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Adsorption of Bentazone from Aqueous Solutions Using Silica Particles

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***Abstract*— Among various water purification and recycling technologies, adsorption is a fast, inexpensive and universal method. The development of low-cost adsorbents has led to the rapid growth of research interests in this field. We have studied the kinetics and thermodynamics of the adsorption of bentazone on silica as a function of agitation time, adsorbent dose and temperature in a batch process. We tried to find the best fitting between experimental data and several theoretical models (Langmuir, Freundlich, Brunauer-Emmett-Teller (BET) and Temkin). As a result, the adsorption isotherms follow a BET model. The adsorption kinetics was analyzed by using pseudo first order and pseudo second order models. Thermodynamic parameters of adsorption process (ΔG, ΔS and ΔH) were computed. The effect of contact time on the removal efficiency of studied substances was investigated. The highest removal efficiency of bentazone was achieved by the adsorption on silica particles. The adsorbent investigated exhibited potential applications in water decontamination and treatment of industrial and agricultural waste waters.**

***Index Terms*—Adsorption, bentazone, herbicides, silica particles.**

I. INTRODUCTION

Environmental protection has become a priority all over the world in the last years. Pollution of surface and ground waters causes risk to human health because of the potential hazards of their contents in inorganic and organic compounds. Pesticides are a group of hazardous compounds that may pollute water due to their extensive application in agriculture as insecticides, repellants, fumigants, fungicides, herbicides and plant growth regulators. The contamination of surface and ground water has increased, and this affects the environment and the health of human beings [1].

Although pesticides, as trace pollutants, are found in the environment in very low concentrations, they are responsible for considerable toxicity effects found in nature [2].

However, biological processes are necessary to remove the organic matter associated with contaminated waters (around 80%), in order to lower inconveniences in the subsequent treatment stages. The most popular tertiary treatments include adsorption and oxidation processes [3]- [5]. There are several procedures available for pesticides removal from water and soil which include photocatalytic degradation [6], ultrasound combined with photo-Fenton treatment [7], advanced oxidation processes [8], aerobic degradation [9], electrodialysis membranes [10], ozonation [11] and adsorption. Powdered silica is widely used in adsorption of organic solutes from the aqueous phase [12]. Zhao et al prepared mesoporous silica materials and used them for adsorption of organic pollutants in water [13].

Bentazone (3-isopropyl -(1H)-2,1,3-benzothiadiazin -4(3H)-one-2,2-dioxide, Fig.1) is a contact post-emergence herbicide which can provide effective control of broad-leaf weeds and sedges in many crops, such as beans, corn, rice, peanuts and peas. It is absorbed by the leaves and has a short herbicidal effect [14].

Bentazone is very mobile in soil, and therefore it has the potential to contaminate surface water. It is stable to hydrolysis, but it is photodegraded in less than 24 hours in water and soil and it is degraded aerobically (its half life varies from 7 days to 14 weeks). Although its degradation is relatively fast, bentazone and its metabolites are contaminants.

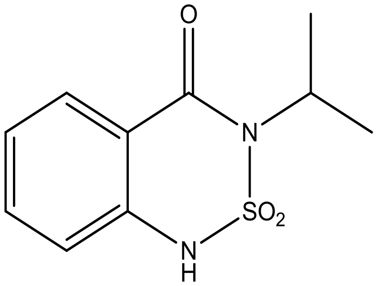

Fig.1: Bentazone molecular structure.

Sorption to solid phases is a key process for the environmental fate of potentially toxic and bioaccumulative pollutants. Adsorption is a simple, easy and economical method for removing substances from aqueous media and soils. An adsorption isotherm is a curve describing the phenomenon governing the retention or mobility of a substance from the aqueous media or aquatic environments into a porous solid-phase at a constant temperature, pH and ionic strenght. In the literature we can find thousands of isothermal adsorption measurements on a wide variety of porous solids. Despite this diversity, most of these isotherms, which are the result of physical adsorption, can be conveniently grouped into six classes according to the IUPAC classification. The first five types of classification (I to V) were originally proposed by Brunauer, Deming, Deming and Teller and they are known as BDDT (also referenced as Brunauer classification). Type VI isotherm is more recent and it is known as step isotherm; it is a rare class but it is interesting from a theoretical point of view [15].

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Isotherms provide valuable information about the characteristics of the solid adsorbent (Fig.2).

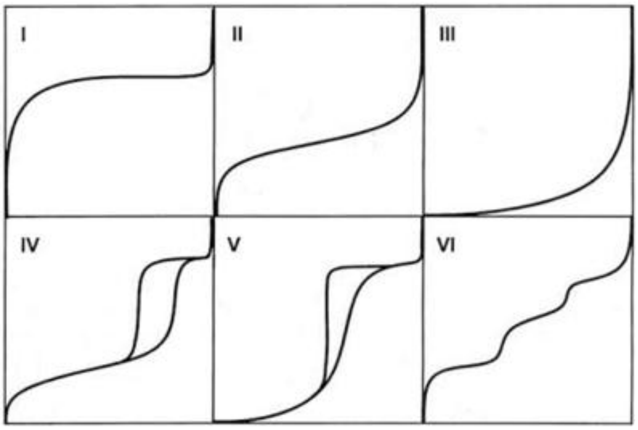

Fig.2: Six different IUPAC adsorption isotherms.

II. MATERIALS AND METHODS

A. *Solid Characterization*

Measurements were performed on FTIR Bruker Equinox 55, between 400 and 4000 cm^{-1}, with a resolution of 4 cm^{-1}. All solid samples were mixed with pure dry KBr in an agate mortar to a fine powder. Tablets were formed applying 4 ton/m^2 by means of a press.

i) Adsorbate: Bentazone

The herbicide bentazone (molecular formula: $C_{10}H_{12}O_3N_2S$; molecular weight: 240.3 g/mol; solubility in water: 0.5 g/L, mp = 138-139ºC [16]) was synthesized and purified according to modified version of literature procedures [17]. The product was analyzed by FTIR spectroscopy, GC-MS and HPLC- MS.

Fig.3, shows the IR spectrum of bentazone. A sharp peak is observed at 750 cm^{-1} due to ortho substitution of benzene ring. At 1700 cm^{-1} the spectrum shows a peak corresponding to the stretching of C=O bond. There are three peaks at 1356 cm-1 own to vibration of SO_2 group. A broad band is observed between 2900 and 3200 cm^{-1} due to vibration of N-H bond.

Fig.4 shows the chromatogram obtained for bentazone and its ESI-MS spectrum.

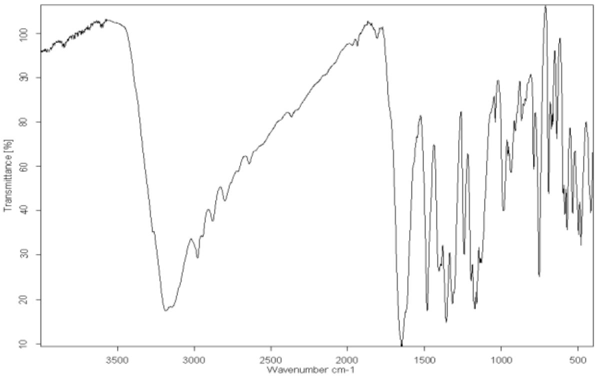

Fig.3: FTIR spectrum of bentazone.

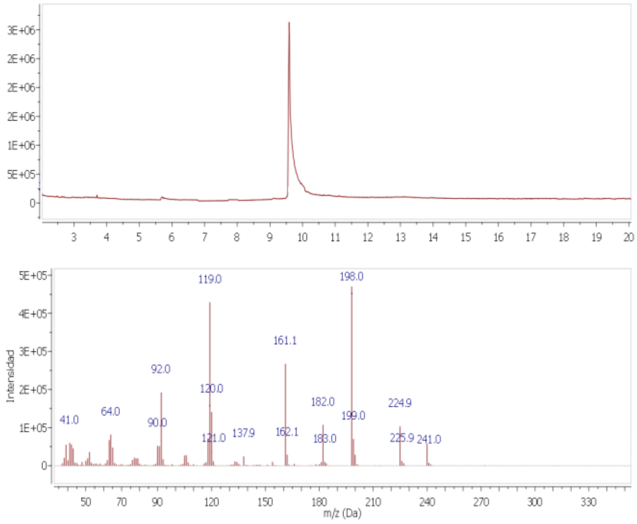

Fig.4: ESI-MS of bentazone.

ii) Adsorbent: Silica

Silica particles were dried in a crucible for 15 h at 120ºC and then in a muffle for 3 h at 250ºC, and stored in a desiccator. Silica was characterized by FTIR spectroscopy [18]. Specific surface area and pore distribution were determined by BET method.

IR spectrum of the silica is shown in Fig.5. A broad band is observed between 3400 and 3500 cm^{-1} due to symmetric and asymmetric vibrations of Si–O–Si groups. Likewise, vibration bands Si-O-Si corresponding to the symmetric and asymmetric vibrations are located at 810 and 1107 cm^{-1}, respectively. The small shoulder observed near 960 cm^{-1} is assigned to the Si-OH groups. The band appearing at 1629 cm^{-1} is attributed to flexing of the SiO-H group.

Identifying the pore structure of the adsorbent, which is commonly determined by the adsorption of inert gases, is an essential procedure before designing the adsorption. There are various methods for determining the specific surface of a solid, for example, N_2 adsorption [19], adsorption of H_2O [20], titration with NaOH [21]. N_2 adsorption technique was used to determine the specific surface area of silica and pore size distribution using BET theory. The BET surface area is 263.7389 m^2/g, and the Langmuir surface area is 3204.0138 m^2/g. The external surface area (236.5320 m^2/g) and the micropore area (27.2069 m^2/g) were determined by t-plot method. The method of Barrett, Joyner, and Halenda (BJH) is a procedure for calculating pore size distributions from experimental isotherms using the Kelvin model of pore filling. It applies only to the mesopore and small macropore

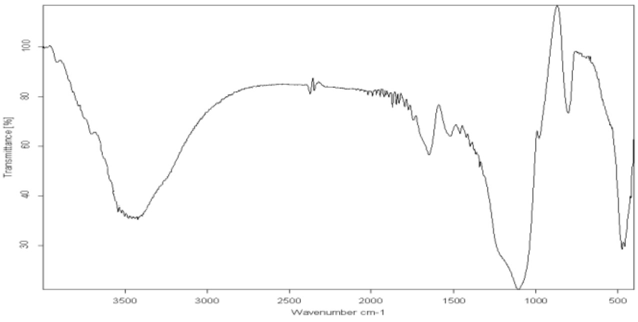

Fig.5: FTIR spectrum of silica particles.

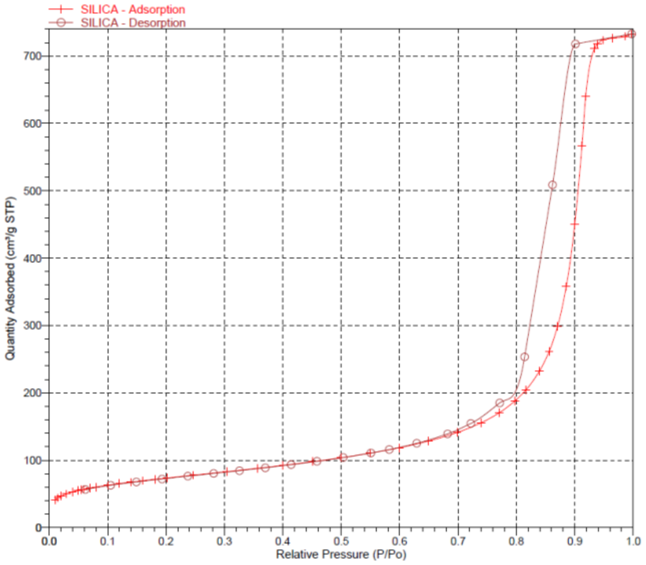

Fig.6: N_2 adsorption on silica.

size range. BJH adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å is 280.464 m^2/g. Average pore width is 176.9270 Å. Therefore, the solid has mesopourus characteristic which could be verified by N_2 adsorption isotherm (Fig.6).

The isotherm obtained is type IV. This is characteristic of mesoporous solids, in which adsorption occurs through a multilayer filling mechanism. At low pressures, the isotherm behaves like a type II one, and one of its distinctive features is its hysteresis loop. This is also typical of mesoporous solids. The appearance of the hysteresis loop during the filling of the mesopores is governed by a capillary condensation phenomenon.

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B. *Adsorption Equilibrium Studies*

The objective proposed is to reduce the bentazone concentration from an initial value of C_o to C_e (mg/L) for a single stage batch adsorption system in a solution of volume V (L).

In a batch-equilibration technique, we put 0.050 g of silica particles and 10 milliliters of bentazone solutions (1, 2, 4, 6, 8 and 10 mg/L) into 25 ml conical flasks. Solutions were prepared in 0.01 M $CaCl_2$ in order to maintain constant ionic strength (I=30mM). Initial solutions were set to pH 4.0 using HCl, and no buffers were used (because they may cause precipitation and affect the adsorption). The flasks were magnetically stirred at room temperature (293 K) at 120 rpm for pre-determined time intervals using thermostatic rotary orbital shaker. Once reached the equilibrium time (each system was maintained with agitation for 48 h to ensure equilibration), each conical flask was centrifuged and filtered using nylon filters of 0.45 µm. Each sample was analyzed by HPLC using an isocratic mobile phase MeOH/aqueous NH4Ac 50:50 through a C-18 column (5 µm particle size, 4.6 x 150 mm). The chromatographer was equipped with two in-tandem detectors: a diode array (DAD) and a mass spectrometer single quadrupole. The maximum wavelength was 224 nm. ESI-APCI source in positive mode was used for ionizing samples. The retention times were approximately 3.5 minutes.

The amount of bentazone adsorbed (q_e) was calculated by using the mass balance equation

$$q_e = (C_o - C_e)\, V/m \qquad (1),$$

where C_o and C_e (in mg/L) are the liquid-phase concentrations of bentazone initially and at equilibrium, respectively, V is the volume of the solution (in L) and m is the mass of dry adsorbent used (in g). The amount adsorbed is plotted vs. the concentration of the solution equilibrium. All measurements were performed at least in duplicate.

In several experiences, the temperature and the amount of silica were changed. The adsorption values were measured before and after treatment at their respective adsorption maximum wavelength, and they were used for calculating the amount of bentazone adsorbed qe (mg/g). The effect of adsorbent dose was studied by varying silica dose from 0.025 to 0.065 g for different bentazone concentrations (1; 2; 4; 6; 8 and 10 mg/L). Sodium hydroxide and hydrochloric acid solutions were used for regulating pH.

Temperature studies were also carried out using 10 mL of bentazone solutions (1; 2; 4; 6; 8 and 10 mg/L) setting different temperatures (20, 30 and 40ºC) to evaluate the effect of temperature on the adsorption process.

We also carried out control experiments without silica in order to evaluate the adsorption of herbicide by the container walls. It was found that there was no detectable degradation or adsorption of herbicide by the container walls.

The amount of silica (generally 0.05 g), pH 4.00 and room temperature (20ºC) were maintained in all experiments unless otherwise stated.

Adsorption tests were repeated using water samples drawn from the Río de La Plata as a solvent (instead of distilled water). The results did not differ more than 10% from those made under ideal conditions. These water samples were collected in November 2014 from 10 stations along the shore of the Río de La Plata near the city of Punta Lara (Ensenada, Province of Buenos Aires, Argentina). They were collected with 4 L glass bottles at a depth between 5-15 cm. Glass bottles were carefully washed with distilled water-detergent and rinsed with ethanol, acetone and pesticide grade n-hexane before sampling. Sampling was done from the bow of a slowly moving boat to minimize any possible contamination.

III. RESULTS AND DISCUSSION

A. *Effect of Contact Time on Adsorption*

The effect of contact time on herbicide concentration is shown in Fig.7.

It is observed that the curve shows a plateau after approximately 35 h, indicating that the adsorption reached equilibrium.

Adsorption kinetics

Two models [22]-[26] were tested in order to explain the adsorption behavior of silica particles: the pseudo first order and pseudo second kinetic models.

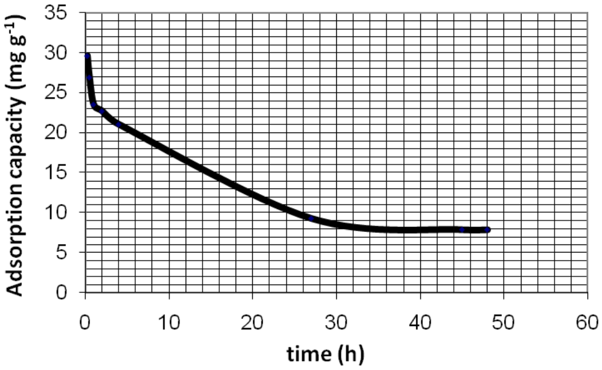

Fig.7: Effect of contact time on herbicide concentration.

i) Pseudo first order equation

The pseudo-first-order equation is generally expressed as [27]

$$dq_t/ dt = k_1 (q_e - q_t) \qquad (2),$$

where k_1 is the pseudo-first-order rate constant. After integrating and applying conditions (q_t= 0 at t = 0 and q_t=q_t at t=t), then (2) becomes

$$\log(q_e – q_t) = \log q_e – (k_1/2{,}303)t \qquad (3),$$

where q_e is the amount adsorbed at equilibrium.

ii) Pseudo second order equation

If the rate of adsorption is a second order mechanism, the pseudo-second-order kinetic rate equation is expressed as

$$dq_t/dt = k_2 (q_e – q_t)^2 \qquad (4),$$

where k_2 is the pseudo-second-order rate constant. Integrating (4), then we obtain

$$t/q_t = (1/k_2q_e^2) + (1/q_e)t \qquad (5).$$

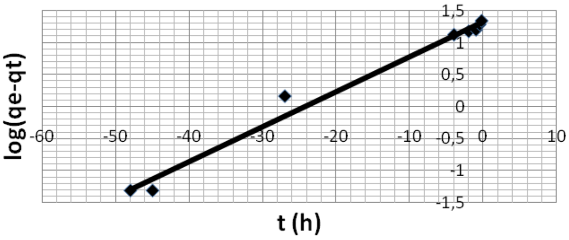

Fig.8: Plot of pseudo-first-order kinetic models.

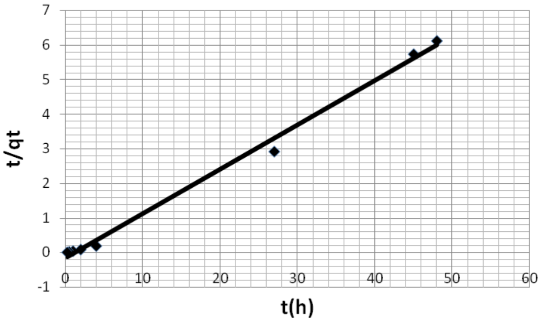

Fig.9: Plot of pseudo-second-order kinetic models.

Plots of pseudo-first-order and pseudo-second-order kinetic models are given in Fig. 8 and 9, respectively.

In order to compare the fit between experimental data and each model, values are calculated and listed in Table 1.

Both models can explain the kinetics, but the R^2 obtained for pseudo-second-order kinetic model is higher than R^2 obtained for pseudo-first-order kinetic model.

Table 1: Kinetic parameters obtained from adsorption of bentazone onto silica.

Kinetic Model	Parameter	Value
Pseudo first order	r^2	0.985
	k_1	0.124
Pseudo second order	r^2	0.995
	k_2	0.103

B. *Adsorption Isotherm*

Different theoretical adsorption models were tested on the observed bentazone-on-silica isotherms: Langmuir, Freundlich, BET and Temkin.

- Langmuir isotherm equation is

$$qe = Q_0bCe/(1 + bCe) \qquad (6),$$

where C_e is the equilibrium concentration of the bentazone solution (mg/L) at equilibrium, q_e is the amount of bentazone adsorbed at equilibrium (mg/g) and Q_0 and b are Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively.

This equation can be linearized (Fig.10) as

$$C_e/q_e = 1/bQ_0 + Ce/Q_0 \qquad (7).$$

- Freundlich isotherm equation can be written as

$$q_e = K_F{\cdot}C_e(1/n) \qquad (8).$$

The logarithmic form of Freundlich (Fig.11) is given as

$$\log(q_e) = \log(K_F) + 1/n{\cdot}\log(C_e) \qquad (9),$$

where q_e is the amount of bentazone adsorbed (mg/g), C_e is the equilibrium concentration of bentazone in solution (mg/L), and K_F and n are integrating constants.

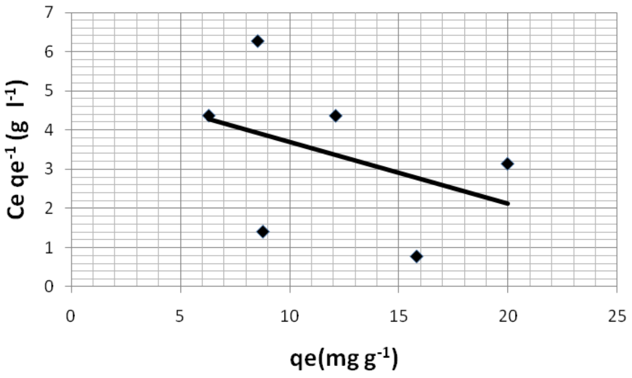

Fig.10: Linearized form of Langmuir isotherm.

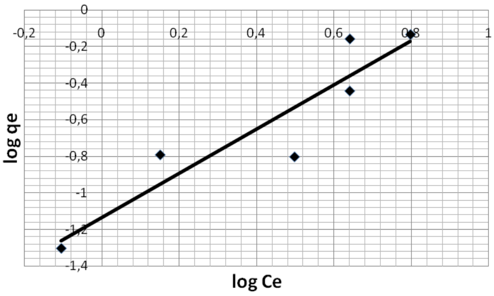

Fig.11: Linearized form of Freundlich isotherm.

- BET equation model is

$$q_e = q_s C_{BET} C_e / [(C_s - C_e) \cdot [1 + (C_{BET} - 1) \cdot (C_e/C_s)]] \qquad (10).$$

The linearized form of BET equation (Fig.12) can be expressed as

$$C_e / [q_e (C_s - C_e)] = 1/qsC_{BET} + (C_{BET} - 1) \cdot C_e / (q_s C_s C_{BET}) (11),$$

where q_s is the theoretical isotherm saturation capacity (mg/g), C_{BET} is related to the energy of surface interaction (L/mg), C_e is the equilibrium concentration (mg/L) and Cs is the adsorbate monolayer saturation concentration (mg/L).

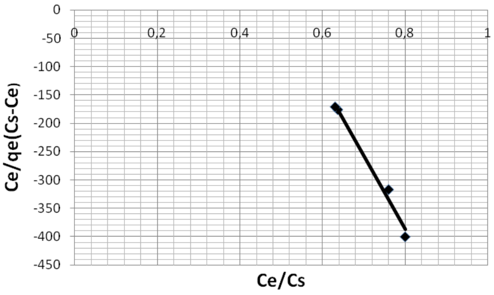

Fig.12: Linearized form of BET isotherm.

- The Temkin isotherm model is given by the equation

$$qe = (RT/b_T) \cdot ln(A_T C_e) \qquad (12),$$

where $(RT/b_T$, in J/mol) corresponds to the heat of adsorption, R is the ideal gas constant, T (K) is the absolute temperature, A_T is a binding constant corresponding to the maximum binding energy and b_T is the Temkin isotherm constant. This equation can be linearized to

$$q_e = (RT/b_T) \cdot ln\ A_T + (RT/b_T) \cdot ln\ C_e \qquad (13)$$

The graphic obtained is shown on Fig.13.

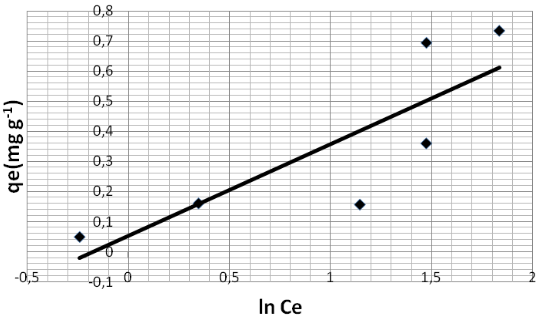

Fig.13: Linearized form of Temkin isotherm.

The analysis of the R^2 values obtained from the linearized forms of the adsorption curves shows that the best fit was obtained for the BET isotherm.

The isotherm can be characterized as a type IV one. The existence of stepwise isotherms can be attributed to a multilayer mechanism. Each section can represent a Langmuir-type isotherm. This is a reasonable assumption based on the monolayer adsorption process. The same behavior is observed in others adsorption studies [28].

C. Effect of Temperature

Fig.14 shows the effect of temperature on adsorption at 20, 30 and 40ºC. The process becomes less effective as temperature rises, being the adsorption exothermic. Similar trends on the adsorption of pesticides onto various adsorbents are also reported in the literature [29], [30].

D. Thermodynamic Parameters

Thermodynamic parameters of the adsorption process, such as ΔH and ΔS, are determined using the Eyring's plot. [22], [30]-[32] Equations (14), (15) and (16) are used for determining ΔH and ΔS.

$$\Delta G = -RT\ ln\ K_c \qquad (14)$$

$$\Delta G_{ads} = \Delta H_{ads} - T\ \Delta S_{ads} \qquad (15)$$

$$ln\ K_c = \Delta S/R - \Delta H/RT \qquad (16)$$

In these equations, $K_c = C_{ads}/C_e$ is the equilibrium constant of the bentazone adsorption equilibrium (which is a ratio of C_{ads}, the bentazone concentration in the adsorbent, and C_e, the bentazone concentration in the adsorbate), R is the ideal gas constant in $Jmol^{-1}K^{-1}$ and T is the temperature in Kelvin.

The isotherms show that the pesticide is adsorbed forming multilayers. The values of the thermodynamic functions are obtained from the first part of the adsorption curve, where interactions adsorbate-adsorbent occur. The highest values of qe are due to adsorbate-adsorbate interactions. Free energy changes (ΔG) were calculated using (14)-(16), and they are presented in Table 2.

The negative value of ΔH shows that the adsorption process is exothermic and the positive value of ΔG indicates a non-spontaneous adsorption. However, the positive ΔG value

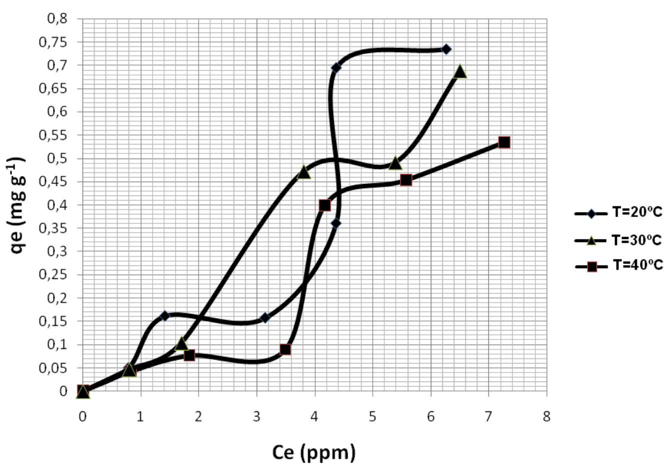

Fig.14: Effect of temperature on bentazone adsorption.

increases as the temperature rises, and this fact indicates that the adsorption spontaneity is disfavored by temperature. The negative value of ΔS shows that adsorbed molecules have less freedom to move over the surface of the adsorbent. These facts are in agreement with other studies of pesticides adsorption onto various materials.

Table 2: Thermodynamic parameters for the adsorption process.

ΔH (kJ/mol)	ΔS (kJ/(Kmol))	ΔG (kJ/mol)	K
-38.04	- 0.148	5.42 (20ºC)	0.999
		6.90 (30ºC)	0.989
		8.38 (40ºC)	0.967

E. Effect of Adsorbent Dose

We also studied the effect of the adsorbent dose on the removal of pesticide. Two different amounts of adsorbent (50 and 67 mg) and six different bentazone solutions (1, 2, 4, 6, 8 and 10 mg/L) were used. Fig. 15 shows that an increase in the concentration of silica particles results in an increase of surface area, with more adsorptive sites for the adsorption to occur. The values obtained for the adsorption capacity rise from 0.160 mg/g (for 0.050 g silica) to 0.845 mg/g (for 0.067 g silica). This curves also adapted to BET isotherm model.

Fig.16 shows the isotherms obtained at the same three temperatures using water from Rio de La Plata as solvent. We can clearly see that there is no more than a 10% difference from the values obtained using distilled water as solvent.

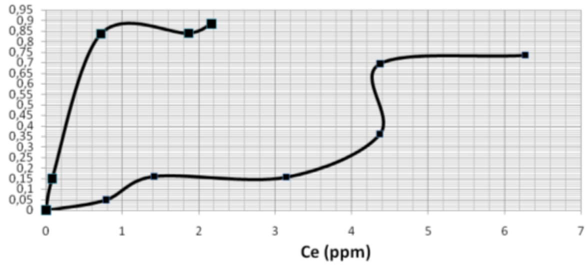

Fig.15: Effect of the adsorbent dose on the removal of pesticide.

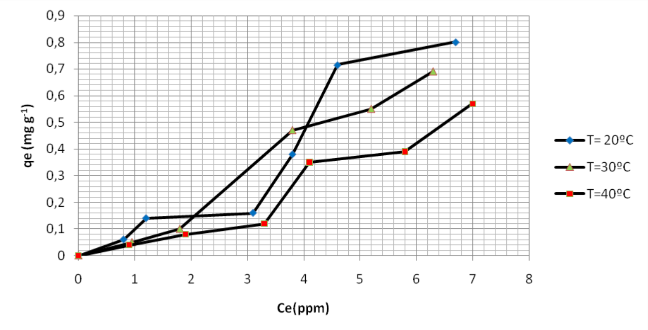

Fig16: Effect of temperature on bentazone adsorption with water from Rio de La Plata

IV. CONCLUSION

The adsorption of the pesticide bentazone was carried out with silica particles as an adsorbent. We concluded that the adsorption of the herbicide bentazone adapts to a type IV isotherm, forming multilayer on the silica surface. From the effect of silica particles dose study, adsorption increases with an increase in silica dose. The adsorption follows a second order kinetics. The adsorption isotherm data were well described by BET adsorption isotherm model. The thermodynamic study reveals that the adsorption process shows a negative value of ΔH, indicating the exothermic nature of adsorption; the positive value of ΔG suggests a non-spontaneous pesticide adsorption process; negative ΔS indicates an increase in the state of order during adsorption.

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