Journal of Environmental Science and Engineering A 10 (2021) 184-197
doi:10.17265/2162-5298/2021.05.004

Optimization of Methylene Blue Pigment Adsorption with Biomass Waste Adsorbent in a Continuous Operating Column

OdysseasKopsidas
Department of Economics, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece

Abstract: The function of adsorption is widespread in industry. After the adsorption process the adsorbent can be discarded after one use. In practice, however, the economics of the process make it necessary to regenerate the adsorbent with the ultimate goal of reusing it. In industry, activated carbon is usually used as an adsorbent which can be regenerated either chemically or thermally. In the present work, a competitive cost adsorbent is used, the raw chickpea straw, which is a discarded biomass by-product. Methylene blue dye was used as the adsorbent. The experiments were performed on bed length columns 15, 25, 75 and 150 cm respectively. The experimental and theoretical points of the adsorption curves for each column length are presented respectively. The experimental diagrams confirm the validity of the Bohart and Adams equation for dilute solutions with low concentrations. Chickpea straw can be offered to the industry as an adsorbent for textile dyes due to its adsorption capacity and low cost. At the same time, from the aggregate diagrams of the dilute solutions listed above, we observe: For Fig. 1 concerning the adsorbents we used we observe that the capacity K_F has a higher value for the ground cork while the lower one for olive ash. Also, for Fig. 2 regarding the adsorbent materials we used we observe n of the isothermal Freundlich has a maximum for olive ash, while a minimum has for two materials lentil straw and ground cork. The database is an important and organizational element of knowledge as its use causes positive economies of scale in the utilization of given scientific knowledge and information. The aim of the present work is to construct an electronic database that includes the existing literature regarding the adsorption conditions of various dyes by some adsorbents.

Keywords: Adsorption, methylene blue, biomass.

1. Introduction

Adsorption is the chemical phenomenon in which various surfaces of solid bodies retain foreign substances from liquids [1]. The surface that holds the substances is called the absorbent, while the holding is called the absorbate [2]. Eleven grams (11 g) chickpea straws were placed in a 15cm bed column, 18.33 g chickpea straws were placed in a 25 cm bed column, while 2,456 g chickpea straws were placed in a 75 cm and a 150 cm bed length column. The pump was calculated at 20 mL/min. Methylene blue, also known as methylene Blue (CI 52015) was used as the adsorbent [3, 4]. The spectrophotometer used in the measurements is an instrument that measures the permeability $T = I_1/I_0$ and gives it as a fraction or percentage in the range 0-1 or 0-100%, respectively. At a special reading scale it gives the absorption directly [5, 6].

The phenomenon of adsorption was first observed on the surfaces of solids, which are sources of attractive forces, because their atoms border one-sidedly with similar atoms of the solid lattice [1]. In this way, however, free affinity units are created on the surface of the solid, which can hold foreign molecules or atoms very strongly [2]. Later, the adsorption phenomenon was observed on wet surfaces, which, however, retain foreign substances with less force than solids [3].

The phenomenon of adsorption is often confused with that of absorption, so it would be appropriate to clarify the difference between the two phenomena [4].

Corresponding author: Odysseas Kopsidas, Ph.D., Post doc researcher, research field: environmental economics.

Absorption is the phenomenon in which the molecules of the foreign substance enter (penetrate) between the molecules of the absorbent medium [5]. Adsorption, on the other hand, is a surface phenomenon, as the adsorbed substance accumulates on the surface of the adsorbent. In fact, the phenomenon of absorption does not occur as it is, but is always accompanied by the phenomenon of absorption in small levels [7, 8].

Database means a collection of systematically formatted related data in which it is possible to retrieve data through on-demand search. American computer scientists report on databases: “When people use the words database, they are essentially expressing the belief that data should be self-identifying and have a schematic structure. This is exactly what the words database describes” [9, 10].

In particular, in computer science and the daily use of computers, the term “databases” refers to organized, distinct collections of related data electronically and digitally stored, to the software that handles such collections (Database Management System, or DBMS) and to cognitive field that studies it. In addition to its inherent ability to store data, the database provides through the design and way of prioritizing data, the so-called content management systems, i.e. the ability to quickly retrieve and update data [11, 12].

In Fig. 1, it is shown the 75 cm plexiglass with absorbent material of chickpea straw and adsorbable aubstance methylene blue and in Table 1, it is shown the database for adsorption of dyes from adsorbents.

2. Experimental Procedure

We record the measurements absorption, concentration (C) that resulted from the spectrophotometer. The adsorbent capacity will be valid:

$$\left(\frac{C_i}{C}\right)^{n-1} - 1 = A \cdot e^{-r \cdot t}$$

The above ratio logged gives:

$$\ln\left[\left(\frac{C_i}{C}\right)^{n-1} - 1\right] = \ln A - r \cdot t$$

Also the initial relation can be resolved with respect to C and used for calculation of the theoretical value of the concentration,

which produced:

$$q = K \cdot C^{\frac{1}{n}}$$

where C, C_i are the concentrations of methylene blue or red reactif 195 (C effluent, C_i influx), t the time, n the inverse of the Freundlich isothermal adsorption gradient, A coefficient and r a constant. At Freundlich adsorption isotherm:

$$\frac{dC}{dt} = \frac{A}{n-1} C_i \cdot \left(A \cdot e^{-r \cdot t} + 1\right)^{-\frac{1}{n-1} - 1} \cdot e^{-r \cdot t}$$

where: q is the amount of methylene blue per unit mass of adsorbent (mg/g), C is the equilibrium concentration of methylene blue in solution (mg/L), $1/n$ is the dimensionless parameter of the Freundlich isotherm and K is its distribution coefficient isothermal Freundlich (L/mg/min) [13-15].

After determining the parameters A, r, n, C_i, then the theoretical value of the concentration C_{theor} is calculated. It is possible to set n = 2.5 instead of determining its optimal value. The standard deviation error could be calculated

$$s = \sqrt{\frac{\sum\left(C - C_{\theta\varepsilon\omega\rho}\right)^2}{n - p}}$$

Fig. 1 Bed length adsorption column 75 cm from plexiglass with absorbent material of chickpea straw and adsorbable substance methylene blue.

Table 1 With the same database for adsorption of dyes from adsorbents.

No.	Topic	Kinetic model order	Model	K_F	n	q_m	K_L	Adsorbate	Adsorbent	Pretreatment	Mechanism	Applications	Authors	Title	Journal	Volume year pages
1	Isotherms		Langmuir					Methylene blue	Hazelnut scells	The shells were washed with deionised water and dried in air overat 1,000 °C for 24 h.		Recycle purpose/color removal from dyehouse effluents	F. Ferrero	Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood Sawdust	Journal of Hazardous Materials	142 (2007) 144-152
2	Isotherms		Langmuir					Acid blue 25	Hazelnut scells	the shells were washed with deionised water and dried in air overat 1,000 °C for 24 h.		Recycle purpose/color removal from dyehouse effluents	F.Ferero	Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood Sawdust	Journal of Hazardous Materials	142 (2007) 144-152
3	Isotherms		Langmuir					Basic Yellow21	Kudzu	Air dried and sieved		Removal of contaminants from waste water	J. Allen	Comparison of optimised isotherm models for basic dye adsorption by kudzu	Bioresource Technology	88 Issue 2 (2003) 143-152
4	Isotherms		Langmuir					Basic Red 22	Kudzu	Air dried and sieved		Removal of contaminants from waste water	J. Allen	Comparison of optimised isotherm models for basic dye adsorption by kudzu	Bioresource Technology	88 Issue 2 (2003) 143-152
5	Isotherms		Langmuir					Basic Red 22	Peat	Milled, air dried and sieved		Wastewater/textiles industries	Gmckay et al.	Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems	Journal of Colloid and Interface Science	280 (2004) 322-332
6	Isotherms		Langmuir					Basic blue 3	Peat	Milled, air dried and sieved		Wastewater/textiles industries	Gmckay et al.	Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems	Journal of Colloid and Interface Science	280 (2004) 322-332
7	Isotherms		Langmuir					Basic Yellow21	Peat	Milled, air dried and sieved		Wastewater/textiles industries	Gmckay et al.	Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems	Journal of Colloid and Interface Science	280 (2004) 322-332
8	Isotherms		Langmuir					Brillant Green	Neem trees	Washed, dried and crushed into a fine powder		Textiles industry	Bhatacharyya and Sarma	Adsorption Characteristics of the Dye, Brilliant Green, on Neem Leaf Powder	Dyes and Pigments	57 (2003) 211-222

Table 1 to be continued

9	Isotherms	Langmuir	Methylene blue	Date pits	Washed, dried, sieved, carbonisation, activation, was hed with 0.1 M H_2SO_4	Textiles industry	Banat et al.	Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters	Process Biocheristry	39 (2003) 193-202
10	Isotherms	Langmuir	Methylene blue	Almond	Dried,mixed with solution $ZnC1_2$, dehydrated activated	Wastewater	Aygun et al.	Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties	Microporous and Mesoporous Materials	66(2003) 189-195
11	Isotherms	Langmuir	Methylene blue	Walnut	Dried,mixed with solution with solution $ZnC1_2$, dehydrated activated	Wastewater	Aygun et al.	Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties	Microporous and Mesoporous Materials	66(2003) 189-195
12	Isotherms	Langmuir	Methylene blue	Hazelnut scells	Dried,mixed with solution with solution $ZnC1_2$, dehydrated activated	Wastewater	Aygun et al.	Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties	Microporous and Mesoporous Materials	66(2003) 189-195
13	Isotherms	Langmuir	Methylene blue	Appricot stones	Dried,mixed with solution with solution $ZnC1_2$, dehydrated activated	Wastewater	Aygun et al.	Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties	Microporous and Mesoporous Materials	66(2003) 189-195

Where n is the measurements that are made and p is the parameters. For the smallest value of the estimation error s (the one that is closer to 0) we will have the optimal value of the parameters.

3. Results of Experimental Procedure

In Table 2, it is shown the experimental data of an adsorption column length 15 cm. In Fig. 2, they are shown the experimental and theoretical points of the sigmoid adsorption curve as a function of (a) volume and (b) time in a 15 cm long column. In Fig. 3, it is shown the flow function over time in a 15 cm long column. In Fig. 4, they are shown the experimental and theoretical points of the sigmoid absorption curve as a function (a) of volume and (b) of time in a 25 cm long column. In Fig. 5, they are shown the experimental and theoretical points of the sigmoidal adsorption curve as a function (a) of volume and (b) of time in a 75 cm long column. In Fig. 6, they are shown experimental and theoretical points of the sigmoid absorption curve as a function of (a) volume and (b) time in a 150 cm long column.

The experimental diagrams confirm the validity of the Bohart and Adams equation for dilute solutions with low concentrations.

4. Theoretical Procedure

When a solution comes in contact with a solid adsorbent, molecules of the adsorbent are transferred from the liquid to the solid, until the concentration of adsorbent in the solution equilibrates the adsorbent to the solid [7, 8]. The elemental equilibrium, at a given temperature, is usually represented by an isothermal adsorption which is the ratio between the amount adsorbed per unit mass of solid and the concentration of adsorbent in solution [9, 10]. Since no equation has been found so far to describe all the mechanisms and shapes of isothermal adsorption, various models describing the phenomenon have been developed which refer to the following: the Langmuir isotherm for adsorption of an adsorbent from a liquid solution; the BET (Brunauer-Emmett-Teller) equation used to describe stratified adsorption [9, 10]; the Freundlich's empirical equation for dilute solutions at low concentrations. It usually describes the adsorption of foreign bodies in a liquid solution of activated carbon [11, 12].

For dilute solutions the Freundlich adsorption isotherm can be written as

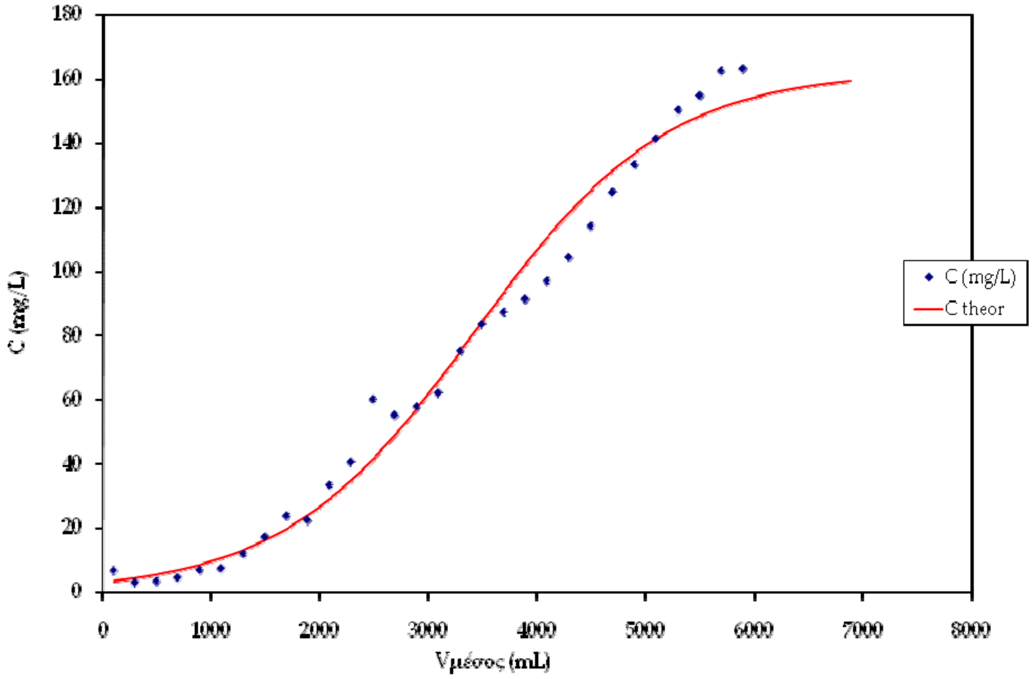
$$q = K_F \cdot C^{\frac{1}{n}}$$

Where q =mg/g of adsorbent, C = mg/L of adsorbent and n, K_F are constant. This equation describes the equilibrium conditions.

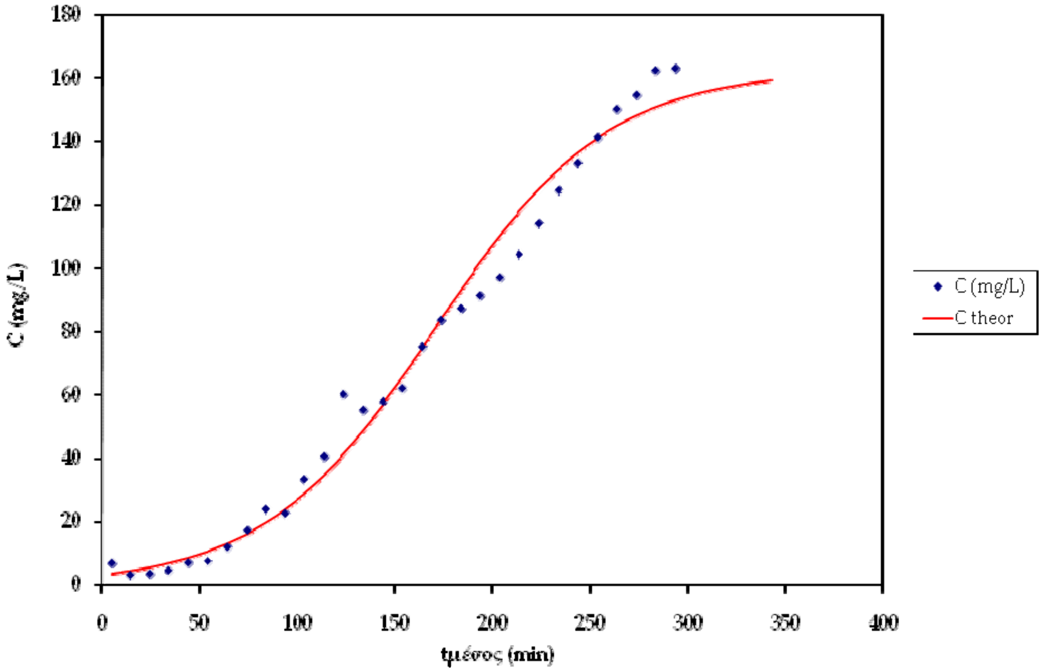
$$\log q = \log K_F + \frac{1}{n} \log C_e$$

Table 2 Experimental data of adsorption column length 15 cm.

C (mg/L)	C_{theor}	dC/dt
6.99	3.62	3.53601214
3.18	4.49	4.368506977
3.62	5.58	5.385462583
4.63	6.91	6.614460019
7.08	8.57	8.120068833
7.57	10.64	9.940840915
12.05	13.16	12.09159886
17.31	16.19	14.57274147
24.00	19.73	17.3312436
22.64	23.90	20.38378922
33.46	28.92	23.76918945
40.64	34.77	27.33076922
60.24	41.43	30.86624139
55.33	48.89	34.17628716
57.95	57.07	37.02412382
62.17	65.75	39.14100777
75.24	74.78	40.36049327
83.68	84.05	40.56833187
87.37	93.18	39.73836732
91.48	101.98	37.96681709
97.11	110.33	35.40453998
104.45	118.07	32.26616499
114.19	125.06	28.79331527
124.68	131.24	25.22302179
133.30	136.59	21.75915399
141.37	141.16	18.51076137
150.32	145.05	15.55109399
154.80	148.29	12.94296652
162.50	150.95	10.70540518
163.12	153.14	8.791913502



(a)



(b)

Fig. 2 Experimental and theoretical points of the sigmoid adsorption curve as a function of (a)volume and (b) time in a 15 cm long column.

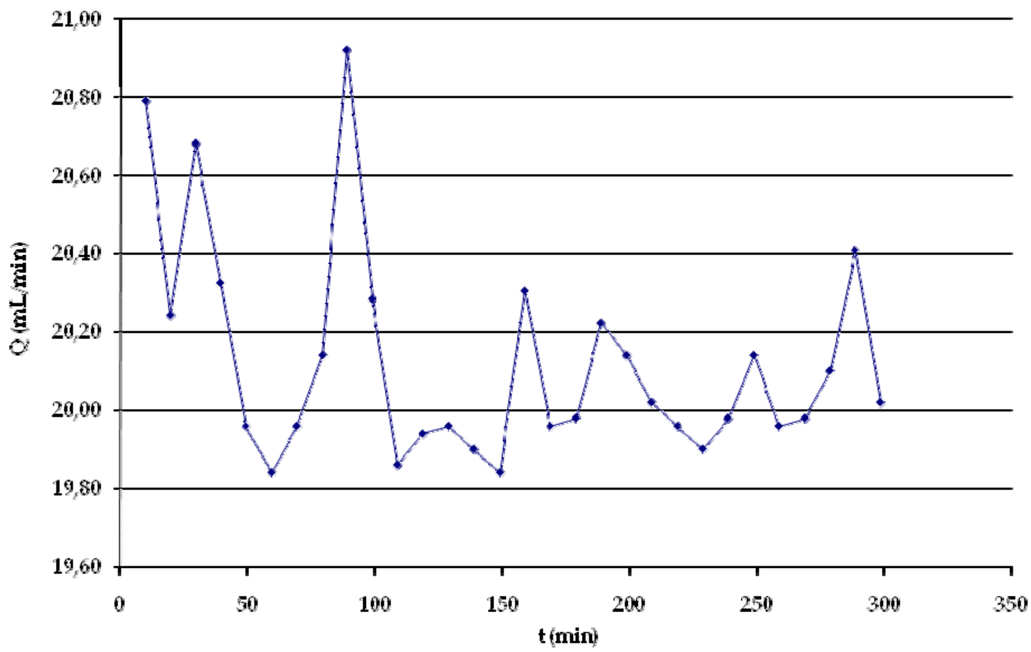


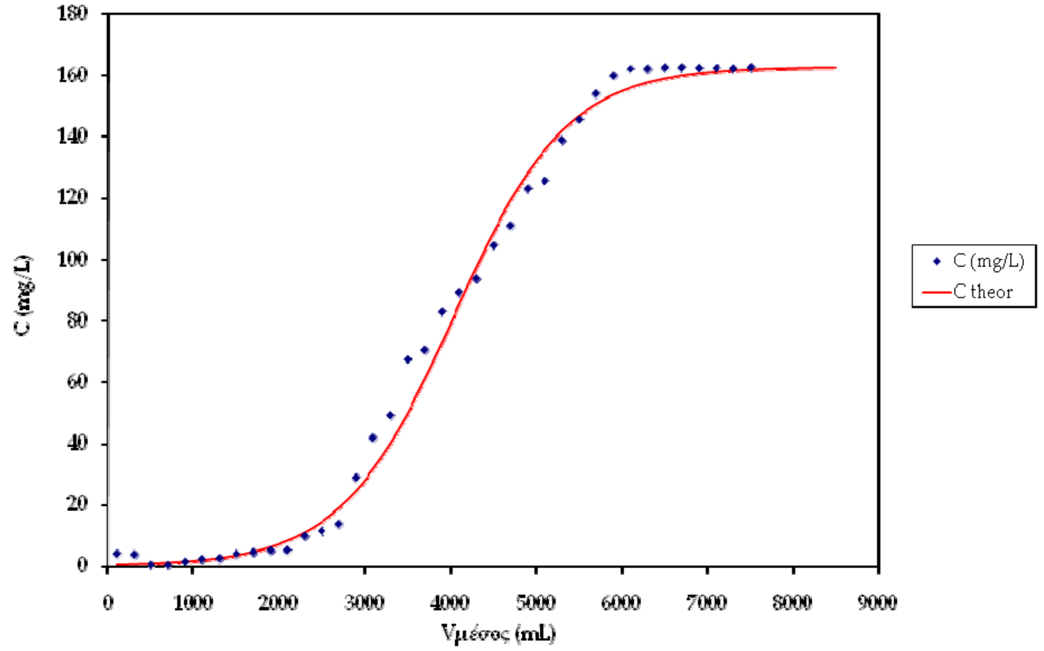
Fig. 3 Flow function over time in a 15cm long column.

Langmuir (1916) adsorption isotherm can be written as

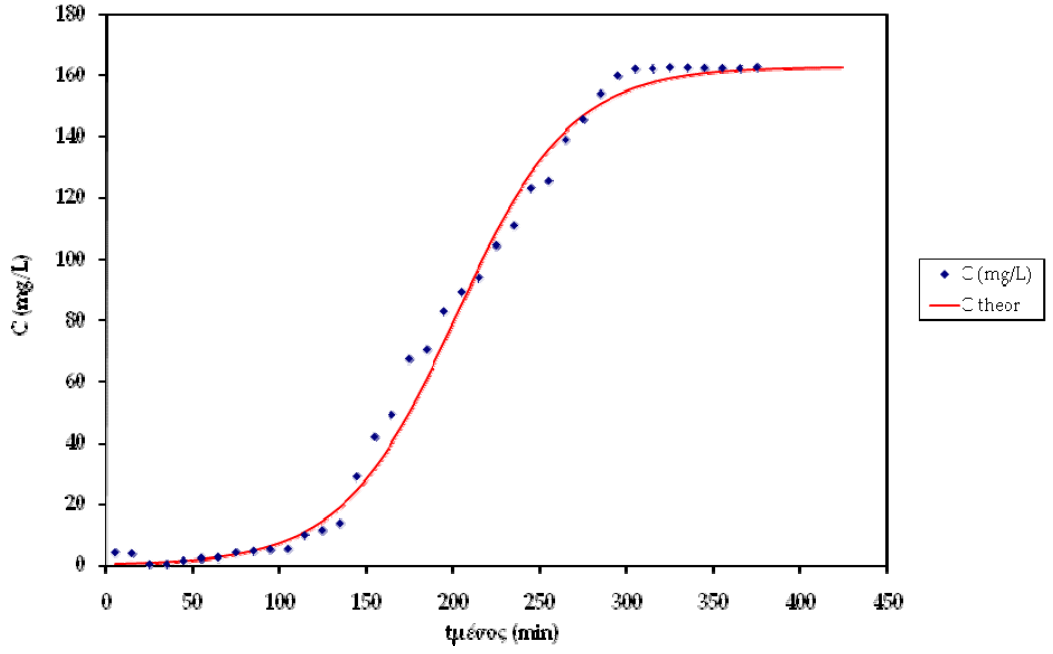
$$\frac{1}{q}=\left(\frac{1}{q_m}\right)+\left(\frac{1}{K_L\cdot q_m}\right)\cdot\left(\frac{1}{C_e}\right)$$

Where K_L is the Langmuir constant associated with the adsorption energy (L/mg) and q_m is the amount of dye absorbed (mg/g) when equilibrium is restored.

Describing the experimental sequence that was followed, we have the following: Place the predetermined amount of H_2O and methylene blue in the 12 flasks (as shown in the proportions in the materials). After filling 1 test tube, take 10 mL from each flask, fill and place cubes in the “Carousel” (the first cuvette is filled with deionized water), for the first 6 bottles we dilute 5:100 and we fill 3 cubes, for the other 6 bottles we do not dilute and we fill 2 cuvettes. Measure the ABS (absorbance) in each sample with the spectrophotometer values for wavelength l = 664 nm for methylene blue and store the values on the PC (Personal computer). Pour 0.5 g of sawdust in each bottle, and stir. After 7 days, take a sample of 10 mL of each solution with a siphon, store them in test tubes and place them in the centrifuge for 5 min to remove sawdust. Repeat steps 2 and 3. Save all the results to the PC.

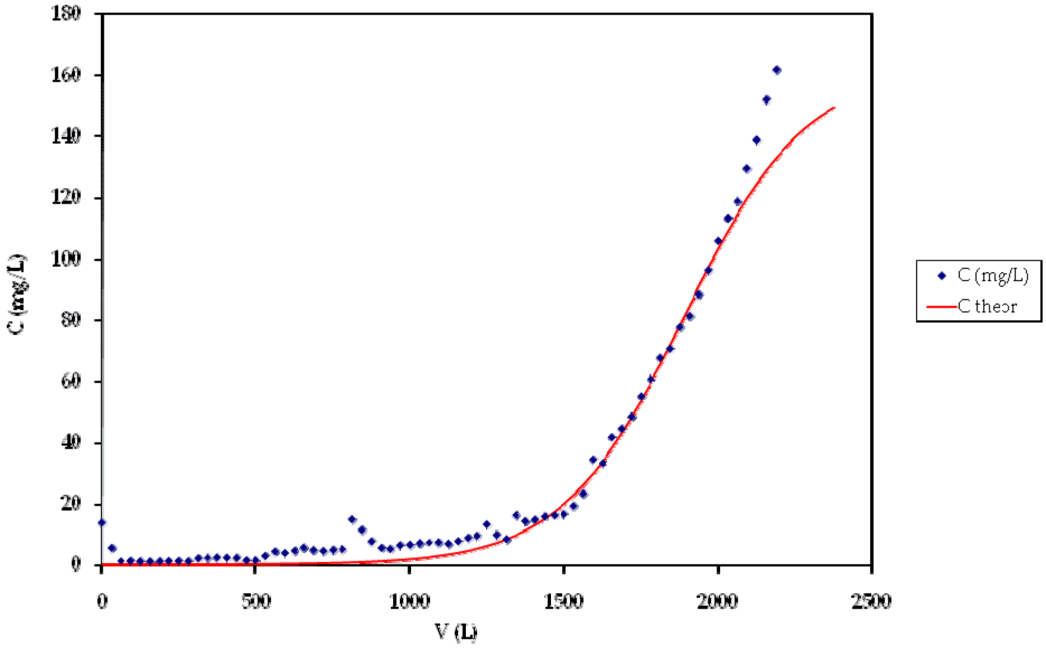


(a)

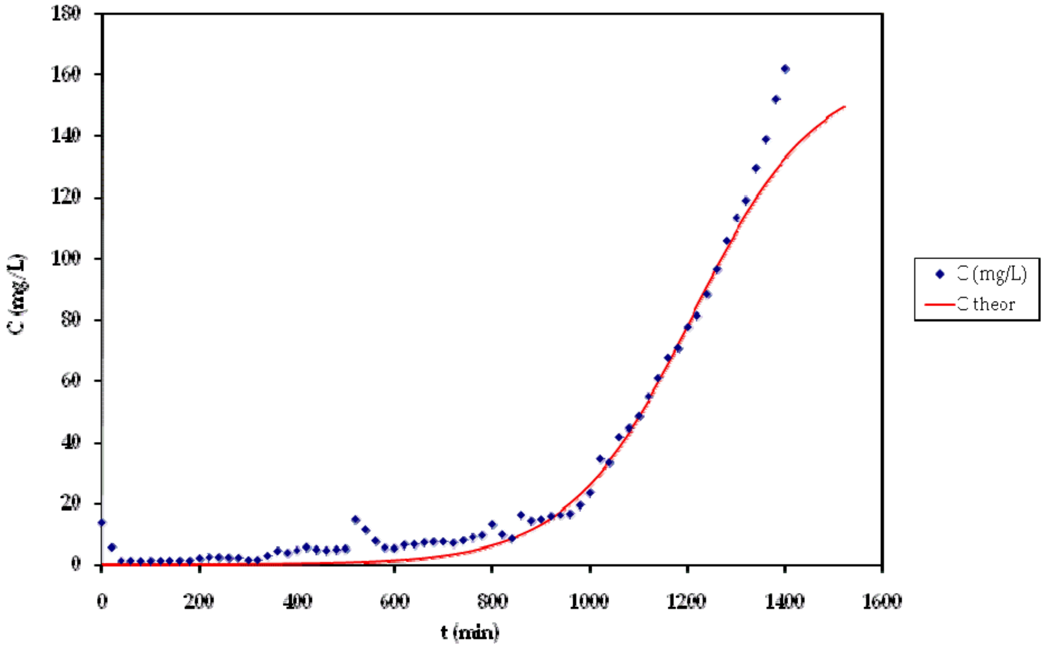


(b)

Fig. 4 Experimental and theoretical points of the sigmoid absorption curve as a function (a) of volume and (b) of time in a 25 cm long column.

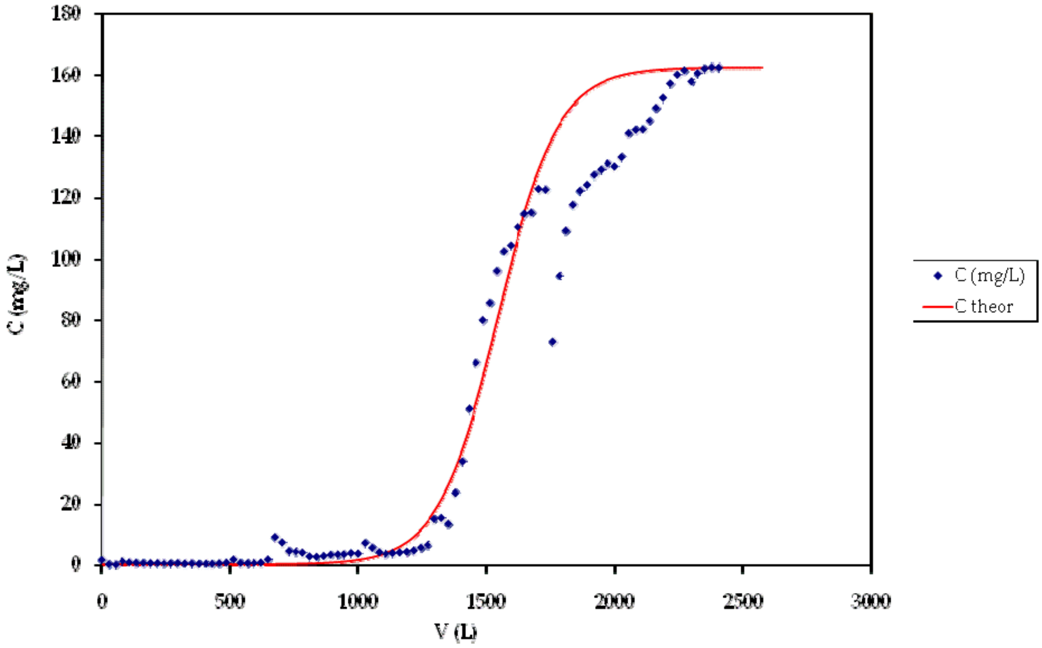


(a)

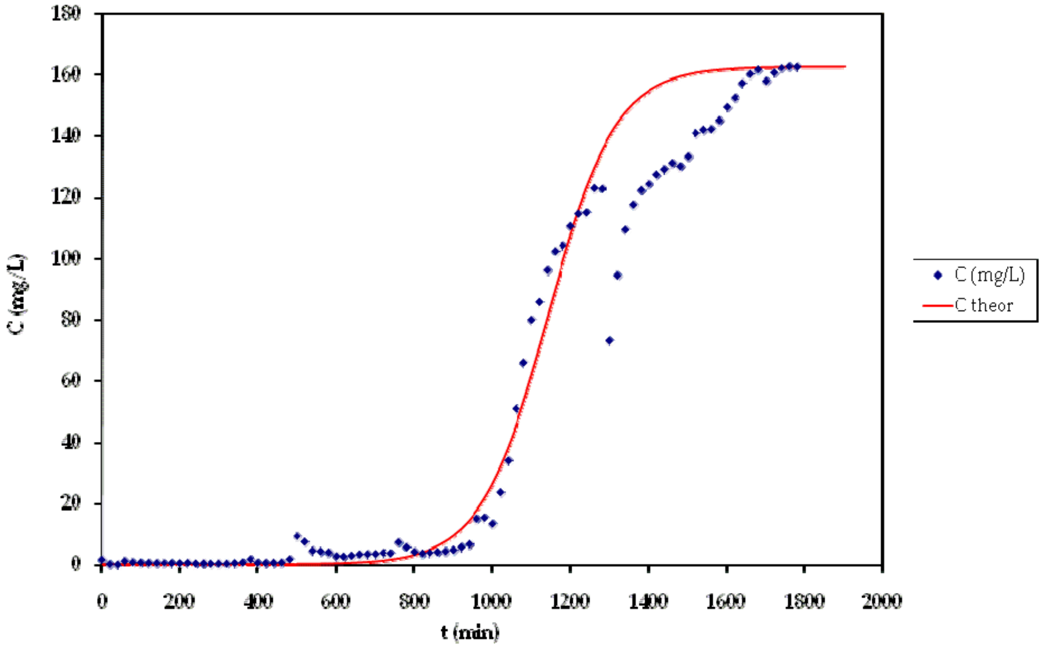


(b)

Fig. 5 Experimental and theoretical points of the sigmoidal adsorption curve as a function (a) of volume and (b) of time in a 75 cm long column.



(a)



(b)

Fig. 6 Experimental and theoretical points of the sigmoid absorption curve as a function of (a) volume and (b) time in a 150 cm long column.

5. Experimental Results

In Table 3, it is shown the experiment 1: raw spruce sawdust, sawdust 0.5 g, methylene blue 20 mg/L and water: 500 mL, adsorption: 100 °C. In Table 4, they are shown the variables for dilute solutions for the values of Table 3. In Table 5, they are shown the Variables for all solutions for the values of Table 3. In Fig. 7, there is a dilute solution graph for the experimental data of Table 3. In Fig. 8, there is a graph of all solutions for the experimental data of Table 3. In Table 6, it is shown the experiment 2: olive ash, sawdust: 0.5 g, methylene blue 20 mg/L and water: 500 mL, adsorption: 100 °C. In Table 7, they are shown the variables for dilute solutions for values of Table 6. In Table, 8 they are shown the variables for all solutions for values of Table 6. In Fig. 9, there is a dilute solution graph for values of Table 6. In Fig. 10, it is shown the graph of all solutions for values of Table 6. In Table 9, it is shown a repetition of the experiment: olive ash, sawdust: 0.5 g, methylene blue 20 mg/L and water: 500 mL, adsorption: 100 °C. In Table 10, they are shown the Variables for dilute solutions for values of Table 9. In Table 11, they are the variable for all solutions for values of Table 9. In Fig. 11, it is shown a dilute solution graph for experimental data of Table 9. In Fig. 12, it is shown the graph of all solutions for experimental data of Table 9.

Table 3 Experiment 1: raw spruce sawdust, sawdust 0.5 g, methylene blue 20 mg/L + water:500 mL, adsorption: 100 °C.

t (h)	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
0.00	133.69	113.94	84.24	42.98	34.47	17.30	12.89	9.98	6.74	4.32	2.99	2.02
168.00	111.31	83.08	54.80	25.46	14.54	4.28	3.36	2.88	1.70	0.81	0.40	0.28
C_e	111.31	83.08	54.80	25.46	14.54	4.28	3.36	2.88	1.70	0.81	0.40	0.28
q	22.39	30.87	29.45	17.52	19.93	13.02	9.52	7.09	5.04	3.51	2.58	1.74
$\log C_e$	2.046517	1.919487	1.73874	1.406	1.162	0.632	0.527	0.46	0.229	-0.09	-0.39	-0.56
$\log q$	1.349986	1.489467	1.46906	1.244	1.3	1.115	0.979	0.851	0.702	0.546	0.412	0.24

Table 5 Variables for all solutions for the values of Table 3.

$\log K_F$	0.628757
$1/n$	0.457399
K_F	4.253602
n	2.186274
R	0.963642
R^2	0.928606

Table 4 Variables for dilute solutions for the values of Table 3.

$\log K_F$	0.6043
$1/n$	0.6074
K_F	4.0211
n	1.6463
R	0.9888
R^2	0.9776

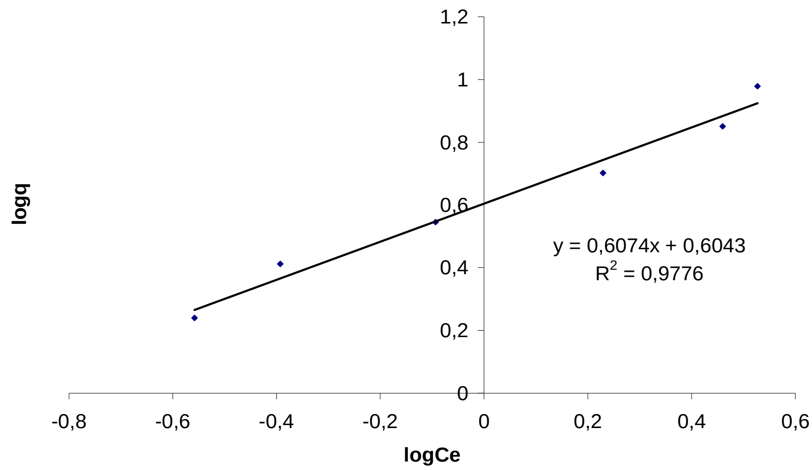


Fig. 7 Dilute solution graph for the experimental data of Table 3.

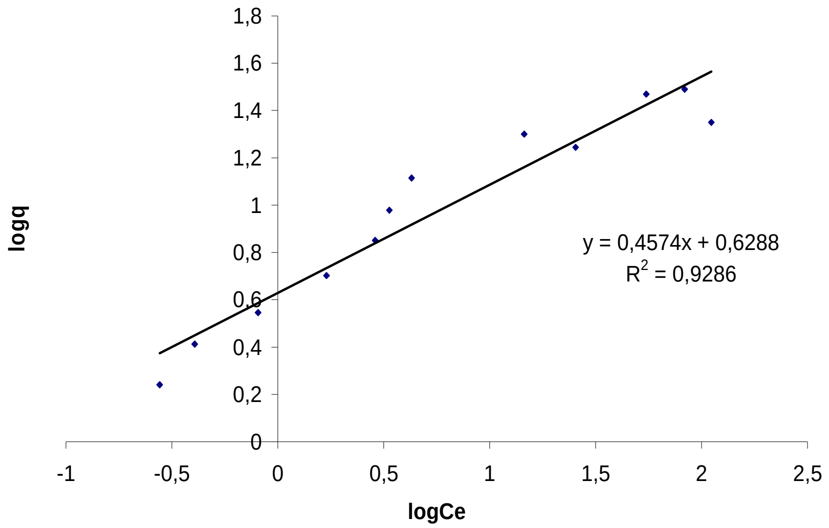


Fig. 8 Graph of all solutions for the experimental data of Table 3.

Table 6 Experiment 2: olive ash, sawdust:0.5 g, methylene blue 20 mg/L + water: 500 mL, adsorption: 100 °C.

t (h)	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
0.00	140.10	97.41	78.13	49.14	33.61	18.74	12.55	9.69	7.08	4.26	3.16	1.46
168.00	124.95	94.44	73.07	44.51	26.30	13.07	9.51	6.77	5.44	3.50	2.30	1.02
C_e	124.95	94.44	73.07	44.51	26.30	13.07	9.51	6.77	5.44	3.50	2.30	1.02
q	15.14	2.97	5.07	4.63	7.31	5.67	3.04	2.93	1.63	0.75	0.86	0.44
logC_e	2.096746	1.975148	1.86373	1.648	1.42	1.116	0.978	0.83	0.736	0.544	0.361	0.009
log$q$	1.180268	0.472325	0.70469	0.666	0.864	0.754	0.482	0.466	0.213	-0.12	-0.07	-0.36

Table 7 Variables for dilute solutions for values of Table 6.

logK_F	-0.4265
$1/n$	0.9168
K_F	0.3746
n	1.0907
R	0.9462
R^2	0.8953

Table 8 Variables for all solutions for values of Table 6.

logK_F	-0.21059
$1/n$	0.572908
K_F	0.615757
n	1.745481
R	0.860552
R^2	0.74055

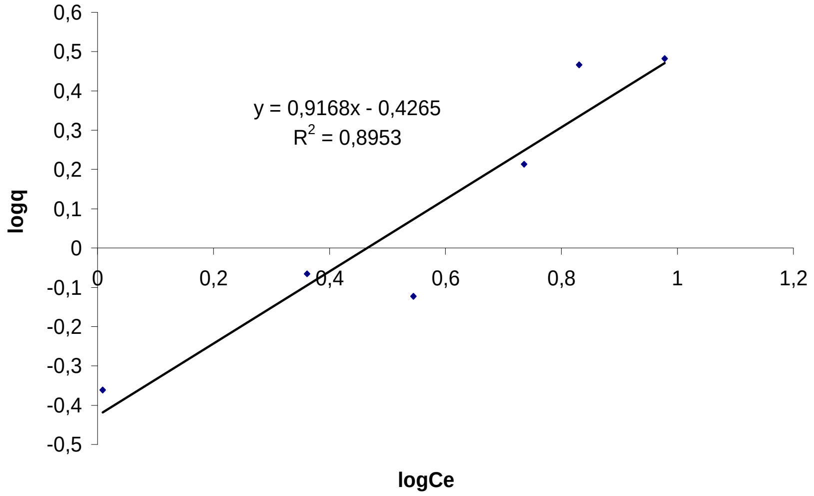


Fig. 9 Dilute solution graph for values of Table 6.

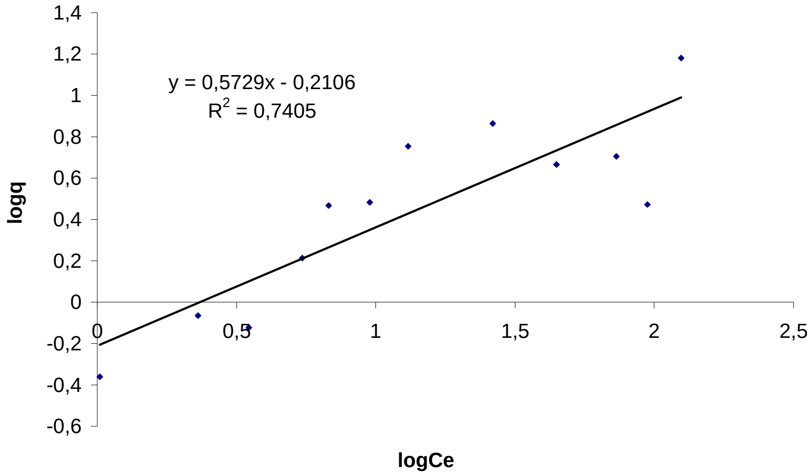


Fig. 10 Graph of all solutions for values of Table 6.

Table 9 Experiment: olive ash, sawdust: 0.5 g, methylene blue 20 mg/L + water: 500 mL, adsorption: 100 °C(repetition).

t (h)	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
0.00	139.71	105.45	81.05	49.62	34.09	15.87	12.14	9.65	7.10	4.45	3.10	1.27
168.00	132.17	79.86	70.88	34.07	21.17	8.48	9.47	6.46	4.86	2.61	1.45	0.44
C_e	132.17	79.86	70.88	34.07	21.17	8.48	9.47	6.46	4.86	2.61	1.45	0.44
q	7.54	25.60	10.17	15.56	12.92	7.40	2.67	3.19	2.24	1.84	1.64	0.83
$\log C_e$	2.121137	1.902302	1.85054	1.532	1.326	0.928	0.976	0.81	0.687	0.416	0.163	-0.35
$\log q$	0.877421	1.408159	1.00741	1.192	1.111	0.869	0.427	0.503	0.35	0.265	0.215	-0.08

Table 10 Variables for dilute solutionsfor values of Table 9.

$\log K_F$	0.0969
$1/n$	0.4066
K_F	1.2499
n	2.4592
R	0.9639
R^2	0.9292

Table 11 Variable for all solutions for values of Table 9.

$\log K_F$	0.11889
$1/n$	0.543519
K_F	1.314891
n	1.839862
R	0.885033
R^2	0.783283

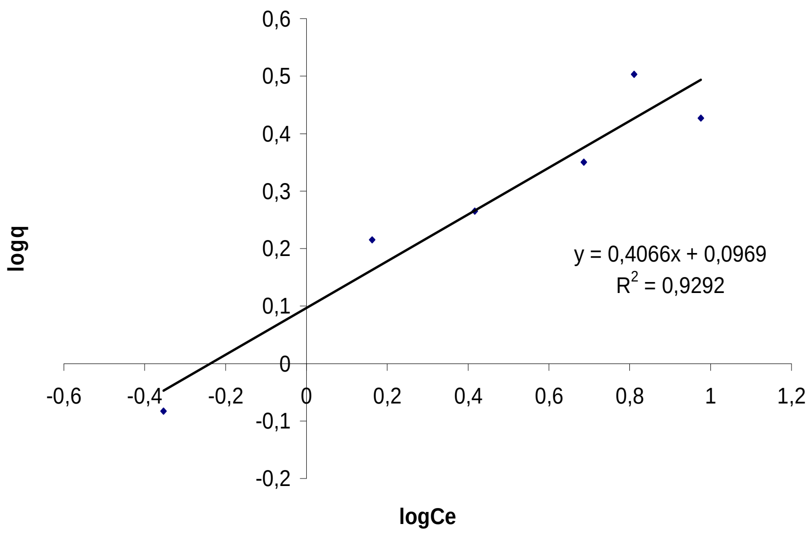


Fig. 11 Dilute solution graph for experimental data of Table 9.

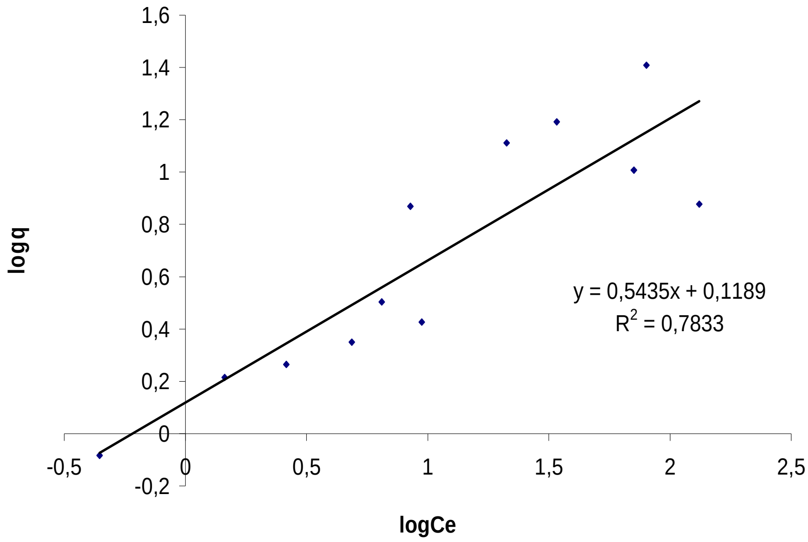


Fig. 12 Graph of all solutions for experimental data of Table 9.

6. Conclusions

The experimental diagrams confirm the validity of the Freundlich equation for dilute solutions with low concentrations. At the same time, from the aggregate diagrams of the dilute solutions listed above, we observe: For the graph concerning the adsorbents we used we observe that the capacity K_F has a higher value for the ground cork while the lower one for olive ash. Also, for the graph concerning the adsorbent materials we used we observe the *n* of the isothermal Freundlich has a maximum for olive ash while a minimum has for two materials lentil straw and ground cork.

References

[1] Abo-Elela, S.I., and El-Dib, M.A. 1987. "Color Removal via Adsorption on Wood Shaving." *Sci.Tot. Envir*. 66: 269.

[2] Allen, S. J., Gan, Q, Matthews, R., and Johnson P. A. 2003. "Comparison of Optimised Isotherm Models for Basic Dye Adsorption by Kudzu." *Biores. Techn*. 88: 143.

[3] Annadurai, G., Juang, R.-S, and Lee, D.-J. 2002. "Use of Cellulose Based Wastes for Adsorption of Dyes from Aqueous Solutions." *J. Hazard. Mater. B*92: 263.

[4] Batzias, F.A., and Sidiras, D. K. 2004. "Dye Adsorption by Calcium Chloride Treated Beech Sawdust in Batch and Fixed-Bed Systems." *J Hazard Mater* 114 (1-3): 167.

[5] Batzias, F. A., and Sidiras, D. K. 2004. "Optimal Design of Adsorption Tower Equipped with a Novel Packed Biomass Bed for Colouring-Processes-Wastewater Treatment." In *Proceeding of the 16th Intern. Congress of Chem. & Process Eng*., 22-26 August 2004, Prague, Czech Republic.

[6] Batzias, F. A., and Sidiras, D. K. 2001. "Wastewater Treatment with Gold Recovery through Adsorption by Activated Carbon." In *Water Pollution IV: Modelling, Measuring and Prediction*, edited by Brebbia, C.A. Southampton: WIT Press, 3: 533.

[7] Bohart, G. S., and Adams, E.Q. 1920. "Adsorption in Columns." *J. Chem. Soc*. 42.

[8] Carrillo, F., Lis, M. J., and Valldeperas, J. 2002. "Sorption Isother ms and Behaviour of Direct Dyes on LyocelFibres." *Dyes & Pigments* 53: 129.

[9] Chubar, A., Carvalho, J. R., and Correia, M. J. N. 2004. "Heavy Metals Biosorption on Cork Biomass: Effect of the Pre-treatment." *Colloids and Surfaces A: Physicochem, Eng. Aspects*. 238: 51.

[10] Chun, L., Hongzhang, C., and Zuohu, L. 2003. "Adsorption of Cr(VI) by Fe-Modified Steam Exploded Wheat Straw." *Proc.Biochem.* 39 (5): 541-5.

[11] Clark, R. M. 1987. "Modeling TOC Removal by GAC: The General Logistic Function." *J. Am. Wat. Works Assoc.* 79 (1): 33.

[12] Crank, G. 1993. *The Mathematics of Diffusion.* London, New York: Clarendon Press.

[13] El-Shobaky, G. A., and Youssef, A. M. 1978. "Chemical Activation of Charcoals." *Surface Techn*. 7(3): 209.

[14] Garg, V. K., Gupta, R., Yadav, A.-B., and Kumar, R. 2003. "Dye Removal from Aqueous Solutions by Adsorption on Treated Sawdust." *Biores. Techn.* 89: 121.

[15] Hutchins, R. A. 1973. "New Method Simplifies Design of Activated-Carbon Systems." *Chem. Eng.* 80 (19): 133.