 III, (d) 1000

Table 3 - Results relative to Freundlich equation non-linear regression

Data group	k_L	n	correl
150 I	2.602	6.53	0.9575
150 II	2.273	7.71	0.8376
150 III	2.247	7.73	0.8389
1000	68.11	1.63	0.9064

4.5 Crystal violet interaction with SBO-magnetite systems: adsorption kinetics

The absorption curves had a rapid rise at the beginning followed by a stabilized value at the end, the steady state value. The model may reproduce both parts of the curve (Figure 3). However, the ensemble of kinetic constants k_1= 90093.2 mol^{-1} L s, k_2 = 27.15 s and k_3= 1.1 mol^{-1} L s, represents

better the initial points (red line), but the other ensemble, k_1= 1096.6 mol^{-1} L s, k_2 = 2.25 s and k_3= 54.6 mol^{-1} L, represents better the final points (black line).

Table 4 - Results of Langmuir equation non-linear regression

Group	K_L	a_L	Lin.
150 I	45,555	50,791	28670/31426
150 II	40,489	45,662	38054/41990
150 III	44,004	50,878	55111/61045
1000	10,050	16,012	4050/3970

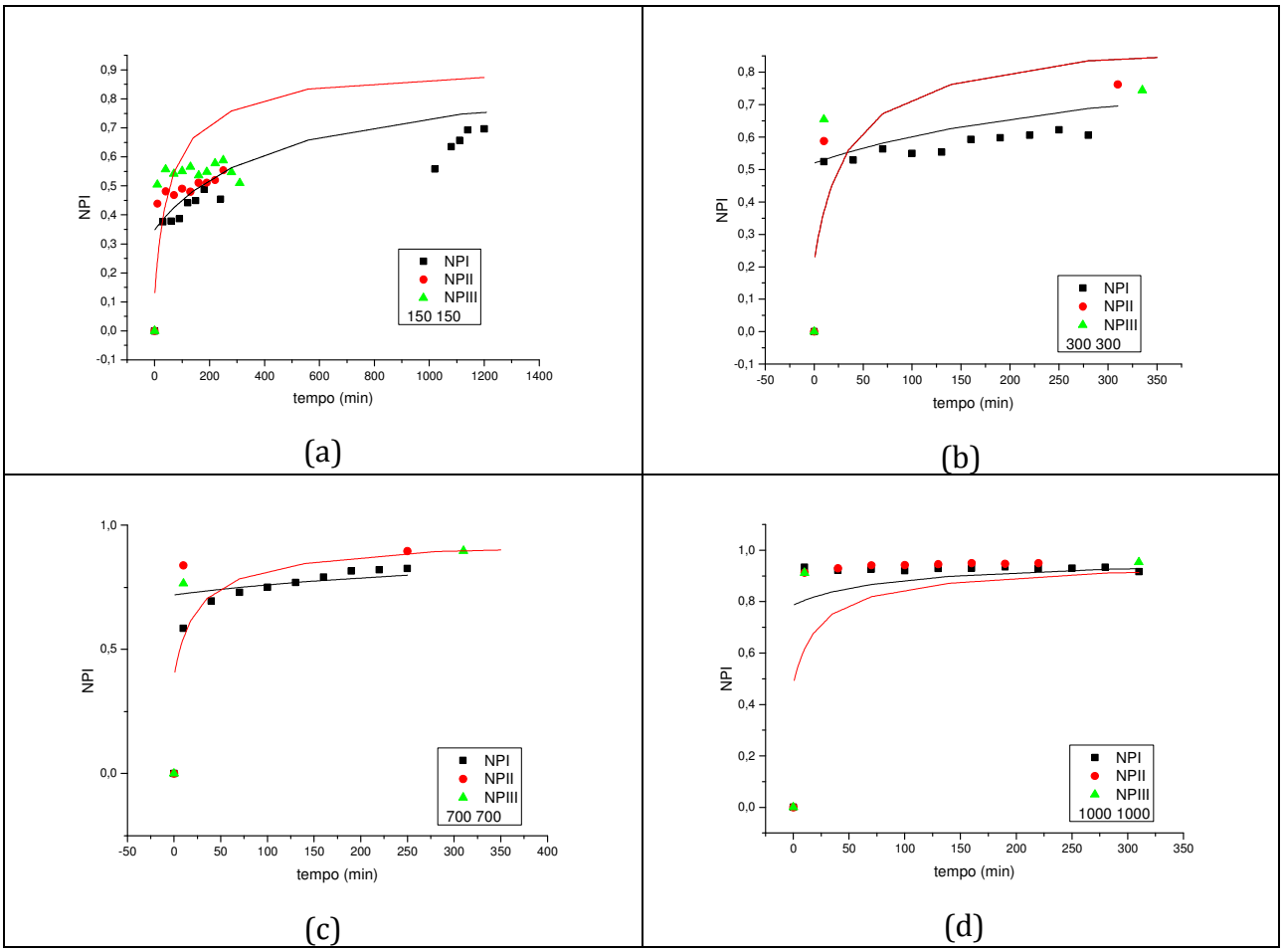

Figure 3 – crystal violet adsorption *versus* time (a) CV= 10 mg/L SBO=150 mg/L; (b) CV= 10 mg/L SBO=300 mg/L; (c) CV= 10 mg/L SBO=700 mg/L; (d) CV= 10 mg/L SBO=1000 mg/L. Lines: black (-) k_1= 90093.2 mol^{-1} L s, k_2 = 27.15 s and k_3= 1.1 mol^{-1} L s; red (-)k_1= 1096.6 mol^{-1} L s, k_2 = 2.25 s and k_3= 54.6 mol^{-1} L.

5. CONCLUSIONS

The algorithm here used allows to estimate the number n of the N_2 layers adsorbed in SBO-containing materials. It is about 95 for 0.05 mg of SBO, between 61 and 84 for 0.1 mg of SBO, and about 81 for 0.5 mg of SBO.

The experimental data relative to crystal violet adsorption on SBO-magnetite systems are fitted by the linearized Langmuir equation (by means of Excel tool), whereas Freundlich equation did not show useful results. The values relative to crystal violet adsorption estimated by non-linear regression are different from those calculated by linear fit. However, the graphics are very similar, which may point out to a singular response surface.

The mechanistic model of crystal violet adsorption may reproduce the rapid rise at the beginning of the curve and the steady state values. However, it is necessary to consider two different ensembles of kinetics constants.

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