“BABEŞ-BOLYAI” UNIVERSITY CLUJ-NAPOCA
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING
CHEMICAL ENGINEERING

ZINC RECOVERY FROM WASTEWATERS BY IONIC EXCHANGE AND ELECTRODEPOSITION

PhD THESIS ABSTRACT

Scientific supervisor
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2015

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Cluj-Napoca, 2015 *Gîlcă Emilia*

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In this summary the notations used for chapters, paragraphs, figures, tables were kept the same as in the thesis.

INTRODUCTION

The aim of the thesis "Zinc recovery from wastewaters by ionic exchange and electrodeposition” is to develop a technology capable for Zn removal as Zn chloride complexes from hot dip galvanizing effluents.

The relevance of the research topic is supported by the fact that the hot-dip galvanizing process generates a considerable volume of highly concentrated solutions with metals. The literature analysis led to the conclusion that beside the classical methods of wastewater treatment, ionic exchange could be a viable and effective technique. As a result, two ways have been proposed:

- Zn removal by ionic exchange
- Zn recovery by electrodeposition

In literature the cationic exchange resins have been extensively applied for Zn removal in cationic form. On the other hand research papers did not cover removal of Zn in anionic form.

The thesis is structured as follows:

- **Part I: Literature overview**
- **Part II: Personal contributions**

Chapter 1 deals with general issues regarding the impact of galvanizing process and ways to treat the effluents, in which, ionic exchange is identified as a viable and effective technique.

In **Chapter 2** are presented the general characteristics of the ionic exchange technique, and the most common isotherm and kinetics models, which are used in the second part of the thesis.

In **Chapter 3** are presented the general aspects for Zn recovery from wastewaters by cathode electrodeposition.

In **Chapter 4** are described the advanced techniques of characterization used: Fourier Transform Infrared Spectroscopy, scanning electron microscopy, optical microscopy and X-ray diffraction.

In **Chapters 5** and **6** are presented and processed by the equilibrium and kinetic models, the experimental results for Zn removal from acid solutions using anionic exchange resins.

In **Chapter 7** are presented the experimental results obtained after anionic exchange resin regeneration in order to increase the Zn concentration in a smaller volume.

In **Chapter 8** are presented in detail the results obtained for Zn recovery by cathodic electrodeposition from the synthetic solutions obtained after anionic exchange resin regeneration.

At the end of the thesis are presented the general conclusions, the scientific work on the thesis topic, bibliography and appendices.

The novelty and the originality of this thesis is to test various anionic exchange resins for Zn removal as Zn complex, $ZnCl_4^{2-}$, followed by its recovery from the solution obtained after resin regeneration using cathodic electrodeposition.

To achieve the thesis goal, the following studies were considered:

- to examine the capacity of several anionic exchange resins for Zn removal as Zn chloride complexes in batch mode and in fixed bed column;
- the applicability of isotherms and kinetic models;
- the ability of different anionic exchange resins to retain and desorb Zn chloride complexes for several cycles of sorption-desorption;
- the possibility to concentrate the metal in a smaller volume in order to be recovered by cathode electrodeposition.

The results were published in different journals: four ISI journals *(Central European Journal of Chemistry, Water Science and Technology, Studia Universitatis Babes-Bolyai Chemia, Desalination and Water Treatment) one article in Bulletin of Romanian Chemical Engineering Society. Also the results were presented at five international and national conferences.*

Keywords: anionic exchangers, ANOVA analysis, electrodeposition, error functions, hot-dip galvanizing, isotherm models, kinetics, Taguchi, thermodynamics, $ZnCl_4^{2-}$.

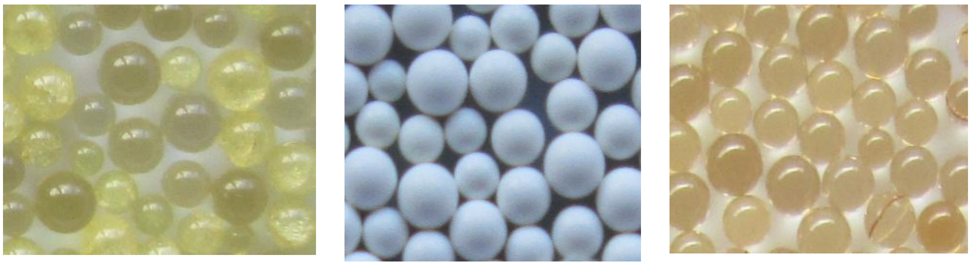
5. ZINC REMOVAL AS ZINC CHLORIDE COMPLEXES BY ANIONIC EXCHANGE RESINS IN BATCH MODE

In this chapter the results regarding the behaviour of anionic exchange resins for Zn removal as Zn chloride complexes from synthetic aqueous solutions in batch mode were presented. The experiments were made taken into account several parameters.

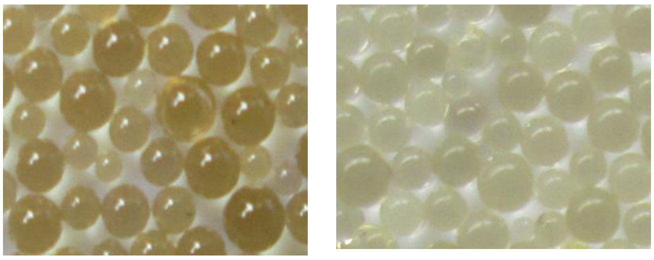
It has also been presented in detail the results obtained using the most common isotherms (Langmuir, Freundlich, Dubinin-Radushkevich, Temkin) and kinetic models. In order to identify the reaction order and rate constant of the ionic exchange process: pseudo-first-, pseudo-second order, intra-particle, film diffusion, Elovich, Bangham and Dumwald-Wagner models were applied. The experimental data and the calculated values obtained by applying different kinetic models were analysed by the most common error function in order to compare the applicability of each model for the investigated process.

5.1. Apparatus and analytical procedure

Several anionic exchange resins (Figure 5.1) for Zn removal as Zn chloride complexes, [$ZnCl_4^{2-}$] were considered for investigations. Before usage, the resins were soaked in double-distilled water for 24 hours and then washed several times.



Amberlite IRA410 Purolite A103S Purolite NRW700



Purolite A400MBOH Purolite A600MB

Figure 5.1 Anionic exchange resins.

Initial Zn solutions (300 to 1100 mg Zn/L) were prepared by dissolving $ZnCl_2$ salt in hydrochloric acid 1M.

5.2. Effect of process parameters for zinc removal using anionic exchange resins

5.2.1. Ionic exchange capacity of anionic exchange resins

The anionic exchange resins were tested in the same conditions by contacting 5 g of resin with 500 mg Zn/L metal solution and stirred for 300 min at 500 rpm.

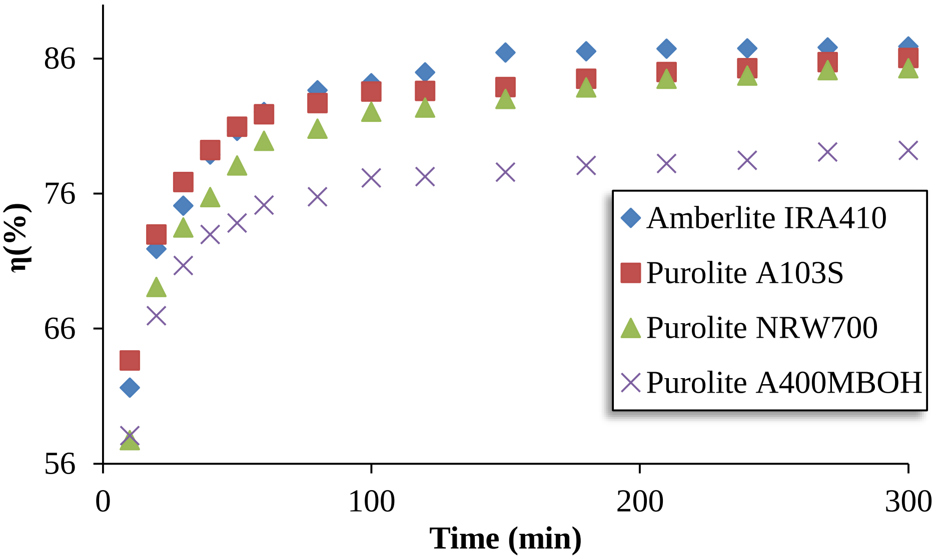


Figure 5.3 Removal efficiency for Zn sorption on different anionic exchange resins; C_0 = 500 mg Zn/L, m = 5 g, V = 100 mL, 500 rpm.

The results presented in Figure 5.3 showed that the percentage of Zn removed increased with the increasing of the contact time. In the first 100 min an increase steep was observed, followed by a slower increase with time up to 300 min. The maximum percent of sorption about 87 % was obtained for Amberlite IRA410 and the minimum percent of sorption about 79 % for Purolite A400MBOH. Based on these data the following tests were made by using Amberlite IRA410 resin.

5.2.2. Effect of stirring rate

The experiments were carried out using 5 g of Amberlite IRA410, which was contacted with Zn solution (100 mL) for 300 min at three different stirring rate 100, 300 and 500 rpm. The results are presented in Figure 5.4.

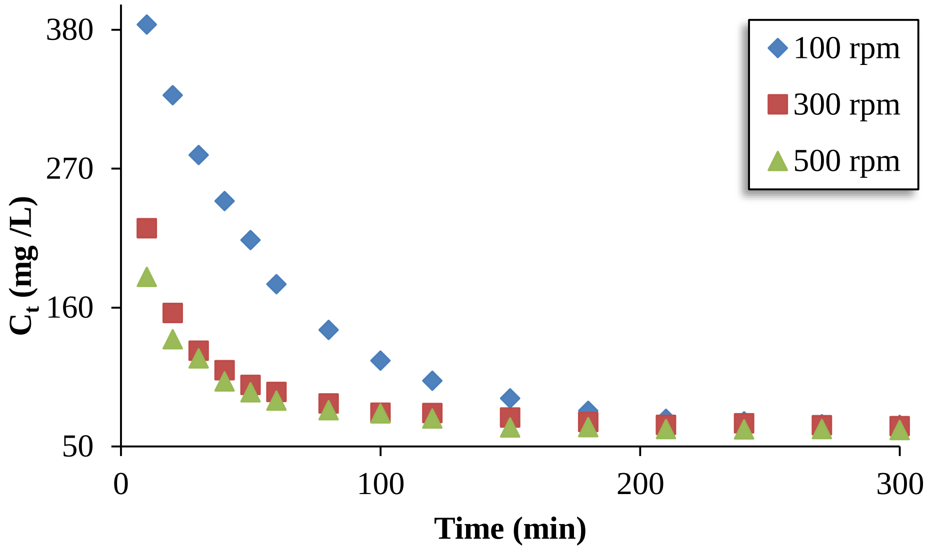


Figure 5.4 Effect of stirring rate on Zn sorption by Amberlite IRA410;
C_0 = 500 mg Zn/L, m = 5 g, V = 100 mL.

The results showed that the sorption process was strongly intensified by an increase of stirring rate from 100 to 300 rpm in the first 150 min, a further increase up to 500 rpm will lead to a smaller increase.

5.2.3. *Effect of resin quantity*

In order to study the effect of resin quantity on Zn removal, the weight of resin added to 100 mL solution was varied from 1 to 5 g. The results are given in Figure 5.6.

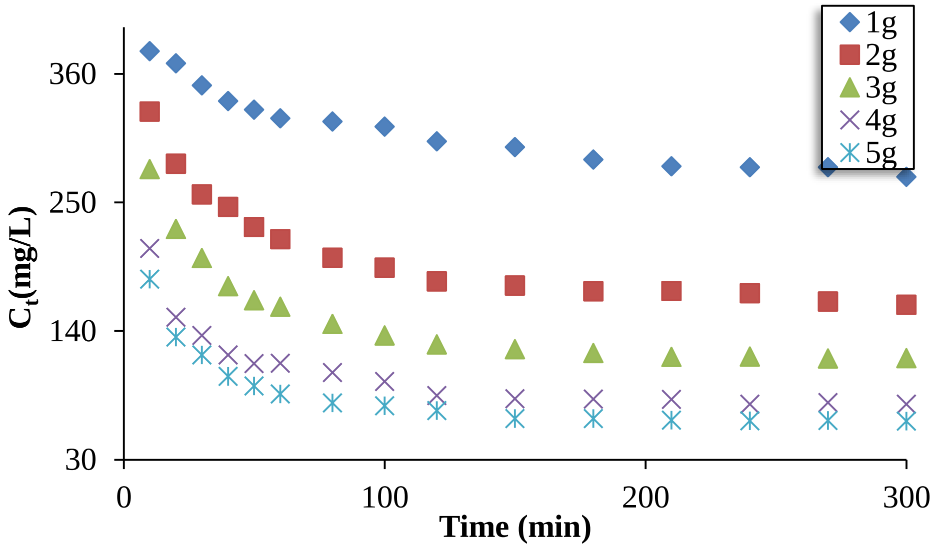


Figure 5.6 Effect of resin quantity on Zn sorption by Amberlite IRA410;
C_0 = 500 mg Zn/L, V = 100 mL, 500 rpm.

An increase in resin quantity will lead to a more rapid concentration drop in the first 50 min.

5.2.4. *Effect of initial concentration*

The experiments were carried out using a fixed anionic exchange quantity which was contacted with 100 mL Zn solution with concentrations between 300 and 1100 mg Zn/L. The obtained results for Zn sorption by Amberlite IRA410 starting from different initial concentration are presented in Figure 5.8.

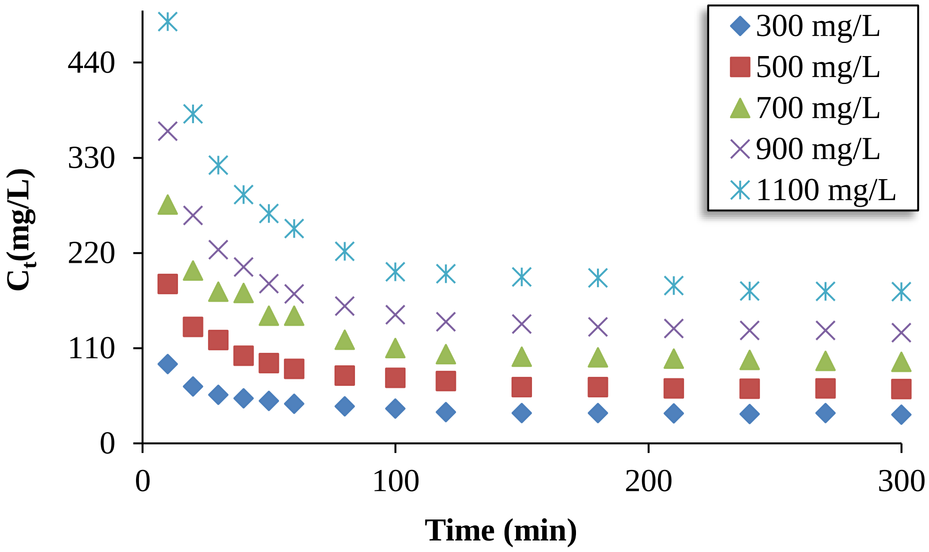


Figure 5.8 Effect of initial concentration on Zn sorption by Amberlite IRA410; m = 5 g, V = 100 mL, 500 rpm.

In this range of concentration, Zn sorption was rapid in the first 10 min, after that, the sorption rate slowly decreases as the process reaches equilibrium. It was noted that removal efficiency at 300 mg Zn/L was 89 % and 85 % at 1100 mg Zn/L.

The results presented in this chapter sections were published in *Central European Journal of Chemistry* 12(8) (2014) 821-828, Removal of zinc ions as zinc chloride complexes from strongly acidic aqueous solution by ionic exchange, authors: Gîlcă E., Măicăneanu A., Ilea P.

5.2.8. *The performance of anionic exchange resin*

The experiments were carried out for six sorption-desorption cycles using 100 mL solution (500 mg Zn/L initial concentration) contacted with 5 g of Amberlite IRA410 resin for 300 minutes. The regeneration of the resin after the sorption cycles was made using double-distillate water.

The results (Figure 5.16) showed that the removal efficiency decrease with the sorption-desorption cycles number and after the third cycle until six cycle remained constant. The decline in efficiency was no more than 10 %. Therefore the resin presented a good potential to retain Zn ions although it has been reused for several times.

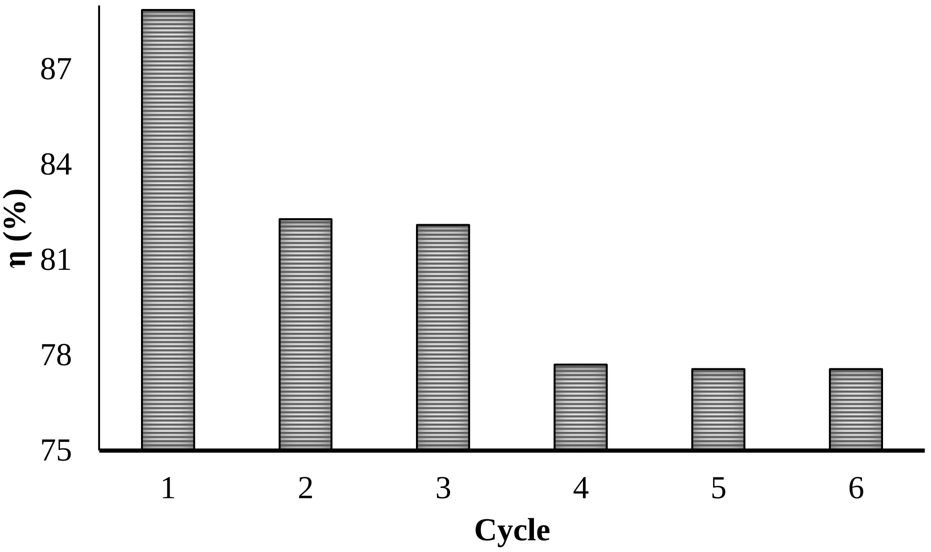


Figure 5.16 Removal efficiency after six sorption-desorption cycles: C_0 = 500 mg Zn/L, m = 5 g, V = 100 mL, 500 rpm.

The results presented in this section were published in *Studia Universitatis Babes-Bolyai Chemia* LX 3 (2015) 173-181, Column and batch regeneration studies for zinc removal on different anionic exchange resins, authors: Gîlcă E.(a)., Măicăneanu A., Ilea P.(a).

5.4. Isotherm models

The equilibrium data were analysed using the most common isotherms model Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906), Dubinin-Radushkevisch (Dubinin & Radushkevich, 1947) and Temkin (Tempkin & Pyzhev, 1940).

From the data presented in Table 5.6, the value of s is 1.29 indicating that the Zn sorption onto Amberlite IRA410 is cooperative.

Table 5.6 Isotherm constants for Zn sorption on Amberlite IRA410.

Model	**Parameters**			**R²**
	Symbol	**U.M.**	**value**	
Langmuir	q_{max}	mg/g	43.47	0.980
	K_L	L/mg	0.18	
Freundlich	s	-	1.29	0.984
	K_F	$mg^{(1-1/n)} L^{1/n} /g^1$	0.37	
Dubinin-Radushkevich	β	mol^2 /kJ^2	$9\cdot10^{-9}$	0.984
	E_L	kJ/mol	7.45	
Temkin	A_T	L/g	2.15	0.966
	G	J/mol	$1\cdot10^{-4}$	

Taking into consideration the calculated value of the mean free energy obtained from Dubinin-Radushkevich isotherm and the constant related to heat of sorption, from Temkin isotherm (Table 5.6), we concluded that the sorption process is physically.

The results presented in this chapter section were published in *Central European Journal of Chemistry* 12(8) (2014) 821-828, Removal of zinc ions as zinc chloride complexes from strongly acidic aqueous solution by ionic exchange, authors: Gîlcă E., Măicăneanu A., Ilea P.

5.5. Kinetics studies

In order to identify the best model for Zn removal as Zn chloride complexes the following kinetics models were taken into consideration: pseudo-first order (Lagergren, 1898), pseudo-second order (Ho & McKay, 1999; Ho & McKay, 2000), intra-particle diffusion (Weber & Morris,1963), film diffusion (Boyd et al., 1947), Elovich (Elovich, 1959), Bangham (Bangham & Burt, 1924) and Dumwald-Wagner (Dunwald & Wagner, 1934).

The kinetics constants for the pseudo-first order (Lagergren, 1898) and pseudo-second order model (1 - 4 forms) are presented in Table 5.7.

The high values of the correlation coefficients obtained and the fact that calculated q_e values are almost similar with the experimental values suggests that Zn sorption on Amberlite IRA410 is best described by the pseudo-second order model.

Table 5.7 Pseudo-first order and pseudo-second order reaction kinetics constants and ionic exchange values for Zn sorption on Amberlite IRA410.

Model	**Parameters**	**Units**	**300**	**500**	**700**	**900**	**1100**
			mg/L	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Pseudo-first order	k_1	1/min	0.010	0.015	0.014	0.012	0.017
	$q_{e,calc}$	mg/g	0.62	1.54	2.44	2.71	5.05
	R^2		0.825	0.909	0.937	0.854	0.889
Pseudo-second order	k_2	g/mg·min	0.057	0.025	0.015	0.013	0.008
1	$q_{e,calc}$	mg/g	5.66	8.49	13.69	16.15	19.72
	R^2		1	1	0.99	1	1
2	k_2	g/mg·min	0.065	0.026	0.018	0.014	0.009
	$q_{e,calc}$	mg/g	5.63	8.46	13.55	16.12	19.53
	R^2		0.993	0.994	0.973	0.998	0.989
3	k_2	g/mg·min	0.625	0.099	0.026	0.014	0.006
	$q_{e,calc}$	mg/g	5.61	8.38	13.48	15.99	19.36
	R^2		0.980	0.974	0.946	0.984	0.965
4	k_2	g/mg·min	0.063	0.026	0.018	0.014	0.009
	$q_{e,calc}$	mg/g	5.64	8.48	13.69	16.15	19.61
	R^2		0.755	0.894	0.891	0.969	0.969
Experimental values	$q_{e,exp}$	mg/g	5.61	8.34	13.47	15.92	19.31

In order to evaluate the displacement of q_e value towards the experimental values, different error functions have been considered. In case of Zn sorption on Amberlite IRA410 resin, the pseudo-second order model produced low values for all errors functions (Table 5.8).

Table 5.8 Error functions for pseudo-first order and pseudo-second kinetic model.

Functions	**Models**				
	Pseudo-first order	**Pseudo-second order**			
		1	**2**	**3**	**4**
HYBRID	311	0.14	0.05	0.004	0.10
ARE	2351	0.86	0.91	0.97	0.87
MPSD	176	3.79	2.36	0.69	3.29
r_s	0.80	0.99	0.99	0.99	0.99
s_{RE}	627	0.28	0.26	0.26	0.27
X^2	40	0.01	0.007	0.0006	0.01
S.E.	6.62	0.78	0.75	0.77	0.77
RMSE	6.16	0.14	0.08	0.02	0.11
ERRSQ/SSE	570	0.29	0.10	0.009	0.21

The intra-particle and liquid film diffusion rate coefficients and intercepts, together with the correlation coefficients are listed in Table 5.9 and 5.10, respectively.

Table 5.9 Intra-particle diffusion rate coefficients for Zn sorption on Amberlite IRA410 at different initial concentrations.

		Region 1 **10 - 40 minutes**		**Region 2** **40 - 100 minutes**		**Region 3** **100 - 300 minutes**	
C_0	D_i	k_{ip}	R^2	k_{ip}	R^2	k_{ip}	R^2
mg/L	cm^2/s	$mg/g\cdot min^{0.5}$		$mg/g\cdot min^{0.5}$		$mg/g\cdot min^{0.5}$	
300	$8.1 \cdot 10^{-7}$	1.20	0.925	1.82	0.973	3.08	0.773
500	$5.2 \cdot 10^{-7}$	0.83	0.952	1.23	0.941	2.07	0.666
700	$5.3 \cdot 10^{-7}$	0.52	0.917	0.75	0.973	1.28	0.991
900	$5.6 \cdot 10^{-6}$	0.43	0.945	0.64	0.985	1.08	0.977
1100	$4.2 \cdot 10^{-6}$	0.37	0.979	0.53	0.999	0.89	0.929
Intercept		3.73 - 9.24		4.89 - 14.3		5.47 - 18.06	

Analysing the results obtained it can be concluded that, in case of Zn sorption on Amberlite IRA410, the intra-particle transport and liquid film diffusion were not the rate-determining step (the intercept values were higher than 0).

Table 5.10 Liquid film diffusion rate coefficients for removal of Zn on Amberlite IRA410 at different initial concentrations.

C_0	**k_{fd}**	**Intercept**	**R^2**
(mg/L)	**(1/min)**	-	-
300	52.66	2.12	0.895
500	37.72	1.39	0.982
700	41.72	1.55	0.972
900	47.47	1.69	0.958
1100	33.69	1.08	0.933

Bangham and Dumwald-Wagner model were applied in order to find if the intra-particle diffusion is the rate-controlling step. The results obtained are given in Table 5.11.

Table 5.11 The kinetics parameters for Zn sorption on Amberlite IRA410.

Model	**Parameters**	**Units**	**300**	**500**	**700**	**900**	**1100**
			mg/L	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Elovich	**α**	**mg/g·min**	2.54	2.00	2.14	2.12	1.90
	ß	**-**	0.29	0.63	0.97	1.18	1.68
	R^2		0.874	0.884	0.908	0.871	0.904
Bangham	**K_0**	**-**	0.50	0.51	0.51	0.51	0.52
	x	**dm/g**	0.05	0.09	0.08	0.08	0.10
	R^2		0.853	0.856	0.885	0.840	0.876
Dumwald-Wagner	**K**	**1/min**	0.01	0.02	0.01	0.01	0.02
	R^2		0.883	0.964	0.974	0.963	0.931

The experimental data do not give a good fit to the Bangham model (low correlation coefficients obtained), for Zn complexes on Amberlite IRA410, therefore intra-particle diffusion is not the rate-controlling step. R^2 values obtained from Dumwald-Wagner model confirmed that the adsorption process was controlled by intra-particle diffusion at initial concentration between 500 - 1100 mg Zn/L.

Also based on R^2 values it has been concluded that experimental data did not fit on the Elovich equation. This suggests that the process governing the Zn sorption on the studied resin is physical. Thus, the obtained results are in agreement with the results obtained from fitting the Temkin and Dubinin-Radushkevich isotherm.

Some of the results presented in this chapter section were published in Central European Journal of Chemistry 12(8) (2014) 821-828, Removal of zinc ions as zinc chloride complexes from strongly acidic aqueous solution by ionic exchange, authors: Gîlcă E., Măicăneanu A., Ilea P.

6. ZINC REMOVAL AS ZINC CHLORIDE COMPLEXES BY ANIONIC EXCHANGE RESINS IN FIXED BED COLUMN

In this chapter the results regarding the behaviour of anionic exchange resins for Zn removal as Zn chloride complexes from synthetic aqueous solutions in fixed bed column were presented. The experiments were made taken into account several parameters. Also the applicability of the kinetics models (Thomas, Adam-Bohart, Clark, Yoon-Nelson, and Wolborska) and the characteristics of the bed were considered. Similarly, the concept of the Mass Transfer Zone was applied in order to properly design the fixed bed adsorption process.

6.1. Materials and methods

A column equipped with a glass frit for support and a layer of glass wool to prevent the escape of the resins beads during operation was used for the experiments. The scheme of the experimental setup is presented in Figure 6.1.

The synthetic solution having different Zn concentrations (300 - 1100 mg Zn/L) was allowed to pass through the column in continuous down flow mode at a given flow rate (1.36 mL/min). The treated metal solution was collected at the outlet of the column every 15 minutes and analysed.

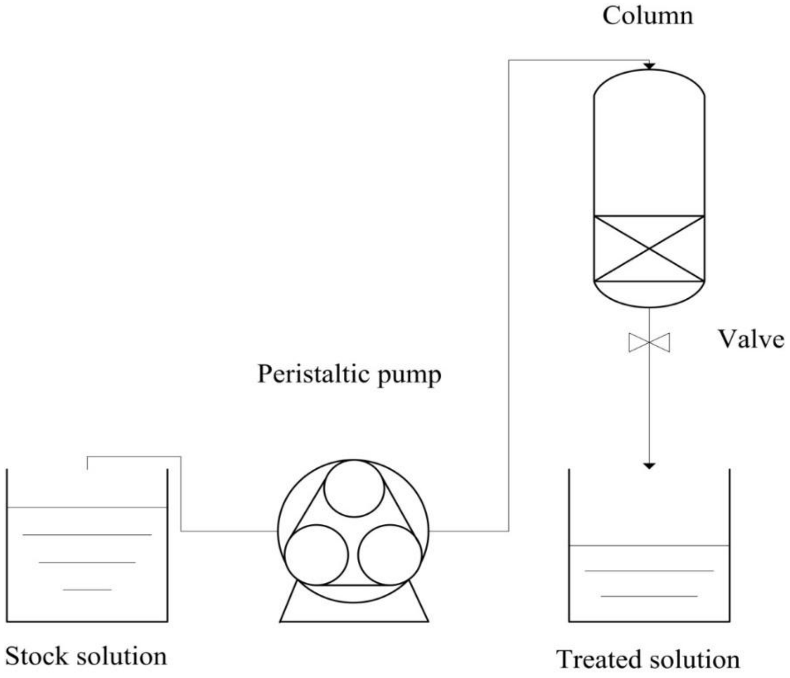


Figure 6.1. Experimental setup.

6.2. Effect of process parameters

6.2.1. *Ionic exchange capacity of anionic exchange resins*

The anionic exchange resins previously tested in batch mode, were tested in a fixed bed column, using 2 g of resin with 1000 mg Zn/L solution (Figure 6.2).

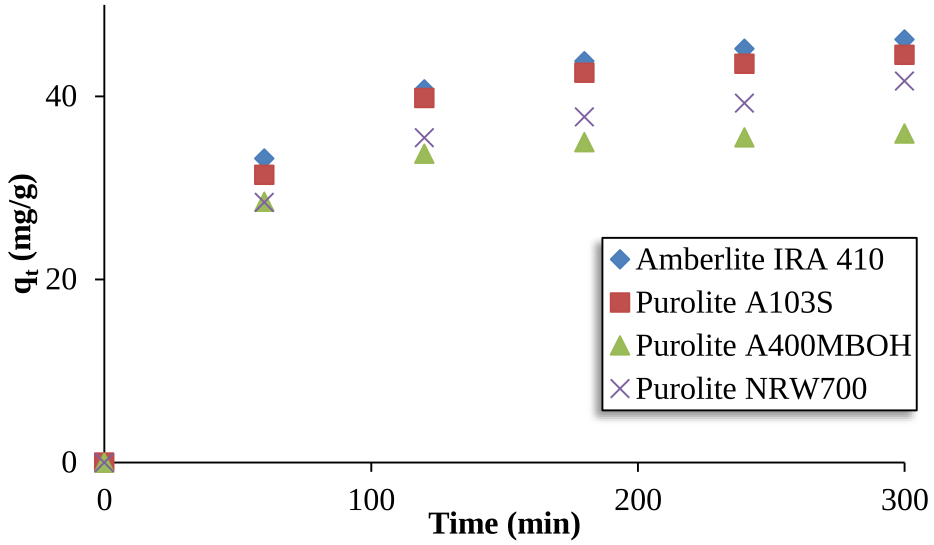


Figure 6.2 Removal capacity for Zn sorption by different anionic exchange resins; m = 2 g, Q = 1.36 mL/min, C_0 = 1000 mg Zn/L.

Based on the obtained data the following series was depicted taking into account their sorption capacity: Amberlite IRA410 > Purolite A103S > Purolite NRW700 > Purolite A400MBOH. The same series was obtained in batch mode.

6.2.2. *Effect of resin quantity*

The breakthrough curves for Zn sorption on Amberlite IRA410 at various resin quantities, 1 - 6 g at an inlet concentration of 500 mg Zn/L are shown in Figure 6.3.

As we expected, Zn sorption was very fast in the first minutes, then the concentration at the column outlet was rapidly increasing as the resin was getting saturated.

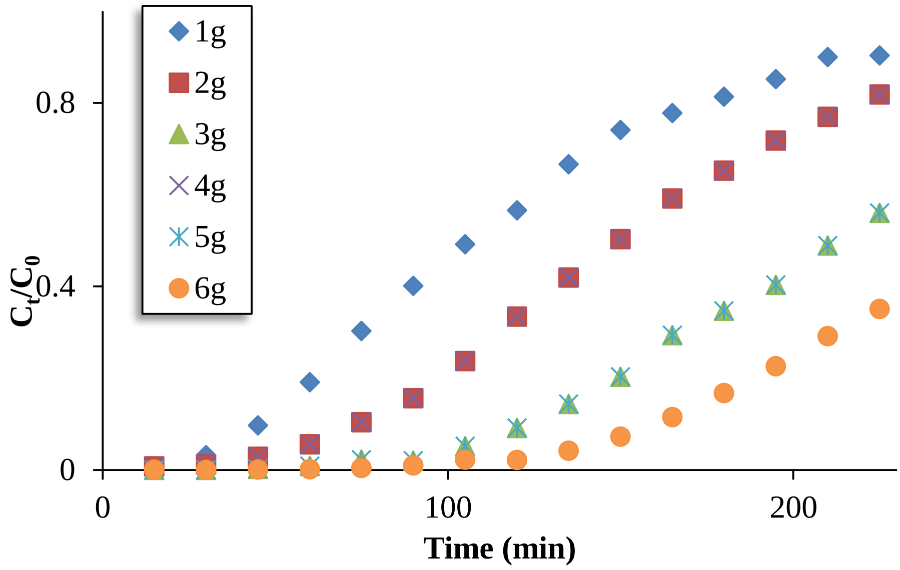


Figure 6.3 Breakthrough curves for Zn sorption onto Amberlite IRA410 using different resin quantities; m = 5 g, Q = 1.36 mL/min, C_0 = 500 mg Zn/L.

6.2.3. *Effect of initial zinc concentration*

The experiments were carried out using 5 g of resin and various initial concentrations ranging between 300 and 1100 mg Zn/L. The obtained results for Zn sorption by Amberlite IRA410 are presented in Figure 6.4.

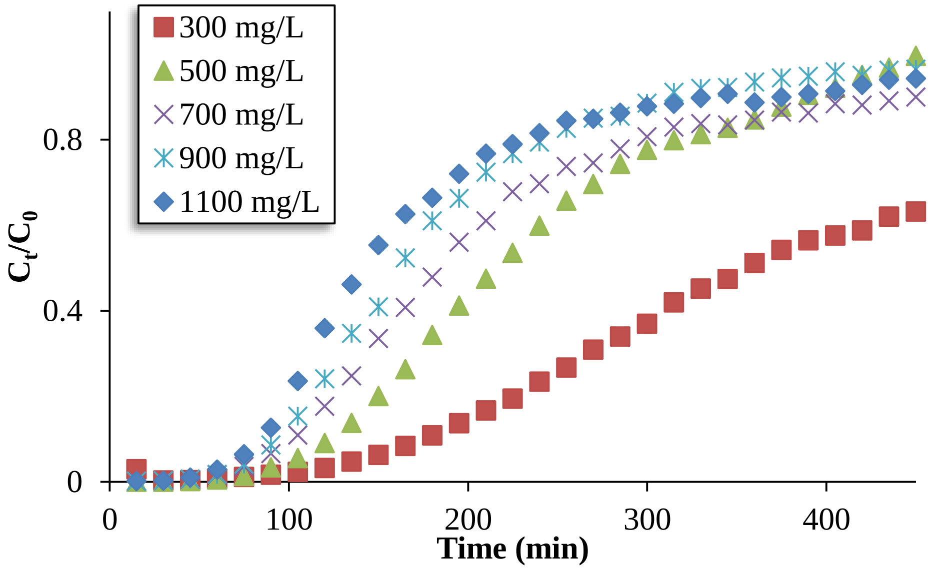


Figure 6.4 Breakthrough curves for Zn sorption onto Amberlite IRA410 using different initial zinc concentrations; m = 5 g, Q = 1.36 mL/min.

As it can be seen, the Zn sorption was very fast in the first 15 minutes, afterwards, the sorption rate slowly decreased as the resin was getting saturated.

In Table 6.1 the values of the following parameters are presented: breakthrough time (t_b) of the breakthrough curves obtained when different initial concentrations and ionic exchange capacities were used at exhaustion time (t_s), 7.5 h. It can be observed that the values of t_b decreased when Zn concentration was increasing. Sorption capacity values were increasing with an increase of the concentration from 28 mg/g (300 mg Zn/L) to 45 mg/g (1100 mg Zn/L). High concentrations quickly saturated the resin, thereby decreasing the breakthrough time.

In Table 6.1 the values of breakthrough time (t_b) at exhaustion time (t_s), 7.5 h for different initial concentrations and ionic exchange capacities used are presented. It can be observed that the values of t_b decreased and the sorption capacity values increased when Zn concentration was increasing. High concentrations quickly saturated the resin, thereby decreasing the breakthrough time.

Table 6.1 The values of breakthrough time and the ionic exchange capacity for different initial Zn concentrations.

C_0	t_b	q_t
mg/L	**h**	**mg/g**
300	2.50	28.32
500	2.25	30.10
700	2.00	39.57
900	1.75	37.43
1100	1.50	45.26

6.2.4. The performance of the anionic exchange resin

In order to evaluate the performance of the Amberlite IRA410, the resin was contacted with the metal concentration for six cycles of sorption-desorption. The results obtained for Zn sorption were presented in Figure 6.5.

By comparing the six cycles curves it can be seen that the breakthrough behaviour remains unchanged with successive regeneration (an increase of sorption-desorption cycles number does not lead to a substantial modification).

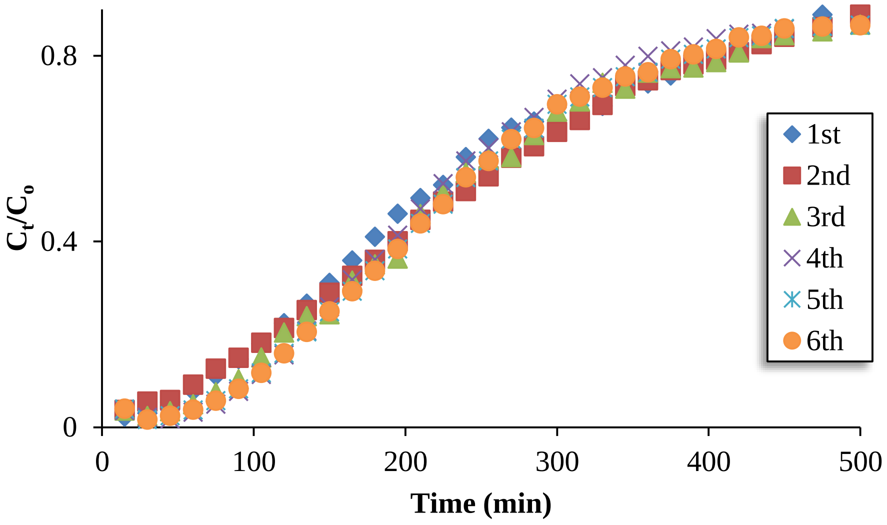


Figure 6.5 Breakthrough curves for Zn sorption during six sorption cycles in fixed bed column; m = 5 g, Q = 1.36 mL/min, C_0 = 500 mg Zn/L.

The regeneration of the resin after the sorption cycles was made using double-distillate water.

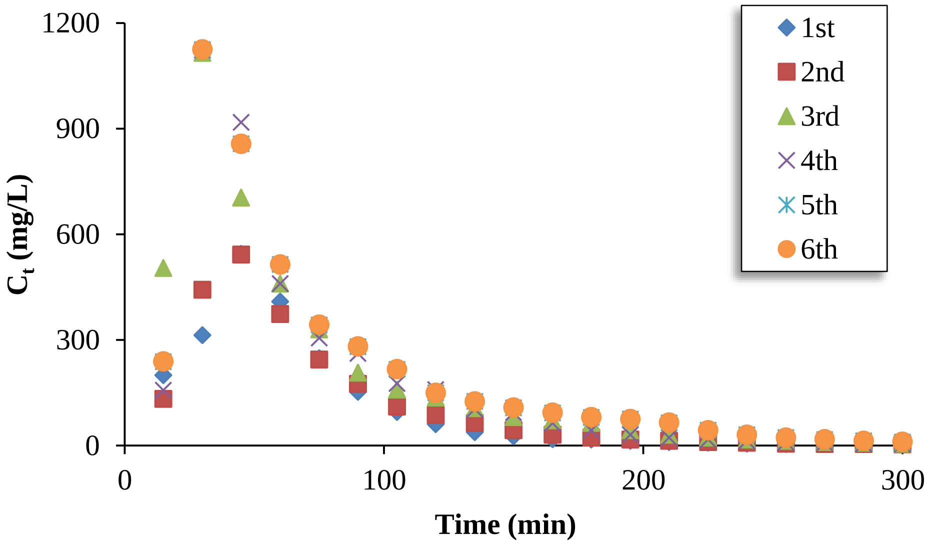


Figure 6.6 Zn concentration during regeneration cycles in fixed bed column: m = 5 g, Q = 1.36 mL/min.

The results obtained showed (Figure 6.6) that in the first minutes the concentration was very high, after that slowly decreased as the resin was regenerated.

The results presented in this section were published in *Studia Universitatis Babes-Bolyai Chemia* LX 3 (2015) 173-181, Column and batch regeneration studies for zinc removal on different anionic exchange resins, authors: Gîlcă E., Măicăneanu A., Ilea P.(a).

6.2.5. FTIR analysis

The FTIR spectra of Amberlite IRA410 resin before (fresh) and after Zn sorption are shown in Figure 6.7.

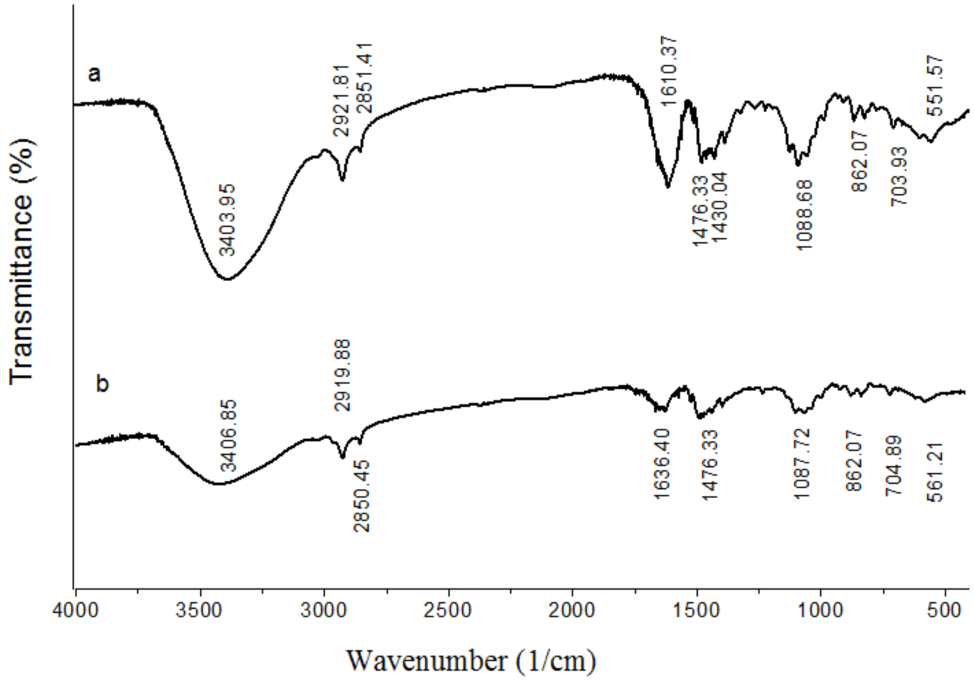


Figure 6.7 The FTIR spectra for Amberlite IRA410; before (fresh) (a) and after Zn sorption (b).

A synthetic solution having 500 mg Zn/L concentration was passed through 5 g of Amberlite IRA410 resin at 1.36 mL/min flow rate for 450 minutes. For the fresh resin, a broad peak at 3403.95 cm^{-1} that was assigned to the stretching vibrations of the –OH group, was observed, Figure 6.7a. A change in peak position to 3406.85 cm^{-1} and a smaller intensity are caused by replacement of –OH groups during the ionic exchange process. The peaks from 3000 - 2800 cm^{-1} range could be assigned to –CH_2 stretching vibration of –CH_3 and –CH_2 functional groups. The peak at 1610.36 cm^{-1} on the fresh Amberlite IRA410 indicates the region of C=C, which corresponds to benzene presented in the matrix of the resin. On Amberlite IRA410 after adsorption, benzene it is present at 1630 cm^{-1}. The region between 1520 and 1000 cm^{-1} is the fingerprint of OH and C–H bending vibration and C–O stretching vibration absorption bands and the peaks at 1500 - 1600 cm^{-1} are due to deformation and skeletal vibrations of C–H in divinylbenzene (Nidheesh et al., 2012; Malkoc & Nuhoglu, 2007; Singare et al., 2011, Awwad & Salem, 2014).

6.3. Reaction kinetic models

The kinetics of Zn sorption on Amberlite IRA 410, was studied taken into consideration the following models: Thomas (Thomas, 1944), Adam-Bohart (Bohart & Adams, 1920), Clark (Clark, 1987), Yoon-Nelson (Yoon & Nelson, 1984), and Wolborska (Wolborska, 1989).

The determined coefficients and relative constants obtained are shown in Table 6.2. The k_{TH} values increased as the resin quantity increased and afterwards slowly decreased with a further increase of the resin quantity. In contrast, k_{TH} decreased with increasing initial Zn concentration. The values of k_{AB}, decreased with an increase of the initial concentration and resin quantity. Based on correlation coefficients obtained, it can be concluded that the Adam-Bohart model does not adequately fit the experimental data for Zn sorption on Amberlite resin.

Table 6.2 Thomas, Adams-Bohart and Clark parameters for Zn sorption at different resin quantities and initial concentrations.

	Thomas			**Adams-Bohart**			**Clark**		
m/C_0	**q_0**	**$k_{TH}\cdot 10^{-5}$**	**R^2**	**$k_{AB}\cdot 10^{-5}$**	**N_0**	**R^2**	**H**	**$r\cdot 10^{-2}$**	**R^2**
g/mg/L	**mg/g**	**L/min·mg**		**L/mg·min**	**mg/L**			**1/min**	
1/500	2.66	3.11	0.82	0.61	86.20	0.50	0.37	1.3	0.85
2/500	30.93	4.22	0.80	2.05	35.15	0.55	0.01	1.5	0.88
3/500	26.76	6.51	0.91	3.70	22.40	0.70	0.04	2.3	0.98
4/500	25.63	6.29	0.97	4.32	18.76	0.88	0.35	1.9	0.99
5/500	25.76	8.56	0.90	7.82	15.27	0.86	0.92	1.9	0.97
6/500	24.56	8.07	0.95	7.62	14.26	0.94	0.98	1.7	0.98
5/300	31.04	4.39	0.92	3.47	20.79	0.86	0.33	0.8	0.96
5/700	46.97	2.49	0.83	1.58	37.79	0.67	0.10	1.1	0.92
5/900	49.41	2.41	0.86	1.32	43.65	0.62	0.21	1.4	0.95
5/1100	57.12	1.75	0.78	1.01	50.68	0.57	0.11	1.2	0.88

Table 6.3 Yoon-Nelson and Wolborska parameters for Zn sorption at different resin quantities and initial concentrations.

Model	**Yoon-Nelson**			**Wolborska**		
m/C_0	**k_{YN}**	**τ**	**R^2**	**h (x 10^{-3})**	**N_0**	**R^2**
g/mg/L	**1/min**	**min**	**-**	**1/min**	**mg/L**	**-**
1/500	0.01	4.06	0.820	1.9	316.91	0.505
2/500	0.02	95.95	0.801	2.6	129.26	0.557
3/500	0.03	123.93	0.919	3.0	82.38	0.706
4/500	0.03	158.10	0.972	2.9	69.00	0.884
5/500	0.04	198.09	0.902	4.3	56.15	0.864
6/500	0.03	224.35	0.954	3.9	52.43	0.942
5/300	0.01	357.92	0.922	2.65	76.45	0.869
5/700	0.01	253.35	0.839	2.19	138.93	0.670
5/900	0.02	218.95	0.867	2.12	160.51	0.628
5/1100	0.01	216.05	0.789	1.89	186.32	0.575

In case of Yoon-Nelson and Wolborska models (Table 6.3) the results obtained suggested that the considered models do not fit properly the experimental data for Zn sorption on Amberlite resin (small correlation coefficients were obtained).

The Clark model provided an acceptable correlation indicating a good applicability for Zn removal on Amberlite resin.

6.4. Characteristics of the adsorption zone

In order to properly design and operate the fixed bed adsorption process, the concept of the Mass Transfer Zone (MTZ) was applied. Therefore its characteristics: fractional capacity (W), height of MTZ (H_Z) and rate of the movement of the MTZ (U_Z) were determined (Namane & Hellal, 2006; Hanen & Abdelmottaleb, 2013). The results obtained are presented in Table 6.4.

In the studied range of concentrations and resin quantities the values of W were between 0.6 - 0.8 and 0.4 - 0.9, respectively. Taken into consideration the values obtained it can be concluded that the resin was not completely saturated and the adsorption phenomenon takes place between 7.90 - 8.56 cm (300 - 1100 mg Zn/L) and 1.70 - 4.75 cm (1 - 6 g).

Table 6.4. Basic design parameters of the sorption column starting from different initial concentrations and resin quantities.

C_0	H_b	W	H_z	U_z	t_f	t_z	Saturation
mg/L	**cm**		**cm**	**cm**	**h**	**h**	**%**
300	9	0.67	7.66	1.53	1.62	5	72
500	9	0.73	7.73	1.47	1.39	5.25	77
700	9	0.78	7.83	1.42	1.18	5.5	81
900	9	0.82	7.94	1.38	0.98	5.75	85
1100	9	0.87	8.00	1.33	0.75	6	89
500	1.8	0.98	1.70	0.48	0.05	3.5	99
500	3.6	0.95	3.24	0.99	0.14	3.25	96
500	5.4	0.92	4.18	1.52	0.19	2.75	94
500	7.2	0.84	4.75	2.11	0.34	2.25	90
500	10.8	0.46	2.41	3.22	0.39	0.75	88

The time required to form MTZ (t_f) greatly increased at 300 mg Zn/L initial concentration (1.62 h) but when the concentration increased the time decreased (less than one hour) (Table 6.4). At 300 mg Zn/L only 72 % saturation at breakthrough point was obtained and at 1100 mg Zn/L the saturation was approximately 89 %. In case of varying the resin quantity, the percentage saturation will increase by decreasing the resin quantity (99 % for 1 g of resin quantity).

6.5. Diffusion parameters

In order to determine the controlling mechanism the mechanical parameter ζ was calculated. If its value is below 1 it indicates liquid film diffusion as rate controlled step and if its value is higher than 1 it indicates the solid diffusion as rate determining step (Inglezakis & Zorpas, 2012). According to the obtained values (Table 6.5), the solid diffusion is controlling the process rate at concentrations between 300 - 900 mg Zn/L and liquid film diffusion at higher concentrations, 1100 mg Zn/L.

Table 6.5 The kinetic parameters for the estimation of the controlling mechanism.

C_0	c	ζ	$Sc \cdot 10^2$	$k_f \cdot 10^{-5}$	a_u	Re
mg/L	**g/s·cm^3**	**-**	-	**cm/s**	**1/cm**	**-**
300	0.02	4.72	226.08	11.48	76.5	0.05
500	0.01	10.57				
700	0.01	11.24				
900	0.14	1.52				
1100	1.09	0.19				

The results presented in this chapter were published in *Water Science and Technology* 71(11) (2015) 1646-1653, Kinetics analysis of zinc sorption in fixed bed column using a strongly basic anionic exchange resin, authors: Gîlcă E., Măicăneanu A., Ilea P.

7. IONIC EXCHANGE-ELECTRODEPOSITION

The following tests were made in order to evaluate the ability of several anionic exchange resins to retain and desorb Zn chloride complexes.

Five anionic exchange resins were tested in the same conditions for one sorption-desorption cycle in batch mode using a higher volume of solution (400 mL) in order to exhaust the resins. The results presented in Figure 7.1 showed that the maximum percent of sorption was obtained for Purolite A600MB and the minimum percent of sorption was obtained for Purolite A400NRW700.

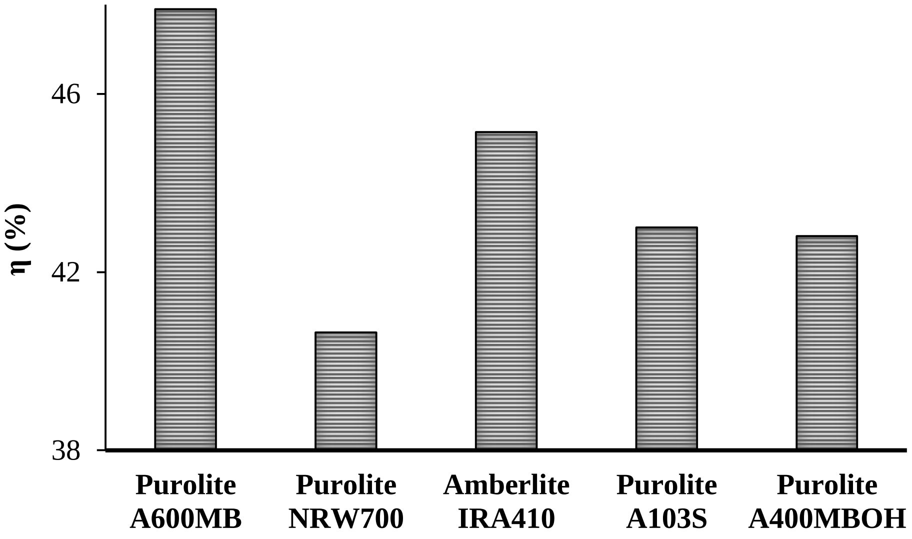


Figure 7.1 Removal efficiency for Zn sorption on different anionic exchange resins.

Taking into consideration that usually Fe is also presented in pickling baths, further sorption-desorption experiments with multicomponent solutions (Zn and Fe) were also considered. The obtained results are presented in Figure 7.2.

In this case the initial Fe concentration remained constant during the experiments (in HCl medium Fe will not form complexes). The removal efficiency at 500 mg Zn/L was 48 % and 37 % at 900 mg Zn/L.

Desorption experiments for all the concentrations were carried out using different volumes of double-distilled water (20 - 80 mL). The results showed that a volume of 80 mL double-distillate water ensured the complete regeneration of the resin. The concentration of Zn in 80 mL was between 1.3 - 1.8 g Zn/L. Taken into account that in this volume the Zn concentration is high the Zn electrodeposition could be applied in order to obtain pure Zn deposits.

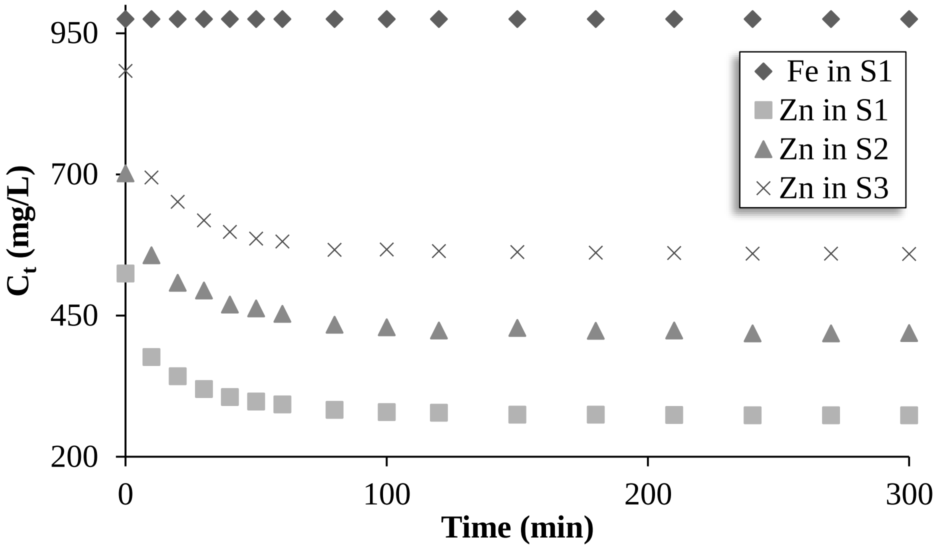


Figure 7.2 Effect of Zn initial concentration on Zn sorption by Purolite A600MB in presence of Fe (S1 = 1000 mg/L Fe + 500 mg/L Zn; S2 = 700 mg/L Zn + 1000 mg/L Fe; S3 = 900 mg/L Zn + 1000 mg/L Fe).

The results presented in this chapter were published in Studia Universitatis Babes-Bolyai Chemia LX 3 (2015) 173-181, Column and batch regeneration studies for zinc removal on different anionic exchange resins, authors: Gîlcă E., Măicăneanu A., Ilea P.(a).

GENERAL CONCLUSIONS

The literature overview has inspired the researches presented in this thesis in order to use an ion exchange-electrodeposition system for Zn removal from hot-dip galvanizing effluences.

The objectives taken into account and presented in the first part of the thesis were achieved in the second part, where personal contributions have revealed the following:

- the following series was depicted based on removal efficiencies in batch mode and fixed bed column: Amberlite IRA410 > Purolite A103S > Purolite NRW700 > Purolite A400MBOH;
- the significant parameters for Zn removal onto Amberlite IRA410 and their optimal levels were: 900 mg Zn/L initial concentration, 293 K, 1 g resin quantity, 2 M acid concentration, 100 rpm;
- the percent contribution value indicated resin quantity ~85 % as the parameter with the highest influence on Zn removal;
- the parameter predicted from the Freundlich isotherm suggests the heterogeneity of the surface of the Amberlite IRA410 resin;
- the kinetics of Zn sorption suggested that the considered sorption process is better described by the pseudo-second-order kinetic model;
- the Dubinin-Radushkevich and Temkin isotherms and also the Elovich kinetic model indicate a physisorption process;
- the Dumwald-Wagner kinetics model indicated intra-particle diffusion model as rate determining step at concentration higher that 500 mg Zn/L;
- the obtained values in fixed bed column showed a classic behaviour: as the quantity of resin increased, the sorption capacity decreased, while with an increase of the initial concentration, the sorption capacity increased;
- the R^2 values for the Clark model indicate a good linearity, while R^2 for the Adam-Bohart model was generally lower than the Thomas model under the same experimental conditions;
- the calculated parameters of the mass transfer zone were presented and discussed in detail;
- the value of the mechanical parameter showed that the rate controlling mechanism was the liquid film diffusion and solid diffusion;

- the electrodeposition testes indicated Zn recovery with current efficiencies between 85 - 95 %;
- the advanced characterization of the Zn deposits obtained showed a hexagonal-like crystalline shape.

The original elements presented in the second part of the thesis were the following:

- the influence of different process parameters for Zn removal as Zn chloride complexes in batch and fixed bed column using anionic exchange resins;
- the ability of several anion exchangers to retain and desorb Zn chloride complexes in order to increase the Zn concentration in the regeneration step;
- the applicability of different isotherms and kinetic models;
- the identification of the optimal process parameters and their levels in batch mode using Taguchi DOE and ANOVA analysis;
- the performance studies of a rotating cylinder electrode in different conditions;
- advanced characterization of the Zn deposits using the following analytical methods: Scanning electron microscopy, X-ray diffraction, optical microscopy.

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Research internship (2 months)

Scientific supervisor Prof. Dr. rer. nat. Dr. h.c. Andreas Bund from Institut fur Werkstofftechnik Fachgebiet Elektrochemie und Galvanotechnik, Technische Universität Ilmenau, Germania

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