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CALORIMETRIC STUDY OF THE IMMERSION HEATS OF LEAD(II) AND CHROMIUM(VI) FROM AQUEOUS SOLUTIONS OF COLOMBIAN COFFEE HUSK

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This work shows the result of the study of the Pb(II) and Cr(VI) ions adsorption by means of a Calvet type calorimeter of heat conduction that can operate at 150ºC. The calorimeter was electrically calibrated to establish its sensitivity and reproducibility, obtaining K=12.95±0.05 W V^{-1} and chemically it was examined with tris-(hydroxymethyl)-aminomethane (THAM)-HCl system, obtaining ΔH=–30.91±0.03 kJ mol^{-1}.

The activated carbon sample obtained from coffee husk and the calorimetric results obtained were related to other techniques used to perform this type of studies.

Keywords: *adsorption isotherm, calibration of calorimeter, immersion calorimetry*

Introduction

Porous solids are one of the most frequently used adsorbents in many applications. During the past decades, these materials have gained great importance because of their application in environmental chemistry and the development of new materials for extraction techniques [1–12].

In the processes of obtaining porous solids with very diverse texture characteristics, it is necessary to control certain variables such as the temperature, carbonisation and/or activation time and activating agents.

These surface characteristics will determine the application and overall performance of the resulting solid.

Some of the most important applications are in gas storage, heavy metal retention and in adsorption process design (e.g. pressure swing adsorption (PSA), vacuum swing adsorption (VSA) and temperature swing adsorption (TSA)) [13–15].

For this reason, it is important to determine very accurately the parameters that characterize these materials, such as surface area, pore distribution, pore volume and the heats of adsorption heats. All of which allow the following [16, 17]:

- the characterization of the adsorbent material from an energetic point of view
- the collection of new data to develop new theories about adsorption and kinetics

Some of the most important methods for the determination of adsorption heat available in the literature include:

- calculation of adsorption heats from equilibrium adsorption data taken at different temperatures. (e.g. adsorption isotherms or adsorption isotheres)
- calorimetric methods: these are usually classified as adiabatic, isothermic, Tian–Calvet and immersion calorimeters [18–22]

This study is the result of the work of our research groups during the past 18 years, combining different developments in the area of calorimetric instrumentation. We have adapted ideas reported in literature to design a new adsorption calorimeter. This new immersion calorimeter was connected to a computational measuring unit, resulting in a novel workstation that measures immersion heat.

Experimental

Description of the newly built calorimeter

Figure 1 shows a complete exploded view of the immersion calorimeter. Its design is not very common and it was not reported previously in the literature.

A detailed view from the inner of the equipment to the exterior of the calorimeter is shown in Fig. 1. In the diagram, part number 13 corresponds to the calo-

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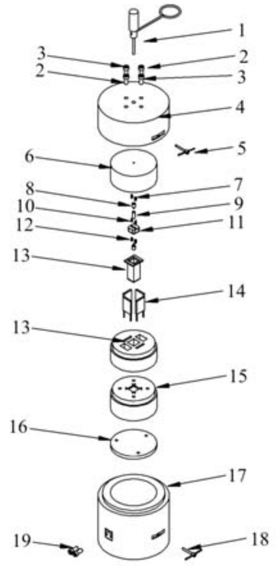

Fig. 1 Exploded view of the immersion calorimeter

rimetric cell made of stainless steel, which is embedded inside a large aluminium block that works as a heat sink (parts number 6, 15 and 16). Due to its thermal diffusion coefficient, the heat sink allows rapid heat conduction to the surroundings of the calorimeter. For this calorimeter, the Nylon block surrounding the equipment permits the rapid stabilization of the temperature (parts number 4 and 17).

The thermal effect was sensed through the four thermopiles connected in series to increase the sensitivity of the micro calorimeter (parts number 14). These thermo elements generate a voltage signal through the feedback effect, which is proportional to the heat flow produced in the cell. In the same matrix, four rectangular holes were made, which lodge four 25×25×2 mm Tellurex reference CZ-1-1.4-1.27-1.14 HT thermopiles connected in series. The thermopiles used are solid in state, made of a quaternary alloy of bismuth, tellurium, selenium and antimony.

This thermoelectric potential was recorded by means of a $6^{1/2}$ digit Aligent multimeter, model 34349 that is connected to a computer through an RS-232 interface.

The upper part of the adsorption calorimeter consists of a Nylon piece (parts number 4), which acts as lid and at the same time has a conic device divided into two parts, which permits the reception of the vial that contains the porous solid without leaving any empty space inside (parts number 1).

Electric calibration of the adsorption microcalorimeter

To establish the correct operation of the calorimeter prior to connecting it to the volumetric adsorption unit, we evaluated its sensitivity by determining the calorimeter constant.

The calibration constant gives the voltage generated by the calorimeter when a given amount of heat is emitted from the inside of the microcalorimetric cell (parts number 12).

There are two methods to determine the calibration constant (K).

Determination of the calibration constant by application of electric power

This method was based on the dissipation of electric work (W_e) by an electric resistor through which an electric current (i) passes for a certain amount of time (t). This generates a voltage (V_t) in the micro calorimeter that is measured.

The calorimeter calibration constant (K) was given by [23]:

$$K = \frac{W_e}{\int V_t \mathrm{d}t} = \frac{V_c i t}{\int V_i \mathrm{d}t} \tag{1}$$

where V_c is the voltage applied to the resistor, i is the current that passes through it, and t is the time expressed in seconds.

Determination of the constant by the stationary state method

This is an alternate method to the one described above, which is useful to compare and evaluate whether the constant (K) assessed by the above method is correct. The method consists of applying a constant voltage (V_c) through the micro calorimeter electric resistor until the voltage generated by the calorimeter (V_t) reaches the condition of stationary state. Under these conditions, K, is given by:

$$K = \left(\frac{V_c i}{V_t}\right)_{\text{stationary}} \tag{2}$$

Microcalorimeter of the precision

To establish the precision of the equipment built [24–29], we determined the heat of neutralization for tris-(hydroxymethyl)-aminomethane (THAM)-HCl.

This system was chosen to agree with the one reported by IUPAC [30] as reference for its use in physical chemistry. Recently, the International Confederation for Thermal Analysis and Calorimetry (ICTAC) made a review of the reference systems used in calorimetry and thermal analysis and recommended THAM-HCl system because of its high enthalpy and fast reaction time.

For this purpose, 0.5 g of THAM were placed in the vial and 10.0 mL of HCl 0.1 N in the calorimetric cell.

Once the signal was stabilized, the vial was broken. This procedure was repeated several times to obtain a statistic sample.

Activation procedure

A sample of Colombian coffee husk was pyrolized in a horizontal controlled atmosphere furnace (Carbolite, CTE 12/75). The sample was placed in a quartz boat, and pushed into the hot zone of the furnace. The sample was heated at 350°C under gas flow nitrogen for 2 h at 100 mL min^{-1} and subsequently activated at 600°C for 2 h in presence of N_2 (100 mL min^{-1} flow rate).

Measurement of adsorption isotherms of heavy metals

In this study the following reagents were used: Lead sulfate ($PbSO_4$) (Merck R.A.); potassium dichromate ($K_2Cr_2O_7$) (Merck R.A.); hydrochloric acid (HCl, Merck R.A.); sodium hydroxide (NaOH, R.A.). All the reagents used were of the highest possible grade. Millipore milli-Q deionised water, with a conductivity of 18.2 MW cm, used for all reagent solutions. The adsorption of Cr(VI) and Pb(II) carried out in a batch process at 298 and 318 K solutions were prepared in deionised water using $PbSO_4$ and $K_2Cr_2O_7$, respectively.

For the sorption isotherm studies the initial concentration of metal varied from 10 to 120 mg L^{-1}. For each solution, the concentration was studied as a function of time. The total time of an experiment was 3 h. During this time, 10 samples were taken at given time intervals. Samples were analysed by atomic absorption (AA) spectrometry.

Adjustments to pH were made with 0.1 mol NaOH or 0.1 mol HCl. During these tests the metal concentration (100 mg L^{-1}), the stirring speed (300 r min^{-1}) and the temperature (298 and 318 K) were kept constant.

The stirring speed, pH and ionic strength (001 M) of the solutions were adjusted to values constants.

Adsorption tests were carried out in the metal concentration range of between 10 and 120 mg L^{-1}. Cr(VI) and Pb(II) concentrations were analysed using a Perkin-Elmer Analyst 300 coupled to a computer and printer.

Determination of the immersion heats

A sample of activated carbon weighed exactly was degassed overnight at 250ºC during 24 h. The calorimetric heat effects of the immersion of the dry activated carbon into aqueous solutions of Pb and Cr were measurements at 298 and 318 K with a designed calorimeter. Usually, 10–20 mg of activated carbon was placed in the cell calorimetric and brought in contact with 8 mL of a given solution.

Results and discussion

Electric calibration of the calorimeter (by applying electric power)

The calibration constants obtained for the calorimeter at operation conditions presents the values at different voltage levels at ranges between 12.34±0.12 and 16.67±0.32 W V^{-1}. These values show the sensitivity of the calorimeter, which is higher than that of other equipment reported in the literature. This increased sensitivity constitutes a significant contribution to the construction of this type of instruments.

Figure 2 shows a typical curve obtained with the calorimeter that corresponds to an electric energy of 1 J inside the cell, which contains distilled water. From this type of curves the calibration constant (*K*) can be obtained.

By stationary state method

Figure 3 illustrates a curve obtained when an electric power of approximately 6 mW dispersed inside the micro calorimetric cell.

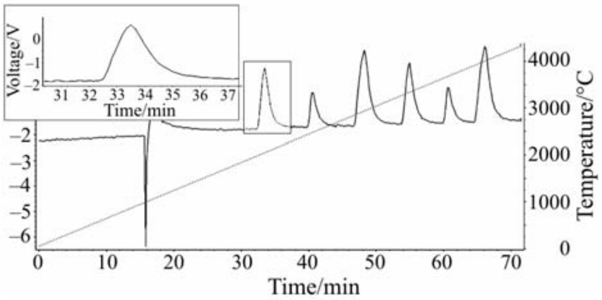

Fig. 2 A typical curve of electric calibration by electrical input

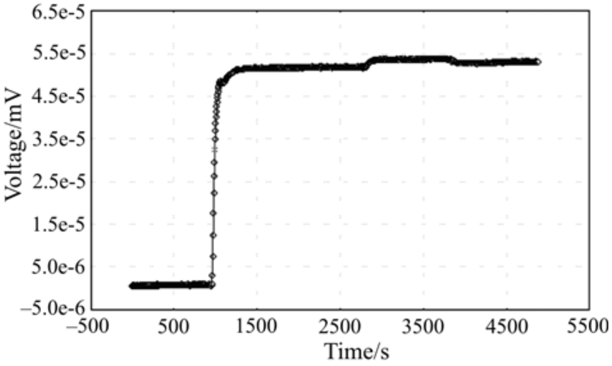

Fig. 3 Curve of electric calibration by stationary state

8 mL of distilled water was placed in the calorimetric cell and the system allowed thermal stabilization. This was confirmed by the stability of the baseline. The readings of thermometric potential were started and different heating powers were set, in a range between 20 and 200 mW, which dispersed inside the cell through a heating electric resistance of 22 ohm and 10 W. The potential readings were continued until the stationary state was reached, which allowed to identify the maximum potential achieved by the system when a specific heating power was dispersed inside it.

Once the stationary state was reached, the heating was stopped and the cooling curve of the system was performed, from different potential levels. Table 1, presents the results obtained when a stationary heating power was dispersed in the cell, which produces a potentially stationary output too. The relation between these magnitudes provides information about the sensitivity and the instrumental constant. Table 1 shows the recording time in seconds for each electric heating. The heating power in mW; the potential difference, ΔE, in mV; the sensitivity, S, in V W^{-1}; and the equipment constant, k, in W V^{-1}.

Table 1 Determination of the sensitivity and the calorimetric unit constant

Recording *t*/ s	Heating power/ mW	ΔE/ mV	*S*/ V W^{-1}	*k*/ W V^{-1}
15000	223.3	4.81	0.079	12.6
	211.2	4.29	0.078	12.9
	124.8	3.70	0.075	13.4
	121.4	3.12	0.073	13.6
30000	19.1	2.82	0.079	12.7
	18.2	2.24	0.079	12.6
40000	25.3	1.65	0.079	12.6
	25.2	2.52	0.078	12.8
	21.5	1.61	0.077	13.0
	21.6	1.01	0.076	13.2
	21.7	0.65	0.076	13.1

S – sensitivity, *k* – calorimeter constant

As it can be observed, as the heating power increases, the output potential of the calorimetric unit increases too, and this occurs regularly. This allows the calculation of the sensitivity of the calorimetric unit. When considering the statistics for the 11 determinations, values of $7.77\cdot10^{-2}\pm8.00\cdot10^{-4}$ V W^{-1} are obtained for sensitivity and of 12.95±0.05 W V^{-1} for the constant of the unit. The values obtained for sensitivity are lower than those obtained in other works [29, 30] and even lower to our previous works [27] in which, we worked with smaller calorimetric cells. However, in this type of cell, there is an advantage in working with small sample quantities.

The values of the constant of calorimeter *vs.* heating power dissipated through of the calibration resistance are shown in Fig. 4. The constant of calorimeter does not vary within the studied range.

Chemical calibration of the immersion calorimeter

Figure 5 shows a curve where the first peak corresponds to the heat of neutralization of THAM-HCl and the second corresponds to the electric calibration signal.

The results shown are in perfect agreement among them and with the values reported in the literature, thus obtaining an average value of –30.92±0.03 kJ mol^{-1}.

Isotherms of adsorption from aqueous solutions for Pb(II) and Cr(VI) and immersion heats

Figures 6 and 7 show the adsorption isotherms from pH controlled solution for solutions of Pb(II) and Cr(VI) for the activated carbon sample obtained from coffee husk; experimental equilibrium data were fitted to the Langmuir and Freundlich isotherm models. These isotherms were mathematically represented as:

$$q=\frac{q_{\mathrm{m}}KC}{1+KC} \tag{3}$$

$$q=KC^{1/n} \tag{4}$$

where q (mg g^{-1}) is the mass of Pb(II) or Cr(VI) adsorbed per mass of adsorbent. C (mg L^{-1}) is the con-

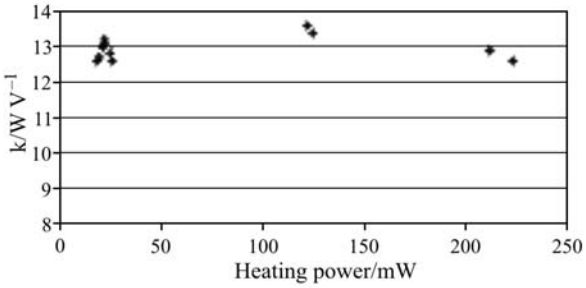

Fig. 4 Determination of the sensitivity and the calorimetric unit constant

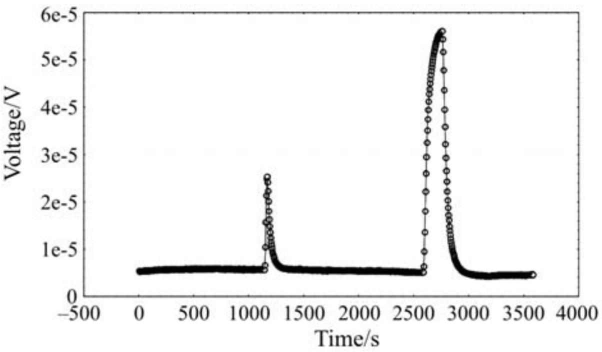

Fig. 5 Curve tris-(hydroxymethyl)-aminomethane (THAM)-HCl system of neutralization

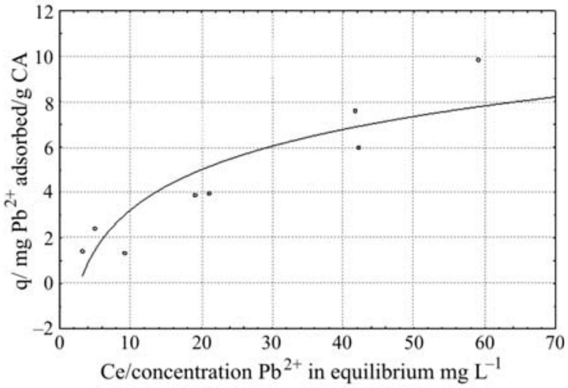

Fig. 6 Adsorption of isotherm of Pb(II) on activated carbon from Colombian coffee husk

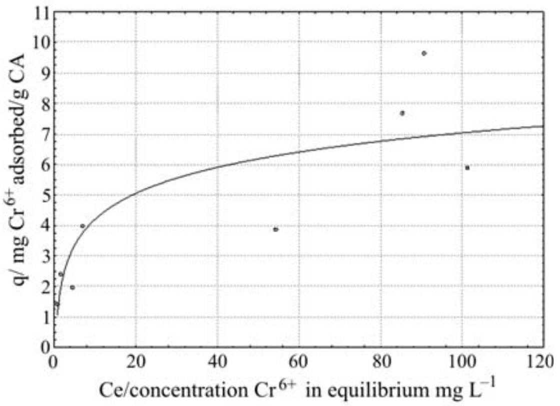

Fig. 7 Adsorption isotherm of Cr(VI) on activated carbon from Colombian coffee husk

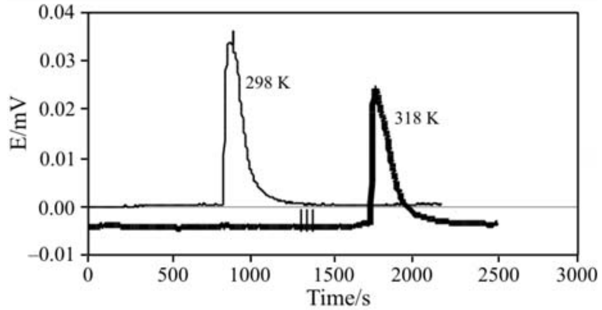

Fig. 8 Curves of immersion of the activated carbon obtained from Colombian coffee husk

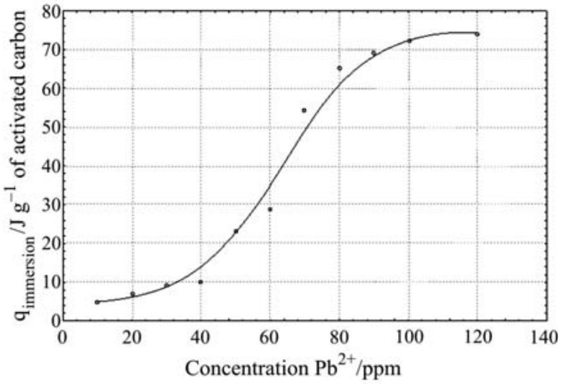

Fig. 9 Immersion heats of the activated carbon in solutions of Pb(II) to 298 K

centration of Pb(II) at equilibrium, q_m (mg g^{-1}) and K (L mg^{-1}) are the Langmuir constants related to the maximum capacity and energy of adsorption, respectively, k (L$^{1/n}$ mg$^{1-1/n}$ g^{-1}) and $1/n$ are the Freundlich constants related to the adsorption capacity and intensity, respectively.

The experimental data fitted better with the Langmuir isotherm than with the Freundlich one since the first one presented smaller percentage deviations.

Effect of temperature on the adsorption isotherm

The effect of temperature on the Pb(II) adsorption isotherm on activated carbon obtained from coffee husk was studied by determining the isotherms at temperatures of 298 and 318 K. It was found that the adsorption isotherms were slightly dependent on the temperature as seen in Figs 5 and 6.

The effect of temperature on K (Langmuir isotherm constant) may be used to estimate the adsorption heat ΔH_{ad}, by means of the following equation [30, 31]:

$$K = k_0 e^{-\Delta H_{ad}/RT} \qquad (5)$$

where k_0 (L mg^{-1}) is the pre-exponential factor, T (K) is the absolute temperature, R (kJ mol^{-1} K^{-1}) is the ideal gas constant and ΔH_{ad} (kJ mol^{-1}) is the adsorption heat.

The experimental values of K were fitted to this equation and the values of K as well as the Eq. (5) were plotted ln$K$ *vs*. $1/T$. In this type graph, it can be noted that the experimental data fitted reasonably well to the Eq. (5). The values of the adsorption heat are $-\Delta H_{ad}$=23.77 kJ mol^{-1}. Thus, the adsorption process on activated carbon is exothermic.

The adsorption of Pb(II) on activated carbon is favoured by lowering the temperature since the Pb(II) adsorption is an exothermic process. Moreover, the adsorption capacity increased very slightly by raising the temperature since the adsorption heat is very low.

At higher temperatures it is observed that the immersion heat is lower, which is related to the smaller amount of adsorbed ion Pb(II) on the surface of the carbon, which allows the follow-up of this procedure by means of the calorimeter.

Figures 9 and 10 show the immersion heats based on the concentration at two different temperatures (298 and 318 K), which compared to the solution isotherms show a correlation between the immersion heats and the solution concentrations in which the immersions are done. The heat results of immersion in carbon samples, demonstrate that the adsorption process of these ions that can be followed on the surfaces of porous solids not

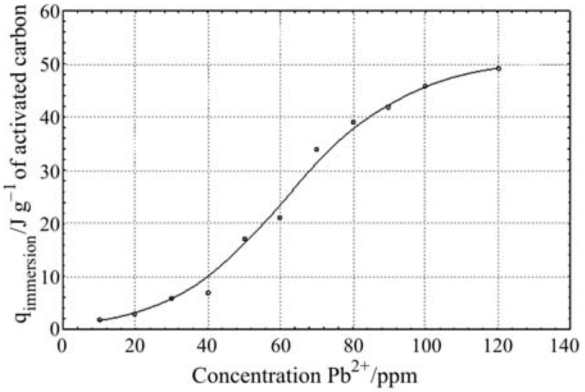

Fig. 10 Immersion heats of the activated carbon in solutions of Pb(II) to 318 K

only by means of aqueous solutions isotherms but also using calorimetry. Moreover, this illustrates the advantages of the built equipment. It is necessary to point out that the obtained immersion heats for the two temperatures differ in magnitudes; for smaller temperature, the heats are greater which can be related to the greater amount of adsorbed ions with respect to the greater temperature. In conclusion, the preliminary results are very promising; they show that calorimeters like this can be used to establish the performance of these types of interactions from the thermodynamic point of view [23–29].

Conclusions

A new calorimeter for heat conduction was built. It was used to determine the adsorption Pb(II) and Cr(VI) on activated carbon obtained from Colombian coffee husk with promising results.

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