„BABEŞ-BOLYAI" UNIVERSITY, CLUJ-NAPOCA

FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

Doctoral School of Chemistry

Sorption of uranium, titanium and iron chlorocomplexes on anionic exchange resins

PhD Thesis Abstract

PhD Student: Eng. MARCU MARIANA CRISTINA

Scientific advisor:

CSI Dr. DAMIAN AXENTE

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(Universitatea Babeş-Bolyai, Cluj-Napoca)

COMISIA DE DOCTORAT:
Preşedinte: Prof. Dr. ION GROSU
(Universitatea Babeş-Bolyai, Cluj-Napoca)
Conducător de doctorat: CSI. Dr. DAMIAN AXENTE
(Institutul Naţional de Cercetare-Dezvoltare pentru Tehnologii Izotopice şi Moleculare, Cluj-Napoca)
Referenţi: Prof. Marcel Ionel Popa
(Universitatea Tehnică Gheorghe Asachi, Iaşi)
CSI. Dr. Vasile Stanciu
(Institutul Naţional de Cercetare Dezvoltare pentru Tehnologii Criogenice şi Izotopice, Râmnicu Vâlcea)
Conf. Dr. Alexandra Csavdari
(Facultatea de Chimice şi Inginerie Chimică, Cluj-Napoca)

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Chapter I. Theoretical part

Keywords: isotopes, enrichment, resins, sorption/desorption, sorption capacities, kinetics, thermodynamics

INTRODUCTION

Natural uranium has three isotopes: ^{234}U (0.0054 at.%), ^{235}U (0.72 at.%) and ^{238}U (99.274% at.) [1]. All these are radioactive, but only ^{235}U is fissionable material that can be used in nuclear power [2]. ^{235}U enriched above natural uranium is called low enriched uranium.

The main enrichment methods are gas centrifugation, gaseous diffusion, distillation, chemical exchange, atomic vapor laser isotope separation, plasma separation process and electromagnetic isotope separation [4].

Since gas diffusion and centrifugation are using toxic compounds, and the electromagnetic enrichment method is expensive, at laboratory or pilot scale, the uranium enrichment by chemical exchange was tested. In France, the chemical exchange, called CHEMEX, was studied at pilot level, based on the isotope effect of the chemical exchange reaction between U (III) in the aqueous phase and the U(IV) in organic phase [6]. Asahi Chemical Industry Company, Japan, developed the enrichment process at semicommercial level based on chemical exchange between U(IV) solution and U(VI) sorbed on anion resin using anion separation columns [7].

The overall aim of the thesis is to study the sorption of uranium, titanium and iron chlorocomplexes on anionic resin in order to determine the experimental conditions to achieve ^{235}U isotope enrichment by chemical exchange method in a separation column filled with anionic exchange resin.

The thesis is divided in two parts: the first one presents a theoretical part on the main aspects of uranium enrichment by chemical exchange. The second one includes the original contributions; the data obtained on uranium, titanium and iron chlorocomplexes sorption, on anionic resins, are presented. The second chapter also contains an experimental study on the sorption kinetics and thermodynamics of U(VI) and Fe(III) on Dowex-Marathon anionic resin. The paper ends with conclusions and references.

Chapter I. Theoretical part

The ^{235}U isotope enrichment can be achieved by chemical exchange between U(IV) chlorocomplexes, in solution phase and U(VI), sorbed on anionic resin. The chemical exchande reaction is illustrated by the following equation [8]:

$$^{238}U(VI)_{(R)} + {}^{235}U(IV)_{(S)} \rightleftharpoons {}^{235}U(VI)_{(R)} + {}^{238}U(IV)_{(S)} \quad (1)$$

where: R refers to the resin phase and S refers to solution phase; and it is characterized by an elementary separation factor α = 1.0013, at room temperature [9].

The elementar separation factor multiplication, α, occurs in the separation column, where the exchange reaction (1) is repeated, the ^{238}U isotope is enriched in U(IV), in solution phase, and the ^{235}U isotope in U(VI), sorbed on resin.

The most used oxidizing agent for ^{235}U / ^{238}U chemical exchange is Fe(III) and the most commonly used reducing agents are Ti(III) and V(II) [13].

The reactions that occur in the separation column, are [17]:

$UO_2^{2+}{}_{(R)} + 2\,Ti^{3+}{}_{(S)} \rightarrow U^{4+}{}_{(S)} + 2\,TiO^{2+}{}_{(R)}$ (in the end of U band) (5)

$U^{4+}{}_{(S)} + 2\,Fe^{3+}{}_{(R)} + 2\,H_2O \rightarrow UO_2^{2+}{}_{(R)} + 2\,Fe^{2+}{}_{(S)} + 4H^{+}$ (in the front of U band) (6)

To achieve ^{235}U enrichment, the reactions (5) and (6) have to be total and have high rate. To understand the sorption mechanisms, the sorption isotherms were studied [48]. The most common sorption isotherms are:

- Langmuir isotherm, with linear form: $\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e$ [50] (8)
- Freundlich isotherm, with linear form: $log q_e = log K_F + \left(\frac{1}{n}\right) log C_e$ [53] (10)
- Dubinin-Radushkevich isotherm, with linear form: $ln q_e = ln q_m - K\varepsilon^2$ [28] (11)

where C_e is the solute concentration, at equilibrium, q_e is the solute amount, at equilibrium, q_m is the maximum sorption capacity.

In order to investigate the sorption mechanism and the rate limiting step, four kinetic models were used:

1. Pseudo first order kinetic model, with linear form [59]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{13}$$

2. Pseudo second order kinetic model, with linear form [61]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{14}$$

3. Elovich kinetic model, with linear form [49]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{16}$$

4. Intraparticle diffusion kinetic model, with the linear form [66]:

$$q_t = k_i t^{0.5} \tag{17}$$

The influence of temperature on the sorption may be positive [79, 80] (increase the sorbed amount on sorbent) or negative [81, 82] (decrease the sorbed amount on sorbent). In the first case, we have an endothermic sorption, when the reaction enthalpy is $\Delta H^0 > 0$, and in the second case, an exothermic sorption, when $\Delta H^0 < 0$. Enthalpies up to 40 kJ / mol, are characteristic to „physisorption" while enthalpies of 40-120 kJ / mol, are specific to „chemosorption", specify MA Zulficar, [84].

Sorption free energy, ΔG^0, shows the process spontaneity and feasibility and it can be calculated with the relation [51]:

$$\Delta G^0 = -RTlnK_C \tag{19}$$

where: K_C is the equilibrium constant for the ions distribution between the liquid and solid phase and it can be calculated with the relation [85]:

$$K_C = \frac{q_e}{C_e} \tag{20}$$

Literature data show that the values of ΔG^0 up to - 20 kJ / mol are compatible with physical sorption and ΔG^0 under - 40 kJ / mol, to chemical sorption, [86].

CHAPTER II. ORIGINAL CONTRIBUTIONS

For for uranium enrichment by chemical exchange is necessary that U(VI) be strongly sorbed on the anionic resin. Taking into account that resins have a high moisture content, we have reported the sorption capacity to wet and dry resin amount. The temperature and hydrochloric acid concentration on the U(VI), Ti(IV) and Fe(III) ions sorption were studied. Since the reduction rate of $U(VI)_{(R)}$ with $Ti(III)_{(S),}$ and the oxidation rate of $U(IV)_{(S)}$ with $Fe(III)_{(R)}$, in the enrichment column have to be high, we tried to determine the reflux reaction kinetics that occurs in the end of uranium band. Then, the sorption reactions kinetics in the front and in the end of uranium band, in uranium enrichment column, were studied. The influence of working conditions were approached in order to determine when the U(VI) and Fe(III) sorption kinetics is favorable.

The thermodynamics of U(VI) and Fe(III) sorption on Dowex-Marathon resin and thermodynamic parameters were determined for both sorption processes.

II.2.1. Determination of resins sorption capacities, in column, for U(VI)

The anionic resins sorption capacity were determined. The results are shown in Table 5. Measurements were made with ± 0.6 mg U(VI) error.

Table 5. Wet ion exchange resins sorption capacity, at room temperature (column determination) [96]

Resin	Sorption capacity (mgU/g wet resin	HCl Concentration (M)
Amberlite IRA-900 Cl	77.44	5
	102.86	7
	130.65	9
Amberjet 4400 Cl	68.38	5
	41.03	7
	36.19	9
	117.77	5

Dowex 1-X8	166.9	7
	187.13	9
Dowex-Marathon	87.75	5
	120.41	7
	128.37	9

II.2.3. Resins sorption capacity determination by batch method for U(VI), Ti(IV) and Fe(III)

The ion exchange resins moisture varies between 58 and 64%. In order to determine the sorption capacity of dried resins in comparison with the wet resins, batch method determination were made.

II.2.4. Factors influencing the dry resins sorption capacity

Effect of temperature on the dry resins sorption capacity are shown in Table 8.

Table 8. Dried anionic resins sorption capacities [96, 98]

Resin	Temperature (°C)	Sorbed Element	Dry resin amount (g)	Dry resin sorption capacity (mg/g)
Dowex - Marathon	22	U(VI)	0.6321	194.32
	30		0.5737	211.20
	50		0.5729	227.45
	70		0.5716	238.63
Dowex-Marathon	16	Fe(III)	0.5715	37.66
	20		0.4119	58.19
	30		0.4003	79.05
	50		0.4081	105.70
	70		0.4000	140.36
	30		0.3966	14.24

Dowex-Marathon	50	Ti(IV)	0.3918	18.05
	70		0.3900	14.48
CEPU-M5	20	U(VI)	0.6873	161.61
	30		0.5191	162.51
	50		0.7486	172.61
	70		0.6711	182.47
Dowex 1-X8	15	U(VI)	0.7150	214.53
	20		0.7431	217.33
	30		0.7332	217.19
	50		0.7591	223.85
	70		0.7667	235.24

In case of CEPU-M5 resin prepared especially for uranium isotope exchange [99], were obtained lower values for capacity than the commercial resins.

II.4. Kinetics and thermodynamics of U (VI) reduction with different reductants

In order to understand the processes occuring at the two ends of uranium band, in the enrichment column, the kinetics and thermodynamics of U (VI) reduction, sorbed on Dowex-Marathon resins, were studied.

II.4.2. Using Ti(III) as reductant

a) U(IV) concentration measurement

Experimental steps of $U(VI)_{(R)}$ reduction with $Ti(III)_{(S),}$ are showed in Figure 13.

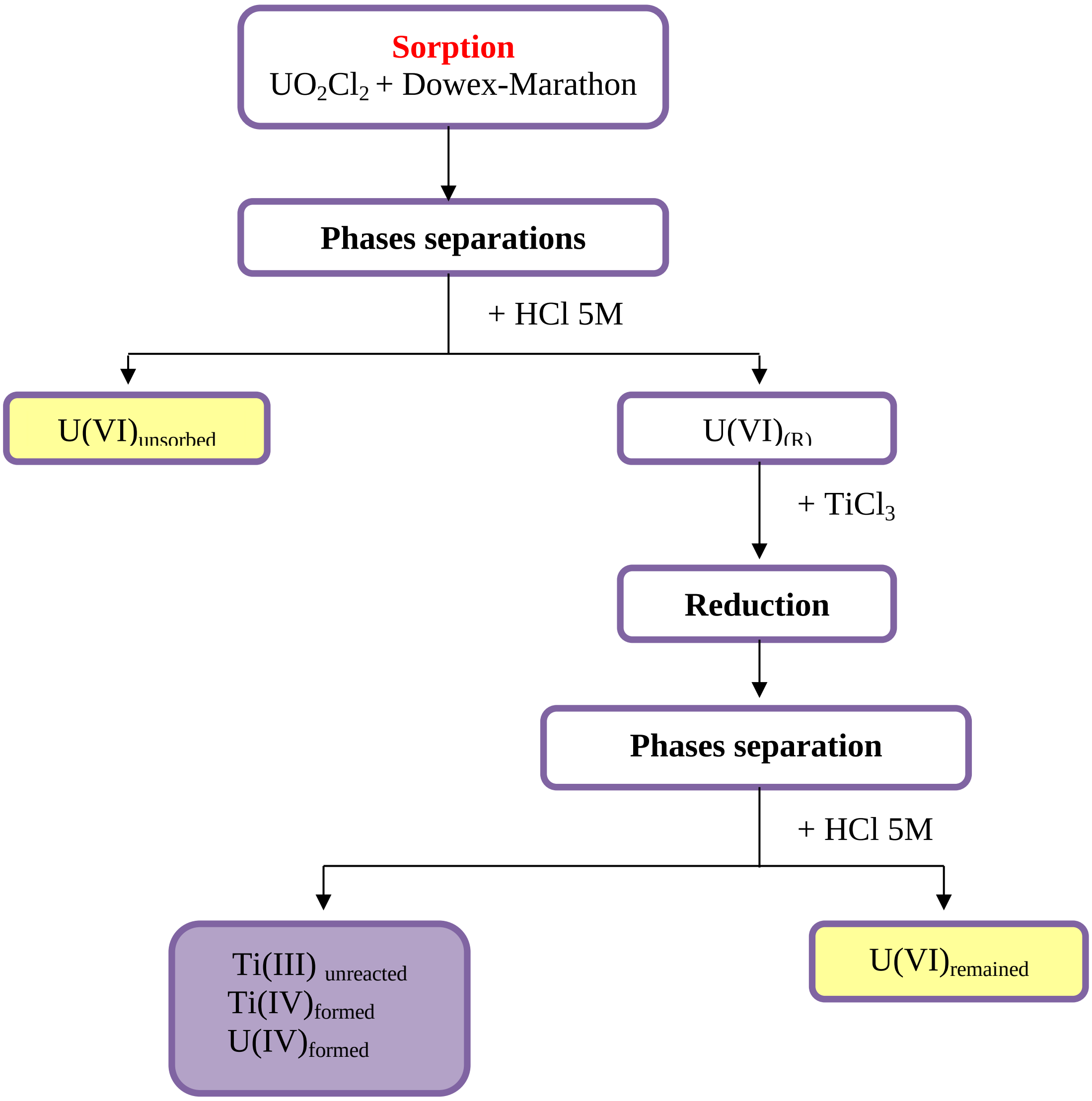

Figure 13. The experimental steps to reduce $U(VI)_{(R)}$ with $Ti(III)_{(S)}$ on Dowex-Marathon resin

The concentration of U(IV) increases with an increase of contact time, Figure 14

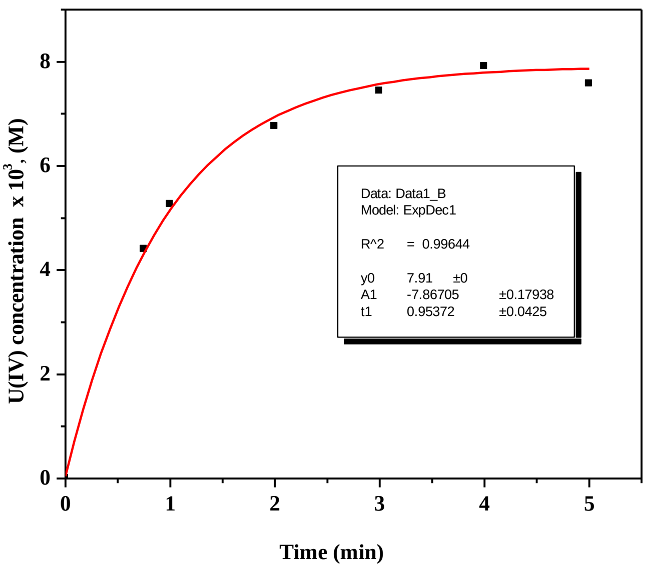

Figure 14. U(IV) Concentration, at room temperature

b) The temperature dependence of the amount of U (IV)

The value of activation energy indicated that we have a diffusion process. The results of these experiments are presented in Table 12.

Table 12. U(VI)$_{(R)}$ reduction experiments with Ti(III)$_{(S)}$

Resin	U(VI)$_{(R)}$ conc. (M)	Ti(III)$_{(S)}$conc. (M)	Temp. (°C)	Medium	E_a (kJ/mol)
Dowex-Marathon	$12.95\cdot10^{-3}$	$35.99\cdot10^{-3}$	21.8-54.8	HCl 5M	12.39
	$13.05\cdot10^{-3}$	$16.85\cdot10^{-3}$	1.4 - 49	HCl 5M	3.21
	$13.10\cdot10^{-3}$	$9.26\cdot10^{-3}$	2 - 23	HCl 5M	1.92
	$13.45\cdot10^{-3}$	$4.65\cdot10^{-3}$	2.2 – 42.6	HCl 5M	8.75
	$4.99\cdot10^{-3}$	$7.79\cdot10^{-3}$	20.4 – 32.4	HCl 5M	-
	$1.52\cdot10^{-3}$	$35.58\cdot10^{-3}$	1.4 – 44.6	HCl 7M	7.48
	$9.62\cdot10^{-3}$	$17.80\cdot10^{-3}$	18.4 – 44.8	H_2SO_4	7.54

				0,05M	
	$3.25\cdot10^{-3}$	$9.10\cdot10^{-3}$	19 – 44.6	H_2SO_4 0,05M	8.18
	$2.22\cdot10^{-3}$	$6.06\cdot10^{-3}$	19 – 44	H_2SO_4 0,05M	10.18
Amberlite IRA-900Cl	$5.36\cdot10^{-3}$	$9.38\cdot10^{-3}$	19.4 - 44	HCl 5M	-
DIAION HPA 25L	$7.94\cdot10^{-3}$	$35.38\cdot10^{-3}$	21	HCl 5M	-

In order to understand the processes that takes place on the resin, we studied the kinetics and thermodynamics of U(VI) and Fe(III) sorption, on Dowex-Marathon resin.

II.5. U(VI) Sorption on Dowex-Marathon resin

II.5.3. Sorption isotherms

The Langmuir, Freundlich and Dubinin-Radushkevich isotherms were studied. Their parameters are presented in Table 13. The correlation coefficient (R^2) is higher for Langmuir isotherm.

Table 13. Isotherm parameters for U(VI) sorption on Dowex-Marathon resin [117]

Langmuir Isotherm			**Freundlich Isotherm**			**Dubinin - Radushkevich Isotherm**		
Q_0 (mg/g)	b (l/mg)	R^2	K (mg/g)	n	R^2	K (mol^2/kJ^2)	q_m (mg/g)	R^2
268.81	1.04×10^{-4}	0.9955	0.232	1.43	0.9883	0.43941	110.55	0.8715

II.6 Sorption kinetics of U(VI) on Dowex-Marathon resin

Sorption kinetics results, for U(VI) onto Dowex-Marathon resin, are shown in Table 14.

Table 14. Kinetic data for of U(VI) sorption onto Dowex-Marathon resin, initial concentration of UO_2Cl_2 solutions dependance [117]

Parameters	**Initial concentration of UO_2Cl_2 solution**				
	0.02M	**0.04M**	**0.05M**	**0.07M**	**0.1M**
$q_{e, exp}$(mg/g)	34.69	67.34	81.66	108.96	142.5
<u>Pseudo first order</u>					
$q_{e, calc}$ (mg/g)	27.23	45.47	60.06	76.98	96.83
k_1 (min^{-1})	11.64×10^{-2}	9.28×10^{-2}	8.9×10^{-2}	8.0×10^{-2}	8.03×10^{-2}
R^2	0.9776	0.9933	0.9948	0.9923	0.9974
<u>Pseudo second order</u>					
$q_{e, calc}$ (mg/g)	38.50	74.02	89.36	119.61	155.76
k_2 (g/mg min)	6.26×10^{-3}	3.40×10^{-3}	2.48×10^{-3}	1.78×10^{-3}	1.46×10^{-3}
h (mg/g min)	9.27	18.62	19.80	25.46	35.42
R^2	0.9990	0.9989	0.9988	0.9977	0.9979
<u>Elovich Eq.</u>					
α (mg/g min)	27.58	55.98	58.98	76.16	111.48
β (g/mg)	14.53×10^{-2}	7.69×10^{-2}	6.13×10^{-2}	4.67×10^{-2}	3.65×10^{-2}
R^2	0.9776	0.9946	0.9951	0.9979	0.9970

Intraparticle difussion					
k_i (mg/g min^{0,5})	2.68	6.11	8.55	10.09	14.21
R^2	0.9948	0.9770	0.9792	0.9959	0.9812

Chi nonlinear test ($\chi 2$) [125], for pseudo first order kinetic model is 55.21 and for pseudo second order kinetic model is 3.69, so the experimental data do not fit to pseudo first order kinetic model.

The activation energy for U(VI) sorption onto Dowex-Marathon resin is: E_a = 6.62 ± 0.16 kJ / mol, which indicates that we measured the E_a for a diffusion, not for a chemical reaction.

II.7. Sorption thermodynamics of U(VI) on Dowex-Marathon resin

Thermodynamic parameters for U(VI) sorption, presented in Table 16, show that U(VI) sorption process is spontaneous and endothermic.

Table 16. Thermodynamic parameters for U(VI) sorption onto Dowex-Marathon resin [117]

t (°C)	**K_C**	**R**	**ΔG° (kJ/mol)**	**ΔH° (kJ/mol)**	**ΔS° (J/mol K)**
20	14.27	- 0.97794	- 6.37	14.57± 0.36	71.48± 1.78
30	17.08		- 7.08		
40	19.28		- 7.80		
50	22.42		- 8.51		
60	28.28		- 9.23		

II.8. Fe(III) sorption on Dowex-Marathon resin

II.8.1. Effect of contact time and iron initial concentration

Sorption equilibrium is reached after about 50 minutes, Figure 26 [129].

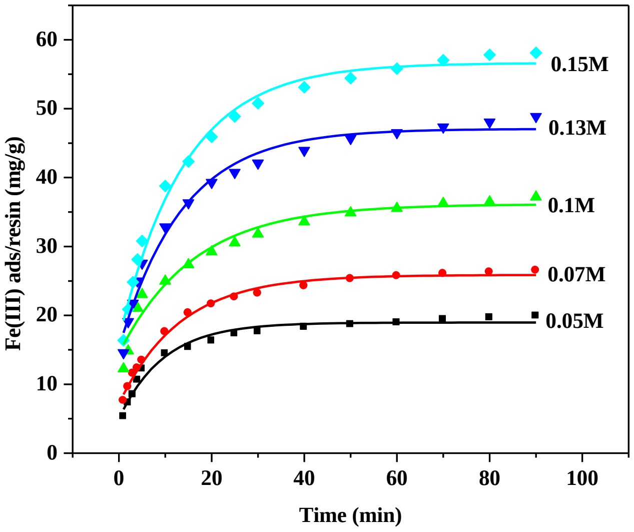

Figure 26. Influence of contact time for Fe (III) sorption onto Dowex-Marathon at 20 ° C [129]

II.8.2. Effect of temperature

With temperature increasing, the sorbed amount of iron onto resin, increases exponentially, Figure 27.

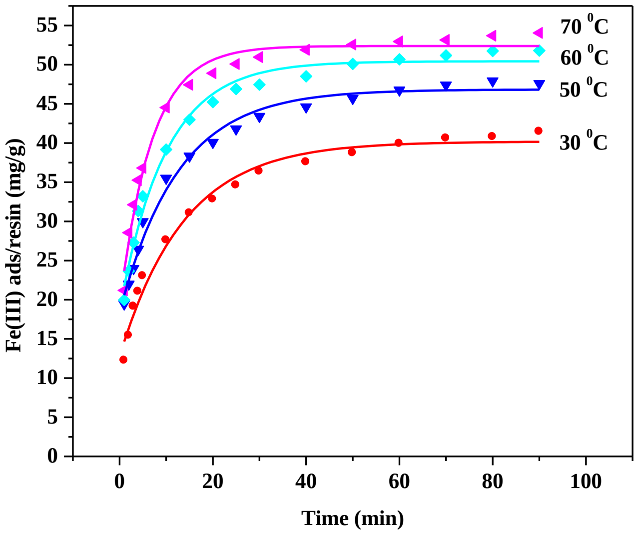

Figure 27. Influence of temperature for Fe(III) of 0.1 M $FeCl_3$ / HCl 5 M, onto Dowex-Marathon resin

II.8.3. Sorption Isotherms

- Langmuir isotherm for Fe(III) sorption is shown in Figure 29:

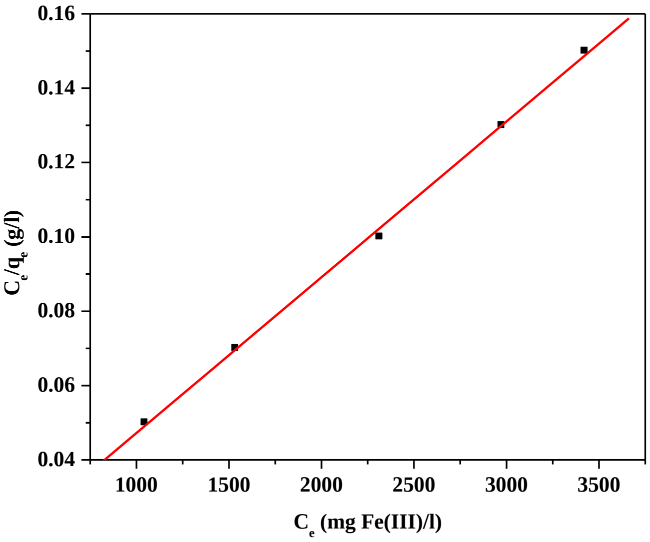

Figure 29. Langmuir isotherm for Fe(III) sorption onto Dowex-Marathon resin (25 ° C, Fe(III) volume solution / sorbent mass = 10: 1) [129]

- Freundlich isotherm for Fe(III) sorption is shown in Figure 30:

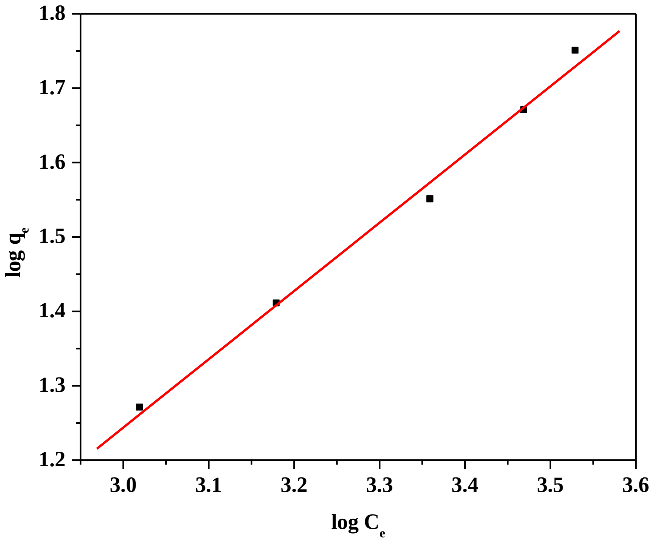

Figure 30. Freundlich isotherm for Fe(III) sorption onto Dowex-Marathon resin (25 ° C, Fe(III) volume solution) / sorbent mass = 10: 1) [129]

- Dubinin-Radushkevich isotherm is presented in Figure 31:

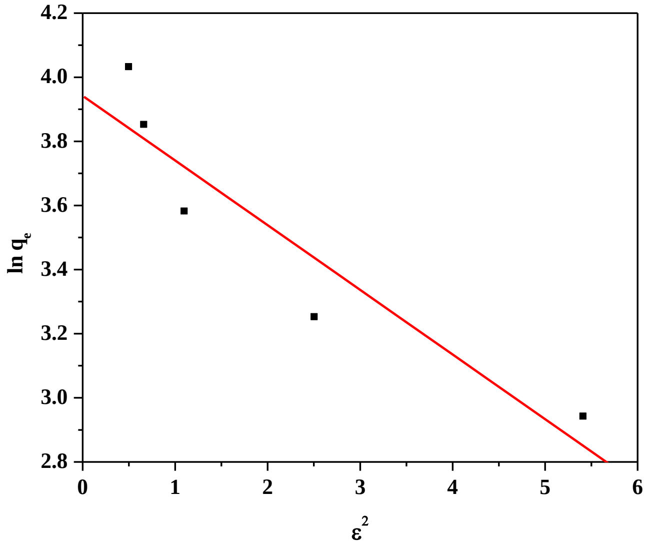

Figure 31. Dubinin-Radushkevich isotherm for Fe(III) sorption onto Dowex-Marathon resin (25 ° C, Fe(III) volume solution / sorbent mass = 10: 1) [129]

Isotherms parameters are listed in Table 17.

Table 17. Isotherm parameters for Fe(III) sorption onto Dowex-Marathon resin [129]

Langmuir Isotherm			**Freundlich Isotherm**			**Dubinin – Radushkevich Isotherm**		
Q_0 (mg/g)	**b** (l/mg)	**R^2**	**K** (mg/g)	**n**	**R^2**	**K** (mol^2/kJ^2)	**q_m** (mg/g)	**R^2**
23.86×10^3	7.84×10^{-3}	0.9988	0.031	1.09	0.9929	0.201	51.52	0.8722

From Table 17, it can be seen that the best correlation coefficient was found for Langmuir isotherm (R2 = 0.9988), which describes a monolayer sorption.

II.9. Sorption kinetics of Fe(III) onto Dowex-Marathon resin

The pseudo first order kinetic model for Fe(III) sorption onto Dowex-Marathon resin , is shown in Figure 32.

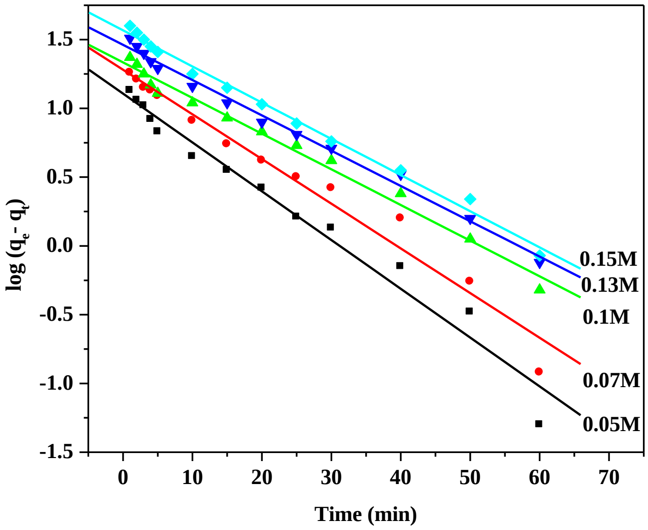

Figure 32. Pseudo first order kinetic model for Fe(III) sorption onto Dowex-Marathon resin at 20 ° C, [129]

The correlation between the experimental data and calculated data, obtained from the predicted kinetic model is expressed by R^2 correlation factor. The results are shown in Table 18.

Table 18. Kinetic data for Fe(III) sorption onto Dowex-Marathon resin, initial concentration of $FeCl_3$ solution dependance [129]

Parameters	**Initial concentration of $FeCl_3$ solution**				
	0.05M	**0.07M**	**0.1M**	**0.13M**	**0.15M**
$q_{e, exp}$(mg/g)	19.00	25.83	36.00	47.28	56.66

Pseudo first order					
$q_{e, calc}$ (mg/g)	12.79	19.11	21.61	28.99	36.97
k_1 (min^{-1})	0.081	0.074	0.059	0.059	0.060
R^2	0.9707	0.9917	0.9865	0.9917	0.9930
Pseudo second order					
$q_{e, calc}$ (mg/g)	20.56	27.76	38.30	50.50	60.90
k_2 (g/mg min)	11.52×10^{-3}	7.36×10^{-3}	5.89×10^{-3}	4.27×10^{-3}	3.24×10^{-3}
h (mg/g min)	4.86	5.67	8.63	10.89	12.01
R^2	0.9992	0.9991	0.9978	0.9985	0.9986
Ec. Elovich					
α (mg/g min)	19.45	20.62	49.61	48.48	45.52
β (g/mg)	0.302	0.217	0.1767	0.1263	0.100
R^2	0.9785	0.9879	0.9929	0.9953	0.9930
Difuzia intraparticulă					
k_i (mg/g $min^{0,5}$)	1.2718	1.5804	2.722	4.0321	5.3240
R^2	0.9702	0.9782	0.9910	0.9815	0.9974

The pseudo second order kinetic model is shown in Figure 33.

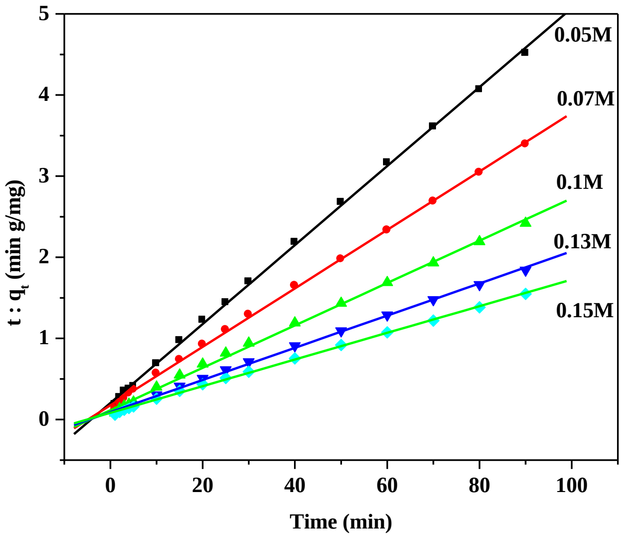

Figure 33. Pseudo second order kinetic model for Fe(III) sorption onto Dowex-Marathon resin, at 20 ° C, [129]

Elovich kinetic model that describes chemisorption, is shown in Figure 34.

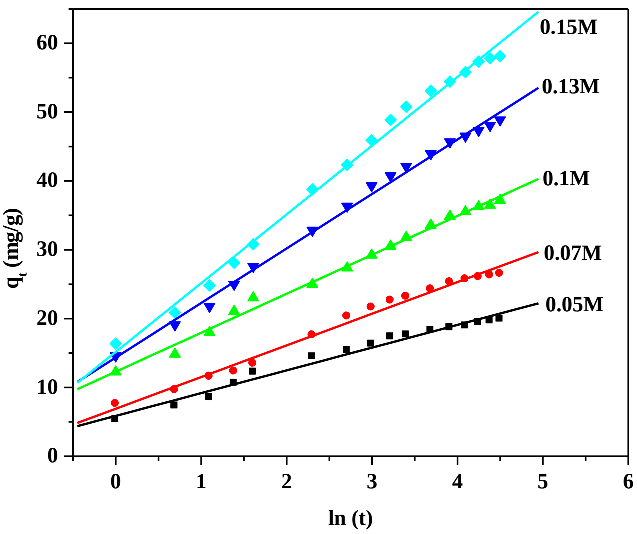

Figure 34. Elovich kinetic model for Fe(III) sorption onto Dowex-Marathon at 20 ° C [129]

Intraparticle diffusion can play a role in the sorption process, Figure 35.

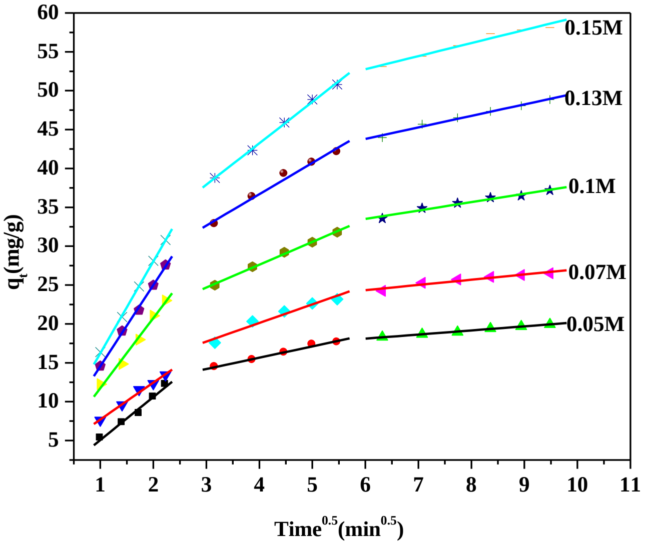

Figure 35. Intraparticle diffusion kinetics for Fe(III) sorption on Dowex-Marathon, 20 ° C, [129]

The activation energy for Fe(III) sorption is: E_a = 7.96 ± 0.2 kJ / mol [129], beeing in the range from 5 to 40 kJ / mol, which indicates a physical sorption process.

II.10. Sorption thermodynamics of Fe(III) onto Dowex-Marathon resin

The thermodynamic parameters for Fe(III) sorption onto Dowex¬-Marathon resin were calculated from the sorption isotherms, the values obtained are presented in Table 20.

Table 20. Thermodynamic parameters for Fe(III) sorption onto Dowex-Marathon [129]

t (°C)	K_C	R	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
30	3.14	–0.9895	–7.91	35.60± 0.89	143.31± 3.58
50	3.87		–10.39		
60	4.51		–12.48		
70	4.80		–13.68		

The thermodynamic parameters shows that we have a spontaneous and endothermic process.

CONCLUSIONS AND CLOSING REMARKS

The main conclusions and observations from this work are:

1. It has been determined that the sorption capacity of anionic resins: Amberlite IRA-900 Cl, Amberjet 4400Cl, Dowex 1-X8 and Dowex-Marathon (wet resin) to U (VI), depends of HCl concentration. With Amberjet 4400 Cl resin exception, other resins have higher sorption capacities, with increasing HCl concentration in the range of 5-9 M. Dowex 1-X8 resin shows higher sorption capacity than the other resins, but it is difficult to work with this. In the case of Dowex-Marathon resin, the sorption capacity increased from 87.75 mg U / g resin, for HCl 5 M UO_2Cl_2 to 128.27 mg U / g resin, for 9 M of HCl solution, therefore, the influence of temperature on the sorption capacity of this resin was studied.
2. It has been determined that the sorption capacity of Dowex-Marathon resin, by column determination, for U(VI), is depending on the temperature. Increasing the temperature between 20-90 ° C, resulted an increase of the sorption capacity by about 64% due to the formation of new active centers on the sorbent surface or to the activation of the sorption step.
3. It has been determined the sorption capacity of Dowex-Marathon resin, by batch method, for U(VI), Ti(IV) and Fe(III), in function of HCl concentration. In the case of Ti(IV) sorption it has been observed that an increase in the HCl concentration from 5 to 8.8 M, the sorption capacity increased for 5 times. In the case of U(VI), the sorption sorption capacity increased from 87.75 MGU / g resin, to 128.37 mg U / g resin, with varying the concentration of HCl 5-9 M, and in case the sorption of Fe(III), the resin sorption capacity increased linearly with the HCl concentration.
4. It has been determined the sorption capacity of Dowex-Marathon resin, by batch method, for U(VI), Ti(IV) and Fe(III), in function of the temperature. In the case of Ti (IV) the sorption capacity was not increased with temperature increasment in the range

30-70 ^{0}C. An explanation for this fact could be that at the higher temperature, the formed titanium complex can not be sorbed onto the resin. For Fe(III), the resin has a sorption capacity of 3.72 higher at 70 ° C than at 16 ° C. For U(VI), the temperature increases led to an increase of the sorption capacity for Dowex-Marathon resin, but not so significant as in the case of Fe(III).

5. Temperature increase on CEPU-M5 and Dowex 1-X8 resins sorption, by batch method, for U(VI), led to a slight increase in sorption capacity, but with these two resins we worked hard because they have very small granules.

6. The spectral determinations were performed by FT-IR method, on Dowex-Marathon, Amberlite IRA-900 Cl and Dowex 1-X8 resins. From these spectra, it was observed that there is no structural difference between the resin before use, and after the sorption experiments, the only difference is observed at 921 cm^{-1} due to the presence of $UO2^{2+}$ ion. This proves that the resins have good mechanical strength and does not change the structure during contact between resin and solution agitation. Neither Dowex 1-X8, showed no structural changes after use. This means that the difficulties in capacity measurements are due to resin porosity, not structural change. The sorbed ions on resins were removed quantitatively by elution with distilled water or weak acid solutions.

Regarding the ions charged sorbed on resins, a theoretical evaluation shows that the complexes sorbed on anion exchanger is dependent on HCl concentration.

7. It has been studied the kinetics and thermodynamics of uranium (VI) reduction, sorbed on the resin with vanadium (III) solution in H_2SO_4 medium because in HCl medium experiments have shown that $U(VI)_{(R)}$ does not react with the V(III) solutions in hydrochloric acid, neither at temperatures up to 155 ° C and HCl concentration of 7 M. The rate constant near to V (III), is $k_1 = 2.87 \times 10^{-2}$ min $^{-1}$ and near to U(VI), the rate constant is $k_2 = 5.53 \times 10^{-2}$ min^{-1}. The activation energy Ea = 34.9 ± 0.9 kJ / mol, is less than that determined for the reduction of U(VI) with V(III), in solution. Thermodynamic parameters were determined: the enthalpy change was: $\Delta H \neq = 35.5 \pm 0.9$ kJ / mol and the entropy: $\Delta S \neq = - 165.7 \pm 3$ J / K.

8. It has been attempted to reduce $U(VI)_{(R)}$ with Ti(III) in HCl solution. It has been found that the rate determining step is not the chemical reaction, but diffusional transport,

because were obtained very low values of the activation energy. In order to understand this behavior, and sorption of U(VI) and Fe(III), were made in HCl 5 M medium, on Dowex-Marathon resin,occur fast enough for use in the enrichment of the ^{235}U isotope column.

9. Equilibrium sorption measurements were made for uranium and titanium chlorocomplexes, in different HCl concentrations. In the case of U(VI), the sorption equilibrium was reached in 40 minutes and in the case of Fe(III) in about 50 minutes. With increasing the concentration of UO_2Cl_2 and $FeCl_3$ solutions, increased the chlorocomplexes amount sorbed on the resin. Their sorption is carried out in steps, a first step is fast and takes place at the surface of ion exchanger, and a second step is gradual and it is that in which the intraparticle diffusion is the rate limiting step of sorption.

10. The sorption mechanism for uranium and iron chlorocomplexes corresponds to Langmuir isotherm. In this case, the correlation coefficient for U(VI) sorption is R^2= 0.9955 and for Fe(III) is R^2 =0. 9988.

11. The sorption kinetic for U(VI) and Fe(III) were analysed using the pseudo first, pseudo second order kinetic models, the Elovich equation kinetic model and the intraparticle diffusion. It was concluded that the U (VI) and Fe (III) sorption process in the hydrochloric solution, can not be described using a single kinetic model.The pseudo second order kinetic model, the Elovich equation (compatible with the pseudo second order kinetic model) and intraparticle diffusion model may be considered in the process U(VI) and Fe(III) chlorocomplexes sorption onto Dowex-Marathon resin.

12. We determined the activation energies for U(VI) and Fe (III) sorption E_a = 6.62 ± 0.16 kJ / mol and Ea = 7.96 ± 0.2 kJ / mol, respectively. Low values for activation energy (<40 kJ / mol), advocates for a physisorption process, not for a chemisorption one, as is clear from the kinetic measurements. These values correspond to those obtained for the sorption energies, from Dubinin – Radushkevich isotherm: E = 1.06 kJ / mol for U(VI) and E = 1.57 kJ / mol, for Fe(III).

13. The thermodynamic parameters for U(VI) and Fe(III) sorption, in the temperature range 20-70 ° C, were determined. In both cases it was observed that the sorption is promoted by temperature increasing the and is regarded as endothermic processes.

Sorption enthalpy, ΔH °, Gibbs free energy, ΔG ° and entropy, ΔS °, thermodynamic parameters were determined.The low values obtained for the sorption enthalpy are an argument for physisorption. Negative values of the free energy of sorption shows that the two sorption processes arising spontaneously.

14. Regarding the use Dowex-Marathon anionic resin in the enrichment process of uranium enrichment in ^{235}U isotope by chemical exchange, it can be said that is not suitable for this purpose. In the front band of uranium, the oxidation of U(IV) in the solution phase, with Fe(III), which is sorbed by the resin,must be occur with high rate. At the other end of uranium band, the reduction of U(VI) which is sorbed onto the resin in chlorocomplexes form with Ti(III), in the solution phase, must have high rate. From this work it is clear that the process of U(VI) and Fe(III) sorption occurs with low rate. Sorption is a reversible process, so that they are sorbed with a low rate, they will desorbed with low rate and the low oxidation kinetics in the end of uranium band, and a low reduction rate in the front of uranium band, are not favorable to the uranium enrichment process in ^{235}U isotope by chemical exchange using Dowex-Marathon resin, even if it has high sorption capacity for U(VI) and Fe(III) chlorocomplexes.

For an efficient uranium enrichment process by this method, will be chosen an anion resin, with high sorption capacity for U(VI) and Fe(III), and with large size of pores, so that the complex ions, comes into contact with the resin, can easily enter into the pores. Thus, the sorption rate will be high, and uranium enrichment in ^{235}U isotope by chemical exchange will lead to favorable results.

Finally, the most important original contributions of this work:

- The kinetic and thermodynamic parameters of the reaction between U(VI) sorbed on Dowex-Marathon resin and V(III) in sulfuric solution, in heterogeneous system were determined and it was concluded that the V(III) can be used as a reducing agent for ^{235}U isotope enrichment by chemical exchange in $U(VI)_{(R)}$ -$U(VI)_{(S)}$ system;

- We developed a method that determines if an anionic resin can be or can not be used in ^{235}U isotope enrichment by chemical exchange in $U(VI)_{(R)}$ -$U(IV)_{(S)}$ system when a solution of Ti(III) is used as reducing agent and a solution of Fe (III) is used as oxidizing agent, in hydrochloric medium. This consists in U(VI) and Fe(III) sorption kinetics measuring onto ion exchange resin, prior to use in the ^{235}U isotope enrichment columns. If the sorption occurs at high rate, it means that the resin is suitable for the isotopic enrichment.

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SCIENTIFIC ACTIVITIES

I. List of published articles in the thesis:

1. E. S. Drăgan, E. Avram, D. Axente, **Cristina Marcu**, *„Ion-exchange resins. III. Functionalization-morphology correlations in the synthesis of some macroporous, strong basic anion exchangers and uranium-sorption properties evaluation”,* Journal of Polymer Science Part A: Polymer Chemistry, 42: 2451-2461, **(2004)**

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4. D. Axente, **Cristina Marcu**, E. S. Drăgan, E. Avram, „*Determinarea capacităţii de adsorbţie a anionitului Dowex-Marathon pentru clorocomplecşii de Ti(IV) şi Fe(III)”,* Revista de Chimie (Bucureşti), 57: 1079-1081, **(2006)**

5. D. Axente, A. Balla, **Cristina Marcu**, „*Reduction of U(VI) adsorbed on anion exchange resin with V(III) in acid solution”*, Journal of Radioanalytical and Nuclear Chemistry, 288: 717-721, **(2011) (IF = 1,52/2011)**

6. **Cristina Marcu**, D. Axente, A. Balla, „*Kinetic and thermodynamic studies of U(VI) adsorption using Dowex-Marathon resin”,* Journal of Radioanalytical and Nuclear Chemistry, 305: 623-630, **(2015) (IF = 1,034/2014)**

7. **Cristina Marcu**, D. Axente, A. Balla, „*Study of Fe(III) adsorption onto Dowex-Marathon resin, as a rate determining step of the U(IV) oxidation in ^{235}U enrichment column”*, Journal of Radioanalytical and Nuclear Chemistry, **(2016) (IF = 1,034/2014)**

II. Oral presentations

1. E. S. Drăgan, E. Avram, D. Axente, **Cristina Marcu**, „*Strong basic anion exchangers with adsorption properties for chlorocomplex uranyl ion”*, PIM, Cluj-Napoca, România, 22 – 24 sept., **(2005)**
2. D. Axente, A. Balla, **Cristina Marcu**, „*Reduction of U(VI) adsorbed on anion exchange resin with V(III) in acid solution”*, PIM, Cluj-Napoca, 29 sept. – 01 oct., România, **(2011)**
3. **Cristina Marcu**, D. Axente, A. Balla, *„Kinetic and thermodynamic studies of U(VI) adsorption using Dowex-Marathon resin”,* Conferinţa Naţională de Chimie, Călimăneşti Căciulata, 01 – 03 oct., România, **(2014)**

III. Poster presentations at national and international conferences

1. D. Axente, **Cristina Marcu**, E. S. Drăgan, E. Avram, „*The determination of adsorption capacity of anion exchange resin Dowex-Marathon for Ti(IV) and Fe(III) chlorocomplexes”,* PIM, Cluj-Napoca, 20 – 22 sept., România, **(2007)**
2. **Cristina Marcu**, D. Axente, A. Balla, „*The kinetics reduction of U(VI) adsorbed on anionit with Ti(III), in HCl solution”*, PIM, Cluj-Napoca, 29 sept. – 01 oct., România, **(2011)**
3. **Cristina Marcu,** D. Axente, „*Kinetic and thermodynamic studies of Fe(III) adsorption onto Dowex-Marathon resin”,* PIM, Cluj-Napoca, 23 – 25 sept., România, **(2015)**