UNIVERSITATEA DIN BUCUREŞTI
FACULTATEA DE CHIMIE
ŞCOALA DOCTORALĂ ÎN CHIMIE

Abstract

Preparation by ion exchange processes and characterization of functionalized ion exchange resins having complex-forming groups

Scientific coordinator **PhD student**

Prof. Dr. Luminiţa Vlădescu ***Cristian Radu***

2012

CUPRINS

Chapter I

ION EXCHANGE RESINS MODIFIED WITH ORGANIC REAGENTS

Despite the progress achieved in instrumental analysis in concentrations of trace elements, the processes of preconcentration and separation of the analytes from the matrix are still indispensable. Based on sorption preconcentration procedures are cosiderat by some specialists exceed those based on liquid-liquid extraction due to simplicity, speed and their ability to give up preconcentration factors. Sorbents obtained by immobilization on solid supports chelating agents proved to be very useful in the preconcentration of trace metals in concentrations in different types of matrices. Their use is advantageous because it can control the sorption capacity and selectivity of the metal by appropriate choice of organic reagent (which will immobilize the sorbent), thereby controlling the efficiency.

The ion exchange resins are well known solutions offered to solve the problems arising from the separation of complex mixtures containing metal cations. Use of chelating reagents in the separation and concentration of metal ions with ion exchange resins usual, is the most widely used. Among the reagents that form complex combinations, organic ones are most suitable because of their selectivity.

In order to obtain complexing ion exchange resins or by physical adsorption, using two methods: static and dynamic method. Common anion exchange resins can be converted into different types of resins functionalized either by synthesis or just by shaking with aqueous reagent. Several authors have discussed loading mechanisms of the functionalized resins functionalized. From studies it can be concluded that the retention of chelating reagents on polymer substrate, in order to obtain complexing resins, generally is involving ion exchange mechanisms and / or adsorption [Olbrych-Sleszynska, 1998].

I.1. Stability of ion exchange resins with complexes forming groups

Stability of chelating resins can be studied spectrophotometrically by measuring the concentration of complexing reagent effluent passed when the resin is treated with eluent. Stability was studied in the presence of complexing resin solutions of acids, bases and salts.

I.2 Literature studies on ion exchange resins to obtain complexes forming groups

A summary of the data in the literature regarding obtaining and characterization of ion-exchange resins with complexes forming groups is presented in Table 1.1.

I.3. Studies on factors influencing reagent sorption in an ion exchange resin

In this section are presented the results of studies in which it was evaluated the sorption potential of anion exchange resins for the treatment of aqueous solutions of organic reagents. Sorption is affected by different parameters such as contact time, initial concentration of the reagent, stirring rate, temperature, pH, particle size and degree of crosslinking of the resin.

Amount of sorbate reactive in resin increases with increasing contact time of phases, with increasing concentration of reagent solution and with resin particle size decreasing. Length of diffusion path from active centers of the ion exchanger are shorter for smaller particles, and thus ion exchange is faster. Differences between stirring speeds determine sorption kinetics change as film thickness surrounding particles changes.

Sorption capacity increases with temperature of reagent solution. Acid dyes sorption is favored by increasing temperature due to increased mobility of reactive molecules with temperature.

Based on the solution pH influence on sorption in resin, it can be concluded that ion exchange mechanism is predominant. Other mechanisms, such as dislikes of reactive molecules and / or between the matrix resin and reactive, play an important role in fixing reagents on sorbents. The emergence double link increases the interaction between dye and the anion exchanger matrix. Physical adsorption and dispersion forces π-π type may result from aromatic nature of the resin and dye [Wawrzciewicz, 2010a].

I.4 Sorption models based on sorption equilibrium and kinetic data used in the study of the process to obtain resins with complex forming groups.

Sorption isotherms characterize how the substance interacts with the sorbent and sorbate and this gives us information about the nature of interactions between the resin and reagent. Of these, the most used were models Langmuir, Freundlich, and Dubinin Radushkevich [Tan, 2008;

Lata, 2008; Bekci, 2008; Hameed, 2009]. Based on the average adsorption free energy, Dubinin theory can predict the sorption type: Physics (1-8 kJ / mol), ion exchange (9-16 kJ / mol) or chemical (> 16 kJ / mol) [Ada, 2009].

Lagergren and Ho models, and Weber Morris intraparticle diffusion model were compared with experimental data obtained from sorption of dyes in the resin Amberlite FPA 51 [Tan, 2008; Lata, 2008; Bekci, 2008; Hameed, 2009].

In the theoretical part of the thesis are presented and discussed articles sorption equilibrium studies and kinetic in synthetic dye / ion exchange resin systems.

Chapter II

Solochrom yellow 2 GS as organic reagent for spectrometric determination of iron (III), copper (II) and uranium(VI) ions

In this chapter are presented the results of a study Spectrometric on interactions between cations Fe^{3+}, Cu^{2+},UO_2^{2+} and 2-hydroxy-5-[(4-sulfophenyl) azo]-benzoic acid disodium salt (also known as Solocrom Yellow 2GS), noted the GAC [Radu, 2009; Radu 2012c; Vlădescu şi Radu, 2012]. Reagent formula is shown in Figure 2.1.

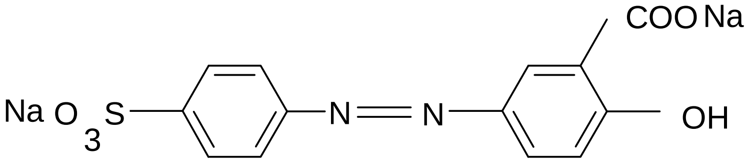


Fig. 2.1: Fig. 2.1: Solochrom yellow 2 GS reagent formula

.

II.1. Study the interaction between Fe (III) ions and Solochrom yellow 2 GS reagent by molecular absorption spectrometry [Radu, 2009].

II.1.1 Influence of experimental parameters on absorption spectra

Wavelength, pH, the amount of organic reagent and concentration of Fe (III) cation influences on the absorbance were studied to determine optimum operating conditions for the determination of iron (III).

II.1.1.1 Absorbance variation by wavelength

Absorbance variation depending on the wavelength was studied by plotting absorption spectra: a solution containing formed compound to reagent blank and solutions containing compound or reagent to water. Fig. 2.2 shows that at a wavelength of 490 nm the solution containing iron (III) and reagent has a maximum absorption, while the solution containing reagent only has a low absorbance, which requires absorbance measurements to be made at λ =490 nm against blank containing only reagent.

II.1.1.2 The influence of pH on the wavelength

Absorbance of each solution was measured at λ = 490 nm against a blank that contained 4 mL GAC 10-3 M in solution with the same pH as the sample. The graph in Fig. 2.3 shows that absorbances of the complex increases with increasing pH, reached a peak in the 2.79 to 2.99 and then decreases. Next, we worked with 10^{-3} M reagent solution in the pH range from 2.5 to 3.0.

II.2.2 Determination of the combining ratio

For determining the Fe (III): GAC combining ratio, 3 methods were used: spectrophotometric titration of Fe (III) by reagent, reagent spectrophotometric titration by Fe (III) and isomolar series method.

All three methods have led to the conclusion that the ions Fe (III) and the reagent form a complex under ratio Fe: GAC of 1:2.

II.1.3 Determination of the stability constant of the complex formed by ions Fe (III) and GAC reagent by nonisomolar solutions series method.

Experimental data and those obtained by the graphic method allowed the calculation of total stability constant $\beta_s = 3.023 \cdot 10^5 \pm 1.55 \cdot 10^5$ L^2/mol^2.

II.1.4. Determination of performance parameters of the spectrometric determination method of iron (III) using acidic yellow chromatic reagent.

To validate the method were determined performance parameters such as linearity range, limit of detection, accuracy and precision. The detection limit was determined from the experimental data according to international rules [ICH Q2A, 1994; ICH Q2B, 1996].

Calibration equation is: $A = 0.0045 + 0.0688\, C$
where: A = absorbance of the sample at $\lambda = 490$ nm; C = concentration of the solution.

The correlation coefficient of the straight line calibration is set R = 0.9997.

Molar absorbance coefficient was calculated as: $\varepsilon = 3750$ L mol^{-1} cm^{-1}.

II.1.5. Interferences

To determine the possible interferences, the UV-VIS were recorded for solutions containing the following cations: Na^+, K^+, Mg^{2+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, UO_2^{2+}, for the working conditions established as optimal for the determination of iron (III) (fig. 2.9). Potentially interfering ions effect on determining ions Fe (III) with organic reagent GAC at $\lambda = 490$ nm in the pH range from 2.79 to 3.00 was studied by adding known concentrations of each ion solution with a concentration of Fe (III) of 4.46 mg / L. Ions: Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, UO_2^{2+} does not interfere when there are in a concentration less than or equal to that of iron (III). Ions Fe (II) did not interfere even when they are in a concentration of 2 times higher than that of Fe (III). Ions Na^+, K^+, Mg^{2+}, Ca^{2+}, Mg^{2+}, Ba^{2+} do not interfere at all.

II.2. Study of the interaction between ions Cu (II) and Solochrom yellow 2 GS reagent by molecular absorption spectrometry [Vlădescu şi Radu, 2012].

II.2.1 Influence of experimental parameters on absorption spectra

Wavelength, pH, the amount of organic reagent and concentration of Cu (II) ions influences on the absorbance were studied to determine optimum operating conditions for determination of copper (II).

II.2.1.1 Variation of absorbance by wavelength

Absorbance variation depending on the wavelength was studied by plotting absorption spectra: a solution containing complex against reagent blank and solutions containing compound or reactive against water. In Fig. 2.10 shows at the wavelength of 435 nm the solution containing copper (II) and reagent has an absorption maximum, while the solution containing reagent only has a low absorbance, which requires absorbance measurements to be made at $\lambda = 435$ nm against blank only containing reagent.

II.2.1.2 The influence of pH on the absorption spectra

Absorbance of each solution was measured at $\lambda = 435$ nm against a blank that contained 4 mL of GAC 10^{-3} M in solution with the same pH as the sample. As shown in Fig. 2.11 absorbance of the complex increases with increasing pH, reached a peak in the 6.30-9.43 then decreases. Next, we worked with 10^{-3} M reagent solution in the pH range 6.30-7.00.

II.2.2 Determination of the combining ratio

For determining the combining ratio Cu (II): GAC 3 methods were used: spectrophotometric titration of Cu (II) by reagent, reagent spectrophotometric titration with Cu (II) isomolar series method. All three methods have led to the conclusion that the ions Cu(II) and the reagent forms a complex under ratio Cu: GAC of 1:2

II.2.3 Determination of the stability constant of the complex formed by ions of Cu (II) and GAC reagent by nonisomolar solutions series method

Experimental data and those obtained by the graphic method allowed the calculation of total stability constant $\beta_s = 1{,}58 \times 10^6 \pm 0{,}4 \times 10^6$ L^2/mol^2.

II.2.4 Determination of performance parameters of spectrometric determination method of copper (II) using acidic yellow chromatic reagent.

To validate the method were determined performance parameters such as linearity range, LOQ şi LOD, accuracy and precision. The detection limit was determined from the experimental data according to international rules [ICH Q2A, 1994; ICH Q2B, 1996].

Calibration equation is: $A = 0{,}0369 + 0{,}1177 \cdot C$

where: A = absorbance of the sample at $\lambda = 435$ nm; C = concentration of the solution.

The correlation coefficient of the straight line calibration is set R = 0,9908.

II.2.5. Interferences

To determine the possible interferences, the UV-VIS spectra were recorded for solutions containing the following cations: Na^+, K^+, Mg^{2+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, UO_2^{2+} , for the working conditions established as optimal for determination of copper (II) (fig. 2.17). The effect of potential interfering ions on determining Cu (II) ions with organic reagent at λ = 435 nm GAC in the pH range from 6.30 to 7.00 was studied by adding known concentrations of each ion solution with a concentration of Cu (II) of 1.0 mg /L. Ions: Fe^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, does not interfere when you are in a concentration greater than that of copper (II). Only ions (UO2) 2 +, in concentrations greater than or equal to that of Cu (II) solution increase the absorbance at λ = 435 nm. Ions Na^+, K^+, Mg^{2+}, Ca^{2+}, Mg^{2+}, Ba^2 do not interfere at all.

II.3. Study of the interaction between UO_2^{2+} ions and Solochrom yellow 2 GS reagent by molecular absorption spectrometry [Radu, 2013].

II.3.1 Influence of experimental parameters on the absorption spectra

Wavelength, pH, the amount of organic reagent and concentration of UO_2^{2+} ions influences on the absorbance were studied to determine optimum operating conditions for determination of U(VI) cations.

II.3.1.1 Variation of absorbance by wavelength

Absorbance variation depending on the wavelength was studied by plotting absorption spectra: a solution containing complex against reagent blank and solutions containing compound or reactive against water. In Fig. 2.18 shows at the wavelength of 397 nm the solution containing UO_2^{2+} and reagent has an absorption maximum, while the solution containing reagent only has a low absorbance, which requires absorbance measurements to be made at λ = 397 nm against blank only containing reagent.

II.3.1.2 The influence of pH on the wavelength

Absorbance of each solution was measured at λ = 397 nm against a blank that contained 4 mL of GAC 10^{-3} M in solution with the same pH as the sample. As shown in Fig. 2.19, the absorbance of the complex increases with increasing pH, reached a peak in the 4.40-4.83 then decreases. Next, we worked with 10^{-3} M reagent solution in the pH range 4.40-4.83.

II.3.2 Determination of the combining ratio

For determining the combining ratio U(VI): GAC 3 methods were used: spectrophotometric titration of U(VI) by reagent, reagent spectrophotometric titration with U(VI) isomolar series method.

All three methods have led to the conclusion that the ions U(VI) and the reagent forms a complex under ratio U(VI): GAC of 1:2.

II.3.3 Determination of the stability constant of the complex formed by ions of U(VI) and GAC reagent by nonisomolar solutions series method.

Experimental data and those obtained by the graphic method allowed the calculation of total stability constant $\beta_s = 1.72 \cdot 10^9 \pm 1.68 \cdot 10^9$ L^2/mol^2.

II.3.4. Determination of performance parameters of spectrometric determination method of copper (II) using acidic yellow chromatic reagent.

To validate the method were determined performance parameters such as linearity range, LOD şi LOQ, accuracy and precision. The detection limit was determined from the experimental data according to international rules [ICH Q2A, 1994; ICH Q2B, 1996].

Calibration equation is: $A = -0{,}019 + 0{,}021C$

where: A = absorbance of the sample at $\lambda = 435$ nm; C = concentration of the solution.

The correlation coefficient of the straight line calibration is set R = 0.989.

Molar absorbance coefficient was calculated as: $\varepsilon = 4985.0$ L mol^{-1} cm^{-1}.

II.3.5. Interferences

In order to establish any possible interferences, the UV – VIS spectra were recorded for solutions containing each one of the following ions: Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Cu^{2+} and the reagent GAC in the working conditions established as optimal for UO_2^{2+} determination. The spectra are showed in figure 2.25 (in the thesis). The effect of potential interfering ions on the spectrometric determination of UO_2^{2+} with the organic reagent Solochrome Yellow 2GS at $\lambda = 397$ nm within *p*H range 4.40 – 4.83 was investigated by adding known concentration of each above ion to a solution containing 1 mg·L^{-1} UO_2^{2+} and 4 mL of 10^{-3} M GAC solution. The ions: Ni^{2+} and Pb^{2+} does not interfere when being in equal or lower concentrations than those of UO_2^{2+}. Only the ions Fe^{3+} and Cu^{2+}, being in the same or larger concentration as UO_2^{2+}, increases the absorbance of the solutions at λ = 397. It was found that: Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+} do not interfere at all.

Chapter III

PREPARATION AND CHARACTERIZATION OF A NEW SORBENT BY UPLOADING SOLOCHROM YELLOW 2 GS ON AMBERLITE IRA 400 RESIN

The aim of the study presented in this chapter is to get a new ion exchange resin having complex-forming groups used in the separation and concentration of heavy metal ions [Radu, 2012b].

III.1. Spectrometric determination of Solochrom yellow 2 GS concentration in solution.

For quantitative determination of acidic chromatic yellow reagent the calibration curve was done (Fig. 3.1 in the thesis) using different concentrations of reagent solutions. Linearity of the calibration curve was checked for reagent concentrations ranging from 1 to 60 mg /mL. Calibration curve equation is: $A = 0.0013 + 0.0383 \cdot C$

where: A = absorbance of the sample at λ = 435 nm; C = concentration of the solution.

The correlation coefficient of the straight line calibration is set R = 1.

Molar absorbance coefficient was calculated as: $\varepsilon = 14040\ \text{L mol}^{-1}\ \text{cm}^{-1}$.

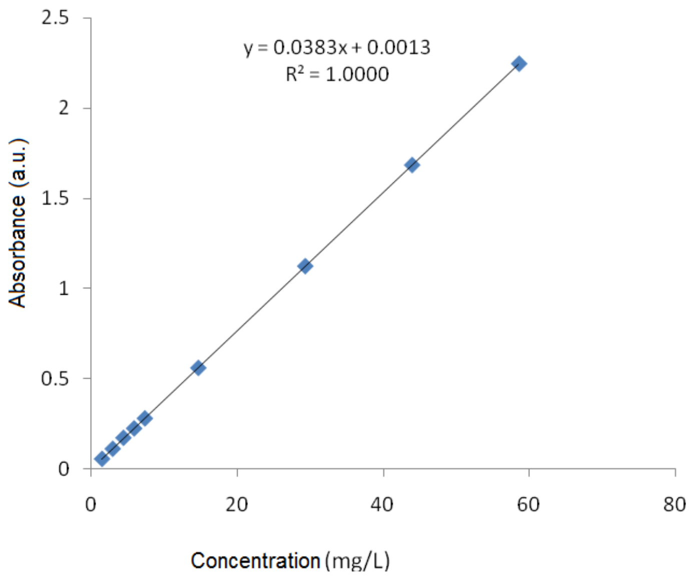


Fig. 3.2 Calibration curve of Solochrom yellow 2 GS reagent

III.2 Distribution equilibria study of reagent solution- ion exchange resin systems

Study of solid-liquid distribution equilibria involving anion exchange resin and acidic chromate yellow reagent solution were made taking into account the influence of the stirring time and the amount of reagent in solution, for the fixation of the dye. It was also studied the influence of solution acidity on the stability of the loaded resin with reagent.

III.2.1. The Effect of Phase Contact Time

The influence of phase contact time on GAC uptake from aqueous solutions with different initial concentrations (366 to 1647 mg/L) by Amberlite IRA 400 (Cl^-) at 20ºC was studied. The results indicated that the amount of dye adsorbed per mass unit of the anion exchanger increased with time and initial GAC concentration. After 15 minutes of stirring, the entire amount of R-dye in aqueous solution was bound to the anion, when the initial concentration of the aqueous solution was 366 mg/L (fig. 3.2). After 30 min of phase contact time, the resin loading changed insignificantly for all the concentrations in the initial solutions. For the initial solution with 1647 mg/L concentration, stirred for: 30, 60 şi 120 minutes, respectively, the equilibrium Q_e values were as follows: 286.22; 292.74; 294.50 mg/g, respectively (fig. 3.3).

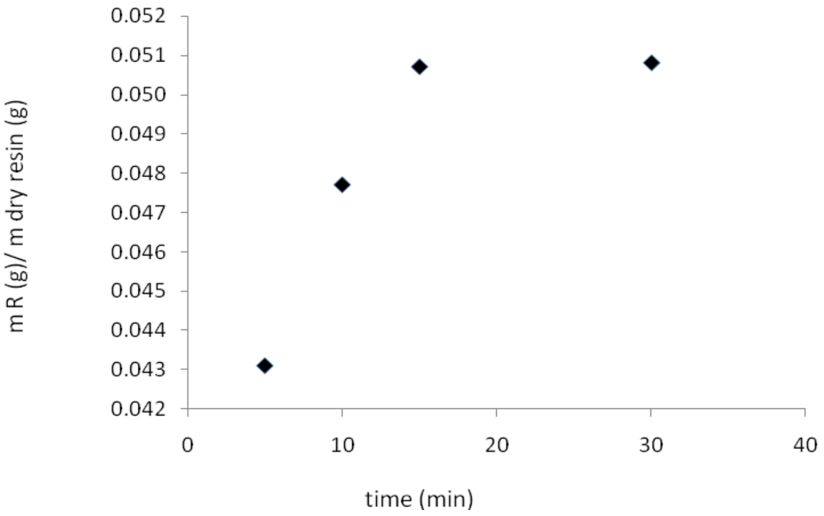


Fig. 3.2: The effect of phase contact time on
GAC fixing on Amberlite
IRA 400 (initial concentration of the reagent 366 mg / L)

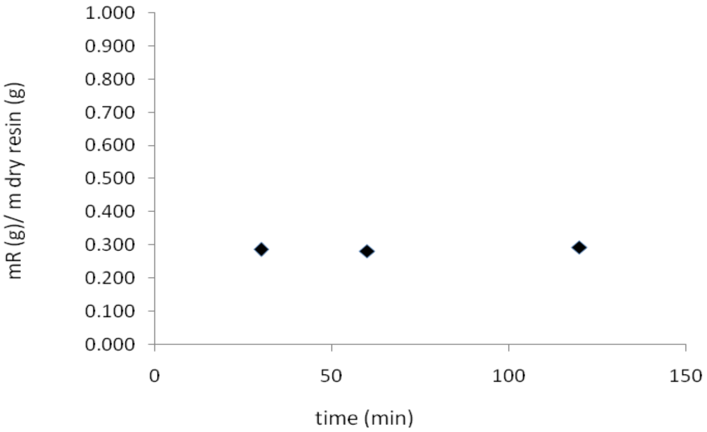


Fig. 3.3: Influenţa timpului de agitare asupra fixării
reactivului GAC în răşină Amberlite
IRA 400 (concentraţia iniţială de reactiv 1647 mg/L).

III.2.2. The Effect of Initial Dye Concentration

S It was found that with increasing initial concentration of dye increases the amount of reagent in resin.

Therefore, for the following initial concentrations: 732, 976 1464 şi1647 mg/L, respectively, the following Q_e values were determined: 103.50; 137.05, 190.72 si 294.50 mg ***R***/g dry resin, respectively (fig. 3.4- 3.6). Based on these results, it is found that for the reagent concentrations above 1647 mg / L in the initial solution, the amount of reagent in resin vary slightly, which leads to the conclusion that it reached maximum sorption capacity of the resin.

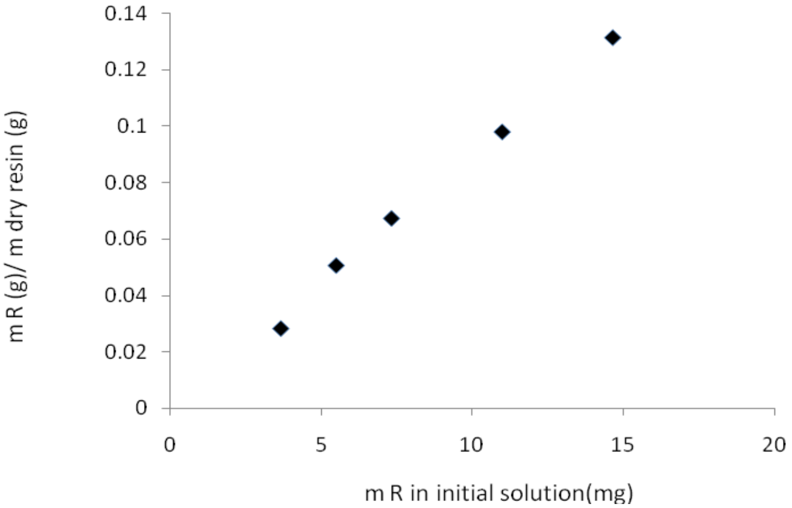


Fig. 3.4: The effect of initial dye concentration over its sorption onAmberlite IRA 400 (contact time: 15 minutes)

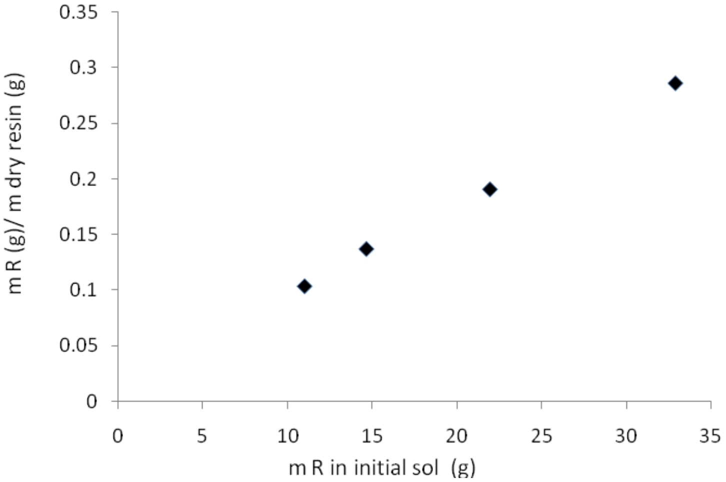


Fig. 3.5: The effect of initial dye concentration over its sorption onAmberlite IRA 400 (contact time: 30 minutes).

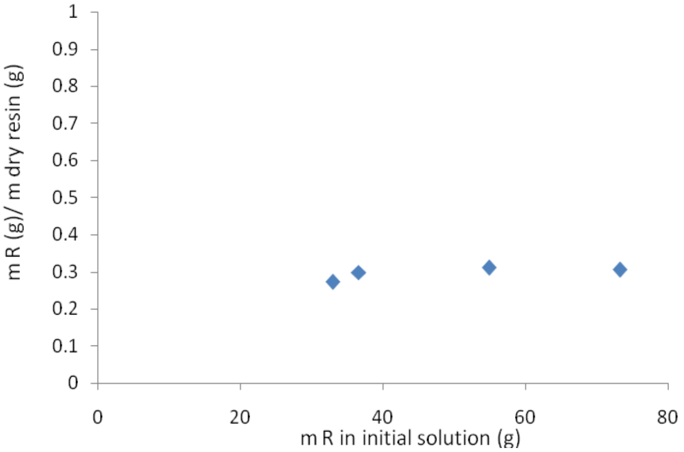


Fig. 3.6: The effect of initial dye concentration over its sorption onAmberlite IRA 400 (contact time: 60 minutes).

III.2.3. The Effect of Acidity on the Stability of the GAC-Loaded Resin

In order to examine the stability of the ***GAC***–loaded resin in acidic solutions, this study used aqueous solutions of HCl in different concentrations. The results are presented in Figure 3.7 below. Figure 3.7 indicates a decrease in the amount of dye from the resin while the concentration of HCl increases. At 0.10 M concentration of the HCl solution, the ***GAC***-loaded resin was stable and, thus it can be used for separation and concentration of cations. The ***GAC***-dye can be removed from the resin by prolonged exposure to a 0.10 M solution of HCl.

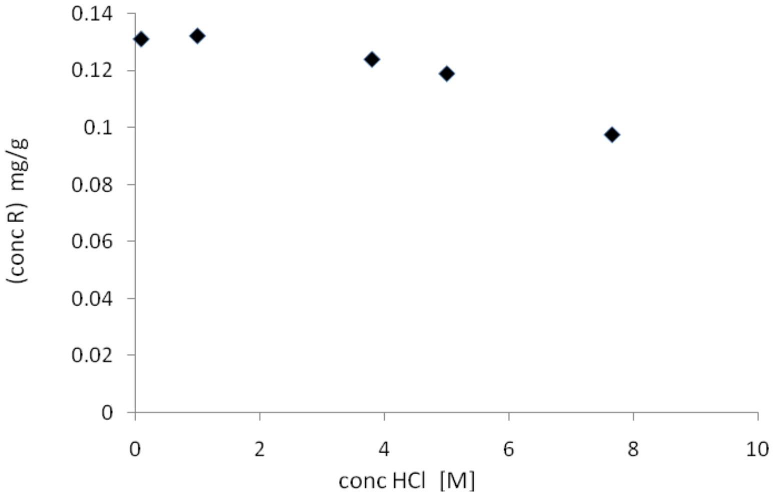


Fig. 3.7 : The Effect of acidity on the desorption of ***GAC***- dye from the Amberlite IRA 400 resin.

III.2.4. Sorption of Iron (III) ions in GAC-Loaded Resin

In order to study the sorption of Fe(III) ions in the ***GAC*** -loaded resin, weighted samples of chelating resin were stirred with aqueous solutions containing different amounts of Fe (III). Figure 3.8 below presents the results. The maximum amount of iron retained in the chelating resin was observed when the amount of ***GAC***-dye loaded in the resin was more than twice the amount of iron.

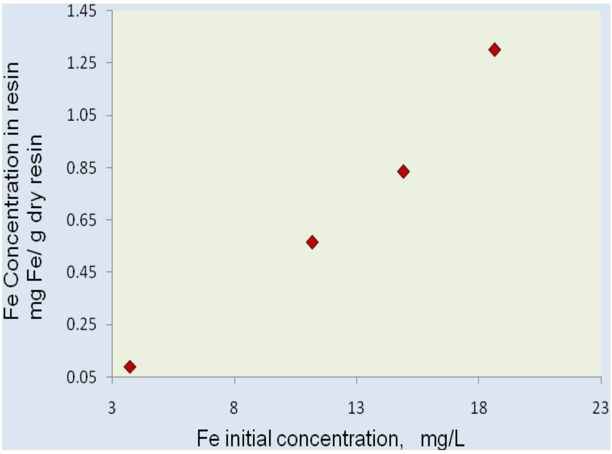


Fig. 3.8 Sorption of Iron (III) ions in R-Loaded Resin.

III.2.5. The effect of acidity on the desorption of Fe(III) from the R-Loaded Resin

Figure 3.9 indicates an increase in the amount of iron that leaves the resin with the increase in the concentrations of HCl solutions mixed with the resin. When the concentration of aqueous solution of HCl was less than 0.10 M, no iron was desorbed from the resin.

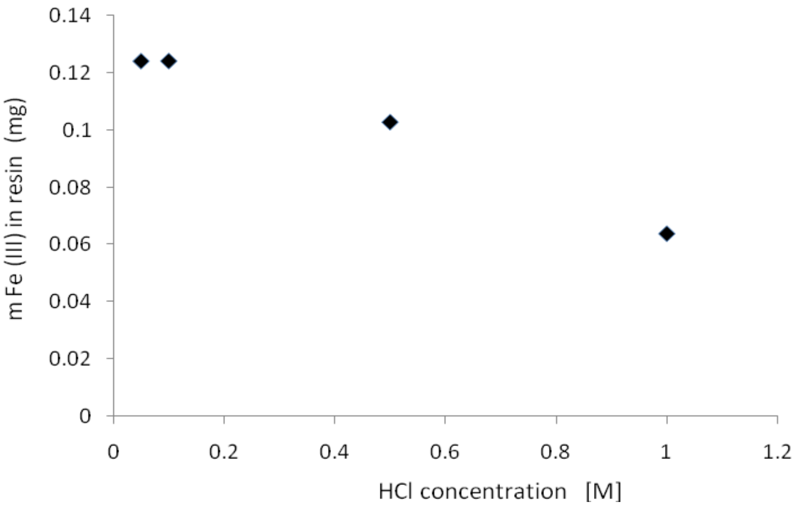


Fig. 3.9: The effect of acidity on the desorption of Fe(III) from the R-Loaded Resin

III.3 Sorption isotherm models

In order to understand the interaction mechanism of between the sorbed dye and the sorbent, as well as the nature of the interaction between the resin and the dye , this paper compared the data from the equilibrium studies with the data obtained by fitting the Langmuir, Freundlich, Dubinin-Radushkevich şi Temkin-Phyzev sorption isotherm models. Fig. 3.10 shows the fitting of the models to the experimental data obtained with the strong basic anion exchanger Amberlite IRA 400 (Cl^-). It exhibits a steep increase at low concentrations, indicating a high affinity for the solute. The coefficients of the isotherm parameters for ***GAC*** sorption in Amberlite IRA 400 (Cl^-), 50 mesh at 20ºC are presented in Table 1. The linearized form of the isotherm models for ***GAC*** equilibrium sorption in Amberlite IRA 400 (Cl^-) are showed in Fig. 3.11-3.14.

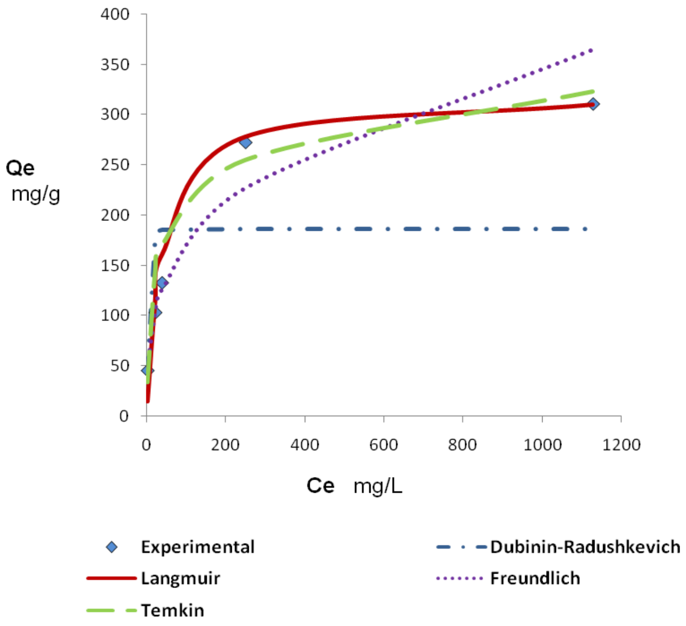
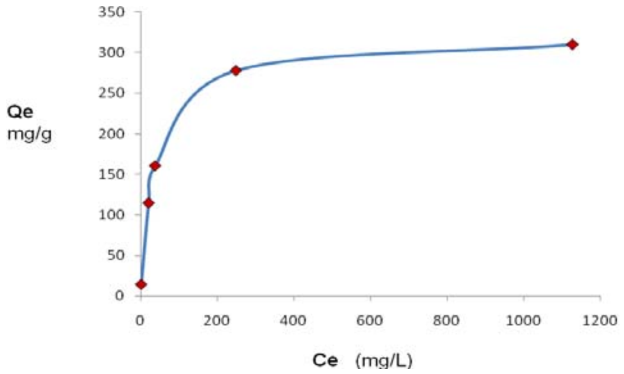


Fig. 3.10: Fitting of the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models to the experimental data of ***GAC*** sorption in Amberlite IRA 400 (Cl^-), 50 mesh at 20ºC.

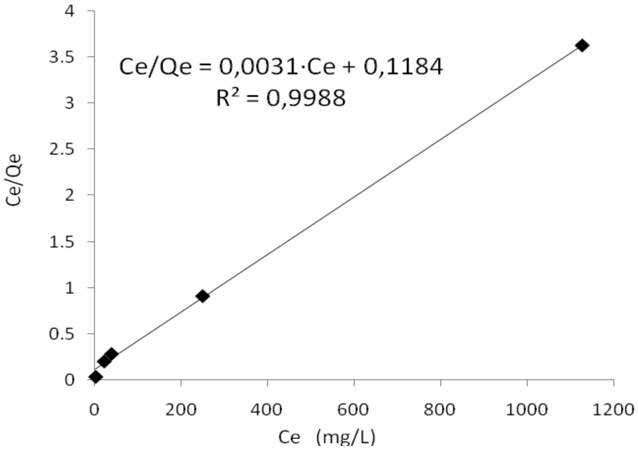
III.3.1 The Langmuir isotherm model

The Langmuir equation represents a better fit of the experimental data compared to the other three isotherm equations. The fact that the Langmuir isotherm fits the experimental data very well confirms the monolayer coverage of dye onto the anion exchanger and also the homogeneous distribution of active sites in/on it.

By fitting the linearized form of the Langmuir isotherm on the experimental data obtained from the sorption of the ***R***-dye on the resin (Fig. 3.11) r^2 the graphic representation of C_e/Q_e as a function of C_e was obtained with the following correlation coefficient $r^2 = 0.998$; this very good correlation confirms that the sorption mechanism was very well described by the Langmuir isotherm model. The maximum monolayer capacity Q_0 for sorption of the dye was 320.51 mg/g (i.e. 0.910 mmol/g). When this value of Q_0 was correlated with the experimental data, the plateau for the plot of Q_e = f(Ce) was observed at 310.98 mg/g (or 0.849 mmol/g) (see Figure 3a). This value is very close to the resin's sorption capacity for the dye; the latter value of 294.50 mg/g was previously obtained from the bath equilibrium study on the influence of ***R***-dye's concentration on its binding to the resin. The Langmuir constant *b*, related to the free energy of adsorption, indicates the affinity of the sorbent for binding of the dye. Its value is the reciprocal of the dye concentration at which half of the saturation of the adsorbent is attained [Mittal, 2009; Wawrzkiewicz, 2010a]. The high value of *b* = 0.026 L/mg obtained for sorption of ***R*** in Amberlite IRA 400 (Cl^-) implied a strong bonding of the dye to this anion exchanger.



a.



b.

Fig. 3.11: Langmuir isotherm (a) and linearized form of Langmuir isotherm (b) for GAC on Amberlite IRA 400, 50 mesh at 20°C.

The essential characteristic of Langmuir isotherm can be expressed by the dimensionless constant called the equilibrium parameter, R_L. R_L values indicate the type of isotherm to be:

irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). In the case of the R-dye's sorption on the Amberlite IRA 400 (Cl^-) resin, the calculated value of the R_L factor was 0.014, indicating that the isotherm was favorable ($0 < 0.014 < 1$)

III.3.2 The Freundlich isotherm model

The Freundlich isotherm describes the non-ideal and reversible adsorption, not restricted to the formation of monolayer. The model is applied to adsorption on heterogeneous surfaces with interactions between adsorbed molecules and it considers that the sites with stronger affinity are occupied first [Mittal, 2009; Greluk, 2009; Wawrzkiewicz, 2010a]. Fig. 3.12 shows the plot of log Q_e versus log C_e, the linear form of the plot indicating the fitting of experimental data to the Freundlich adsorption isotherm. The value of Freundlich correlation coefficient $r^2 = 0.972$ is high, but slightly smaller than that of the Langmuir isotherm.

The value of $1/n = 0.31$ for the sorption system is less than unity which reflects the favorable adsorption of GAC - dye over the entire concentration range used in this study, indicating a strong bond between the acidic dye absorbed and the strongly basic anion exchange resin sorbent. For the Freundlich constant correlated with the adsorption capacity of the adsorbent, the resulting value was $K_F = 43.95$ mg/g, which was smaller than the value obtained by fitting the Langmuir isotherm .

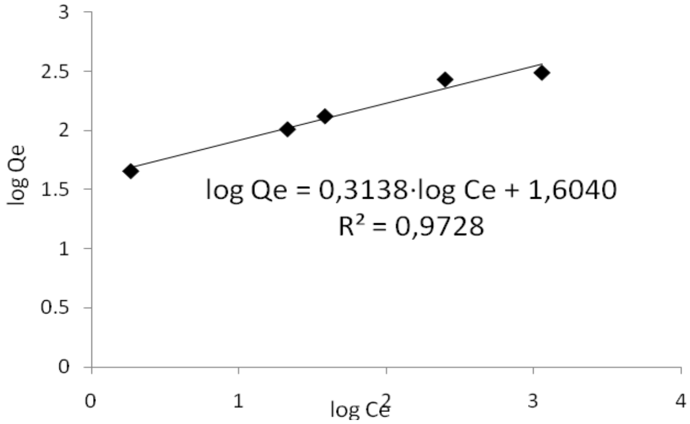


Fig. 3.12: Linearized form of Freundlich isotherm for GAC on Amberlite IRA 400, 50 mesh at 20°C.

III.3.3. The Dubinin-Radushkevich isotherm model

Fig. 3.13 shows the plot of ln Q_e versus ε^2 for the uptake of the R-dye by the anion exchanger. The value of the correlation coefficient r^2 = 0.651 indicated that the Dubinin–Radushkevich isotherm model did not fit well with the equilibrium data when compared with the above two considered models. A linear curve whose negative slopes (β) and intercepts (ln X_m) $1.27 \cdot 10^{-3}$ mol2/kJ2 and 186.20 was obtained. The maximum sorption capacity of the dye, X_m = 186.20 mg/g, was calculated from the preceding values [Mittal, 2009; Greluk, 2009; Wawrzkiewicz, 2010a]. The value of the sorption energy, E = 19.84 kJ/mol (calculated based on the β constant of $1.27 \cdot 10^{-3}$ mol^2/kJ^2) confirmed that the acidic dye's sorption on the strong base anion resin is attained by ion exchange equilibria, but also by chemical sorption.

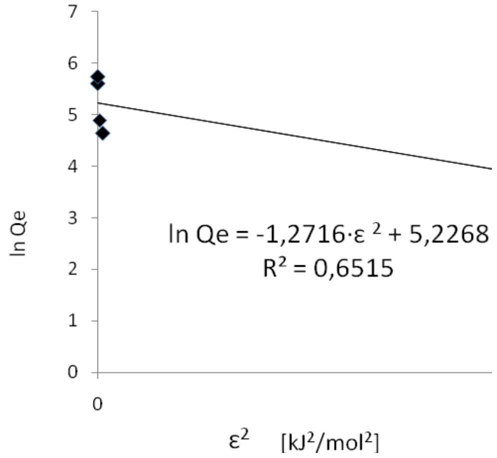


Fig. 3.13: Linearized form of Dubinin-Radushkevich isotherm for GAC on Amberlite IRA 400, 50 mesh at 20°C.

III.3.4. The Temkin-Pyzhev isotherm model

The applicability of the Temkin-Phyzev isotherm was studied by plotting Q_e vs. C_e (Fig. 3.14). The correlation coefficient (r^2 = 0.943) showed that this model fitted well to ***GAC***-dye's adsorption data on Amberlite IRA 400. The heat of sorption, b_T, and the isotherm constant, *A,* (the equilibrium binding constant corresponding to the maximum binding energy) were found to be 54.03 J/mol and 1.14 L/g respectively.

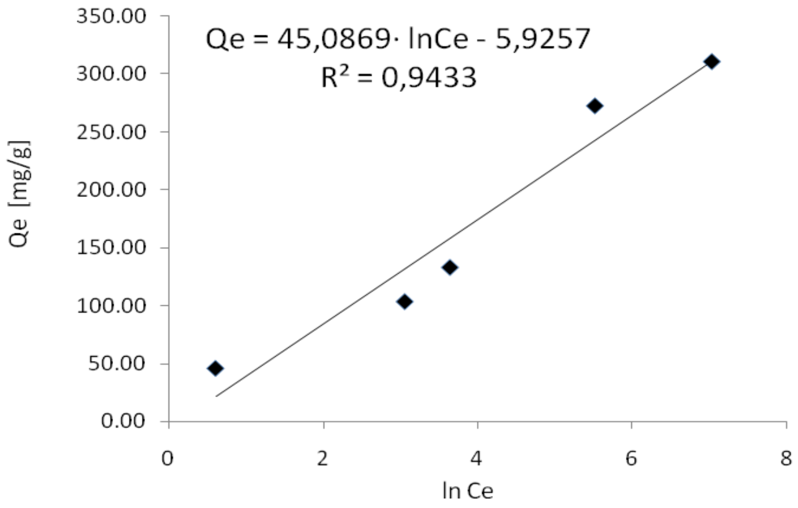


Fig. 3.14: Linearized form of Izoterma Temkin-Pyzhev isotherm for GAC on Amberlite IRA 400, 50 mesh at 20°C.

Chapter IV

PREPARATION AND CHARACTERIZATION OF A RESIN FUNCTIONALIZED WITH A PIRAZOLONIC REAGENT

In this chapter we present the results obtained in experiments performed to obtain and characterize a functionalized ion exchange resin with a organic azopirazolonic reagent derived from sulphanilic acid. Formula of the reagent (denoted R) is shown in Fig. 4.1.

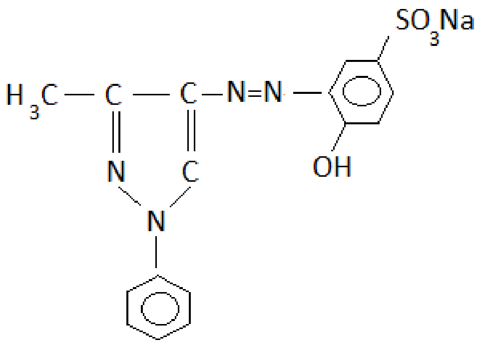


Fig. 4.1: Formula of the organic azopirazolonic reagent derived from *p*-hydroxy-sulfanilic acid.

IV.1. Establishing of the optimum operating conditions to determine spectrometrically the concentration of the reagent solution.

In this chapter we present the results of experiments conducted in order to establish optimal conditions for determining spectrometrically the concentration of Pyrazolone, R reagent. Reagent formula is shown in Figure 4.1.

As shown in Fig. 4.2 (in thesis) at a wavelength of 423 nm the reagent containing solution has an absorption maximum, which requires absorbance measurements to be made at
λ = 423 nm against blank containing only water.

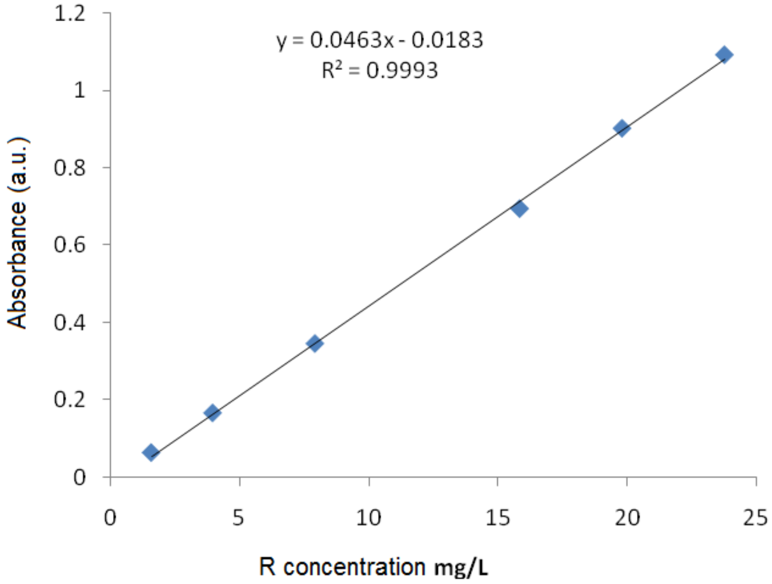


Fig. 4.3 Calibration curve for spectrometric determination of the reagent.

Linearity of the method was verified for R reagent concentrations ranging from 1 to 25 mg/ mL. Calibration curve equation is: *A* = -0.0183 +0.0463 *C.* The correlation coefficient has a value of R = 0.9993. Molar absorbance coefficient was calculated: ε = 16580 L mol^{-1} cm^{-1}.

IV.2. *Preparation of R-loaded Resin*

Study of solid-liquid distribution equilibria involving anion exchange resin and R reagent solution were made taking into account the influence of the stirring time and the amount of reagent in initial soultion. It also was studied the influence of solution pH on the stability of reagent loaded resin.

IV.2.1. The effect of phase contact time

Figure 4.4 shows the influence of shaking time on the sorption of reagent from solutions of different concentrations. For initial reagent solution with a concentration of 1980 mg /L and 0.0534 g of dry resin at a stirring time of 120 minutes, the amount of reactive sorbate at equilibrium was 130.73 mg /g. It was found that by increasing mixing time, increases also the amount of dye in resin. After 120 minutes of shaking a significant increase in the amount of reagent loaded resin.

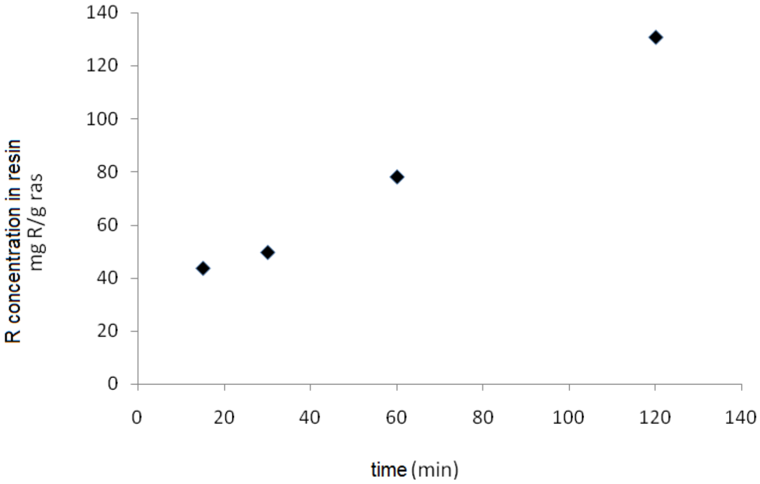


Fig. 4.4: The effect of phase contact time over R reagent sorption on Amberlite IRA 400

4.2.2 The Effect of Initial Dye Concentration

Figure 4.5 shows the influence of the amount of reagent on its sorption from aqueous solutions of different initial concentrations.

Based on these results it was found that with increasing initial concentration of dye increases the amount of dye in resin. It is noted that for reagent concentrations greater than 1584 mg /L in the initial solution, the amount of dye in resin vary slightly, which leads to the conclusion that it reached maximum sorption capacity of the resin.

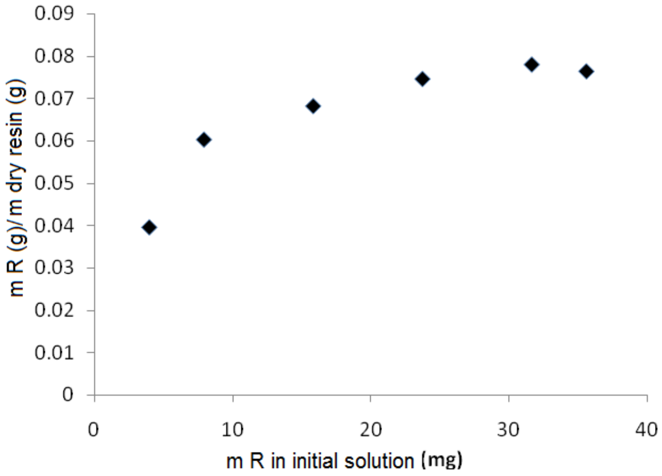


Fig. 4.5: The effect of initial dye concentration over its sorption on Amberlite IRA 400 (contact time: 90 minutes).

IV.2.3. The effect of crosslinking degree

Effect of resin crosslinking degree on reagent binding was studied using Dowex 1 resin, 200 mesh with different degrees of crosslinking. (X2, X4 şi X8).

Figure 4.6 shows an increasing amount of reagent sipped with decreasing the degree of crosslinking of the resin.

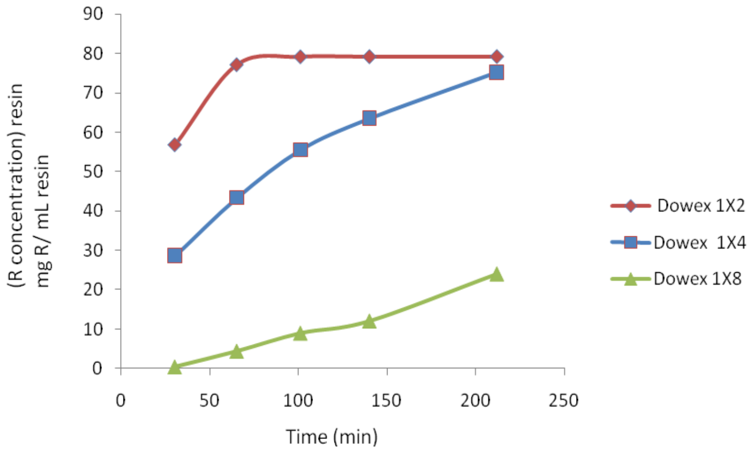


Fig. 4.6: The Effect of crosslinking degree over R reagent sorption on Dowex 1, 200 mesh.

IV.2.4 The Effect of Acidity on the Stability of the R-Loaded Resin

IV.2.4.1 The Effect of aqueous HCl solution on the Stability of the R-Loaded Resin

In order to examine the stability of the ***R***–loaded resin in acidic solutions, this study used aqueous solutions of HCl in different concentrations. The results are presented in Figure 4.7 below. Figure 4.7 indicates a decrease in the amount of dye from the resin while the concentration of HCl increases.

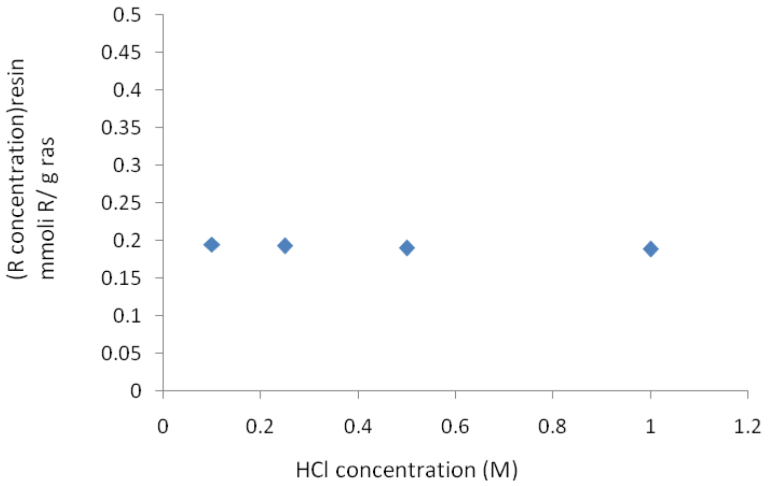


Fig. 4.7 : The Effect of acidity on the desorption of ***R***- dye from the Amberlite IRA 400 resin.

IV.2.4.2 The Effect of aqueous NaOH solution on the Stability of the R-Loaded Resin

In order to examine the stability of the ***R***–loaded resin in alkaline solutions, this study used aqueous solutions of NaOH in different concentrations. The results are presented in Figure 4.8 below. Figure 4.8 indicates a decrease in the amount of dye from the resin while the concentration of NaOH increases.

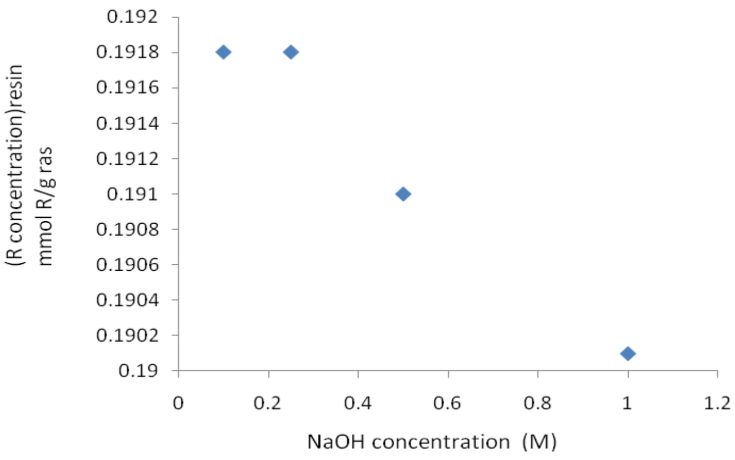


Fig. 4.8: The Effect of alkaline solutions on the desorption of ***R***- dye from the Amberlite IRA 400 resin.

.

Chapter V

STUDIES ON THE ADSORPTION OF THE ACIDIC DYE TELON BROWN 3G BY A STRONG BASIC ANION EXCHANGER

This chapter contains the results obtained in experiments performed for obtaining and characterization ion exchange resins functionalized with organic dye Telon Brown 3G [Radu, 2012a]. Formula reagent (denoted TB) is shown in Fig. 5.1

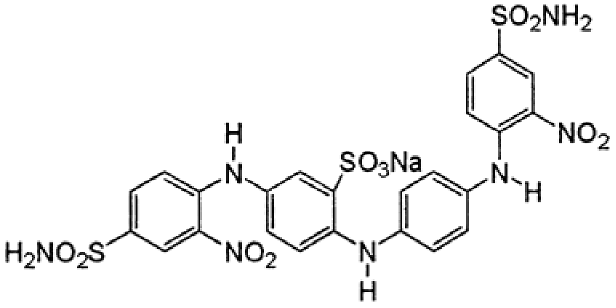


Fig. 5.1: Organic reagent Telon Brown 3G formula.

V.1. Establishing the optimum operating conditions for spectrometric determination of the concentration of the reagent in solution.

In this chapter we present the results of experiments conducted in order to establish optimal conditions for spectrometrically determining the concentration of organic reagent Brown Telon 3G. At a wavelength of 423 nm the reagent solution presents an absorption maximum, which requires absorbance measurements to be made at λ = 431 nm against blank containing only water.

For TB reagent quantitative determination, the calibration curve was drawn using solutions of different concentrations.

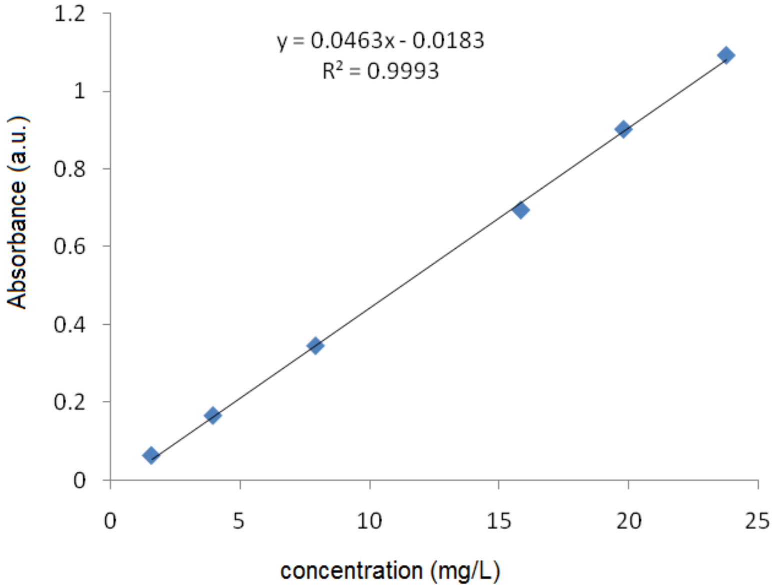


Fig. 5.2b. Calibration curve for spectrometric dtermination of TB reagent in aqueous solution.

Linearity of the method was tested for TB reagent concentrations ranging from 1 to 40 mg /mL. Calibration curve equation is: $A = 0{,}00060 + 0{,}01209 \cdot C$.

The correlation coefficient has a value of R = 0.9999.

V.2. Study of reagent sorption in the anion exchange resin

V.2.1. The Effect of Phase Contact Time

The influence of phase contact time on TB uptake from aqueous solutions with different initial concentrations (100 to 750 mg/L) by Dowex 1- x4, 50 mesh (Cl^-) at 20ºC was studied (Fig. 5.3). The results indicated that the amount of dye adsorbed per mass unit of the anion exchanger increased with time. After 120 minutes of shaking it can be observed a significant increase in the amount of reagent loading of resin unless the reagent concentration in the initial solution is 100 mg /L or unless the situation in which the resin mass was 0,1 g. TB reagent concentrations in Dowex 1 resin (x4, 50 mesh) at equilibrium were: 10,016; 19,848; 29,529; 31,182; 31,485 mg/g for initial solution concentrations: 100, 200, 300, 500 şi 750 mg/L.

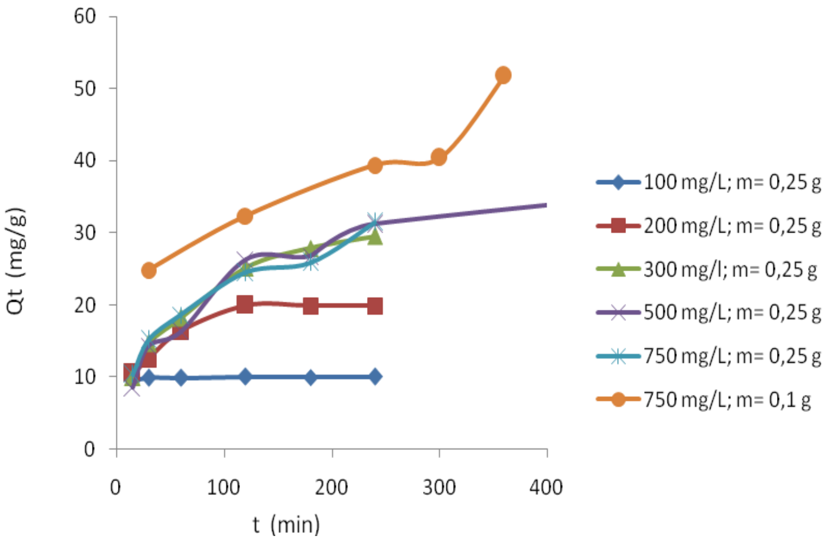
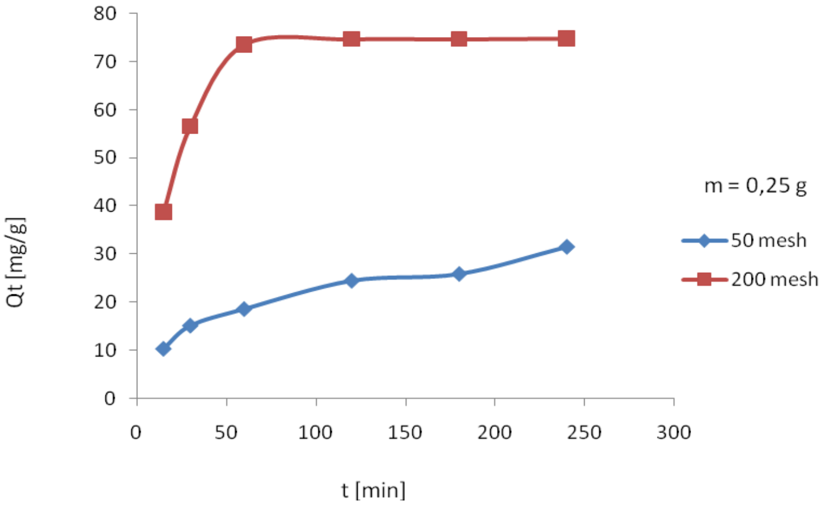


Fig. 5.3: The effect of phase contact time over TB sorption on Dowex 1x4, 50 mesh, from initial solution at different concentrations (100-750 mg/L) at 20°C.

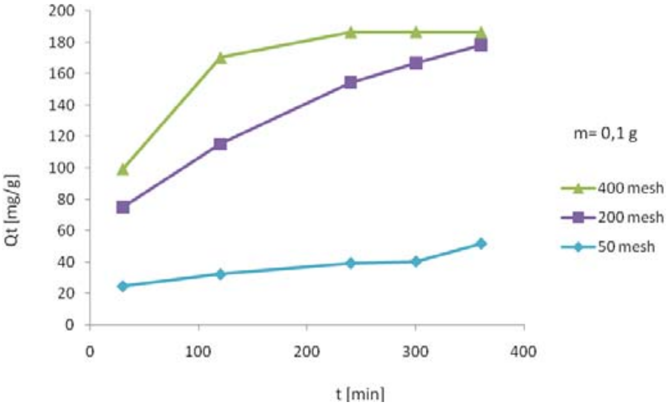
V.2.2 The Effect of Particle Size.

The effect of particle size on reagent sorption in resin was studied using three types of Dowex 1x4 resin having particles with different sizes, namely 50, 200 and 400 mesh.

From Figure 5.4 a and b we can see an increasing amount of reactive sipped with decreasing particle size. The diffusion path lengths of the exchanging ions to and from the active sites are shorter with smaller particle size, so that exchange is more rapid [Dorfner, 1991; Wawrzkiewicz, 2010a].



a .



b.

Fig. 5.4 : The effect of particle size on sorption capacity of Dowex 1 (x4) resin

a. m_{rasina}= 0,25 g; b. m_{rasina}= 0,1 g

V.2.3 The effect of crosslinking degree

Figure 5.5 shows an increasing amount of reagent sipped with decreasing the degree of crosslinking of the resin.

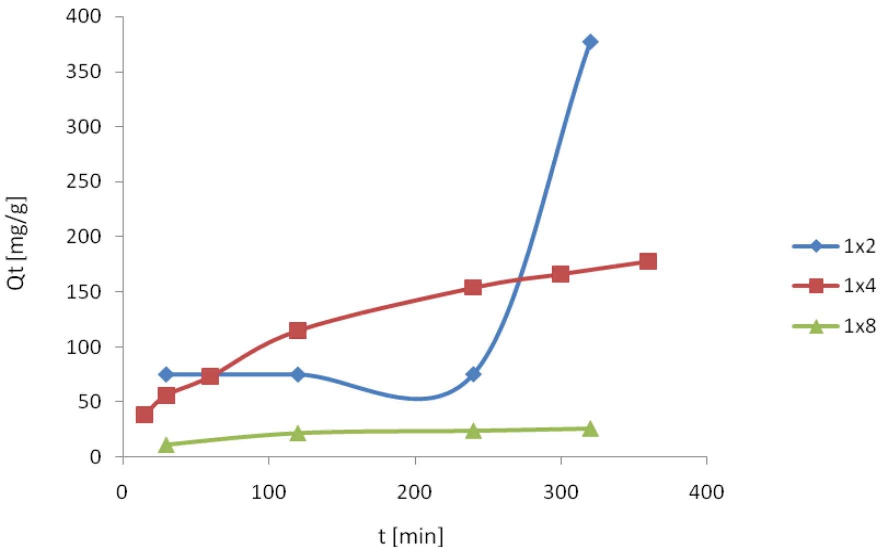


Fig. 5.5: The effect of crosslinking degree for Dowex 1 (200 mesh), on TB sorption from aqueous solution (750 mg/L).

V.2.4 The effect of acidity on the stability of the TB-loaded resin

In order to examine the stability of the TB–loaded resin in acidic solutions, this study used aqueous solutions of HCl in different concentrations. The results are presented in Figure 5.6 below. Figure 5.6 shows that up to a concentration of 4 M hydrochloric acid solution, theTB-loaded resin is relatively stable, the dye remaing fixed in the ion exchanger.

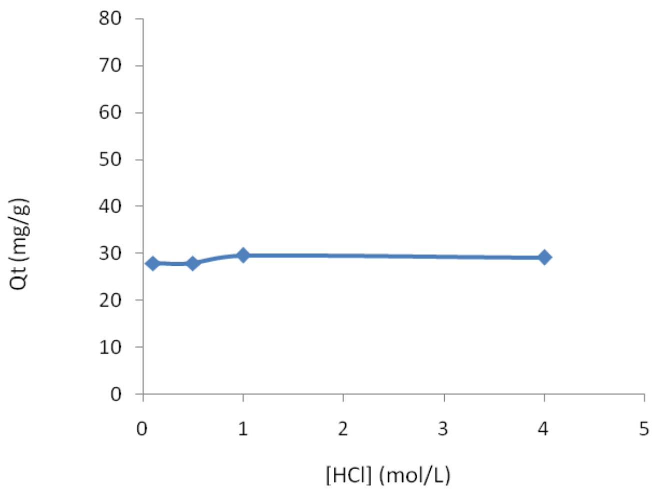


Fig. 5.6: The effect of acidity on the stability of the TB-loaded resin.

V.3 Sorption isotherm models

In order to understand the interaction mechanism of between the sorbed dye and the sorbent, as well as the nature of the interaction between the resin and the dye, this paper compared the data from the equilibrium studies with the data obtained by fitting the Langmuir, Freundlich, Dubinin-Radushkevich şi Temkin-Phyzev sorption isotherm models. Fig. 5.7 shows the fitting of the models to the experimental data obtained with the strong basic anion exchanger Dowex 1 (Cl^-). It exhibits a steep increase at low concentrations, indicating a high affinity for the solute. The linearized form of the isotherm models for TB equilibrium sorption in Dowex 1(Cl^-) are showed in Fig. 5.8-5.11.

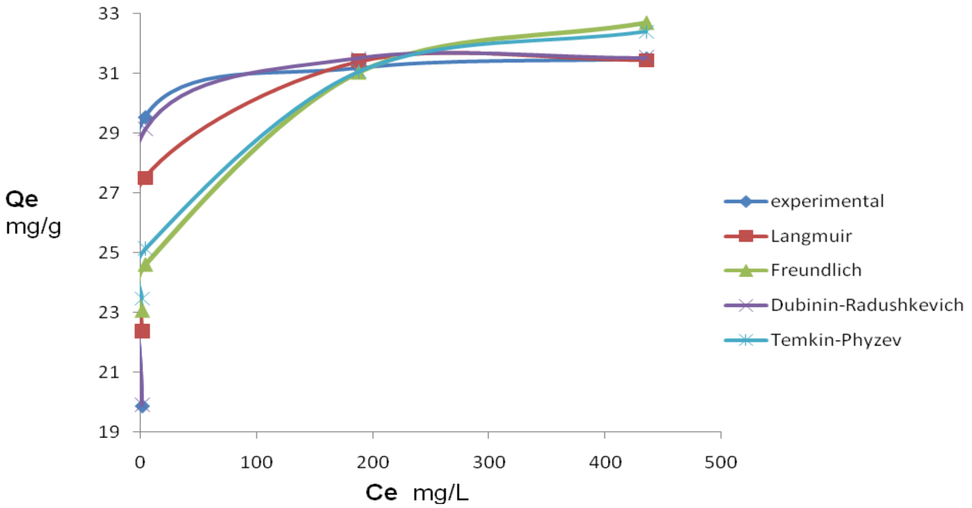


Fig. 5.7: Fitting of the the Langmuir, Freundlich, Dubinin-Radushkevich şi Temkin-Phyzev isotherm models to the experimental data of TB adsorption on Dowex 1 at 20°C .

V.3.1 Langmuir isotherm model

The Langmuir equation represents a better fit of the experimental data compared to the other three isotherm equations. The fact that the Langmuir isotherm fits the experimental data very well confirms the monolayer coverage of dye onto the anion exchanger and also the homogeneous distribution of active sites in/on it.

By fitting the linearized form of the Langmuir isotherm on the experimental data obtained from the sorption of the TB-dye on the resin (Fig. 5.8) r^2 the graphic representation of C_e/Q_e as a function of C_e was obtained with the following correlation coefficient $r^2 = 0.999$; this very good correlation confirms that the sorption mechanism was very well described by the Langmuir isotherm model. The maximum monolayer capacity Q_0 for sorption of the dye was 31.49 mg/g (i.e. 0.045 mmol/g). When this value of Q_0 was correlated with the experimental data, the plateau for the plot of Q_e = f(Ce) was observed at 31.48 mg/g (or 0.045 mmol/g) (see Figure 5.7).

The Langmuir constant *b*, related to the free energy of adsorption, indicates the affinity of the sorbent for binding of the dye. Its value is the reciprocal of the dye concentration at which half of the saturation of the adsorbent is attained. The high value of *b* = 1.58 L/mg obtained for sorption of TB in Dowex 1 (Cl$^-$) implied a strong bonding of the dye to this anion exchanger.

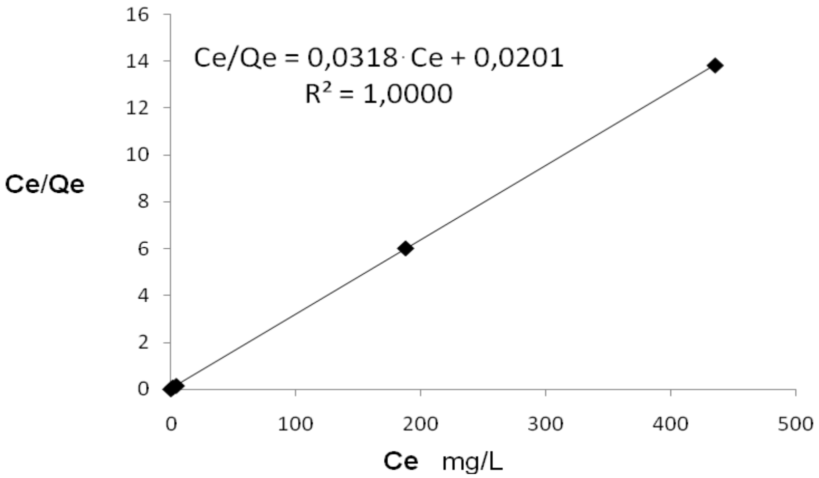


Fig. 5.8b: Linearized form of Langmuir isotherm for TB on Dowex 1 (Cl^-), 50 mesh at 20°C.

In the case of the TB -dye's sorption on the Dowex 1 (Cl^-) resin, the calculated value of the R_L factor was 0.00084, indicating that the isotherm was favorable (*0*< 0.00084<*1)*.

V.3.2. Freundlich isotherm model

Fig. 5.9 shows the plot of log Q_e versus log C_e, the linear form of the plot indicating the fitting of experimental data to the Freundlich adsorption isotherm. The value of Freundlich correlation coefficient r^2= 0. 0.604 is low. The Freundlich isotherm represents the poorer fit of experimental data than the Langmuir equations. For the Freundlich constant correlated with the adsorption capacity of the adsorbent, the resulting value was K_F = 22.45 mg/g, which was smaller than the value obtained by fitting the Langmuir isotherm .

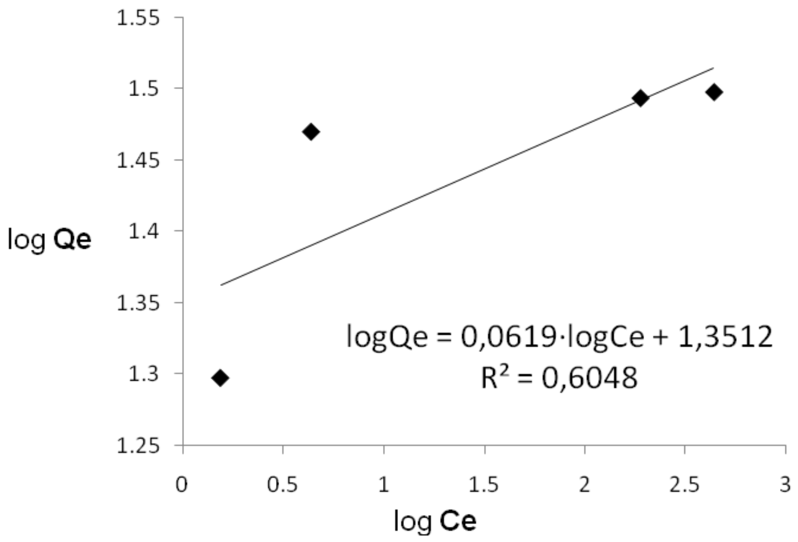


Fig. 5.9b: Linearized form of Freundlich isotherm for TB on Dowex 1 (Cl^-), 50 mesh at 20°C.

V.3.3. Dubinin-Radushkevich isotherm model

Fig. 5.10 shows the plot of ln Q_e versus ε^2 from Eq. (5) for the uptake of the ***TB***-dye by the anion exchanger. The value of the correlation coefficient r^2 = 0.997 indicated that the Dubinin–Radushkevich isotherm model fit well with the equilibrium data when compared with the above two considered models. A linear curve whose negative slopes (β) and intercepts (ln X_m) 310.9 · 10^{-3} mol2/kJ2 and 186.20 was obtained. The maximum sorption capacity of the dye, X_m = 31.51 mg/g, was calculated from the preceding values. The value of the sorption energy, E = 1.27 kJ/mol (calculated based on the β constant of 310.9 · 10^{-3} mol^2/kJ^2) confirmed that the acidic dye's sorption on the strong base anion resin is attained by physical sorption.

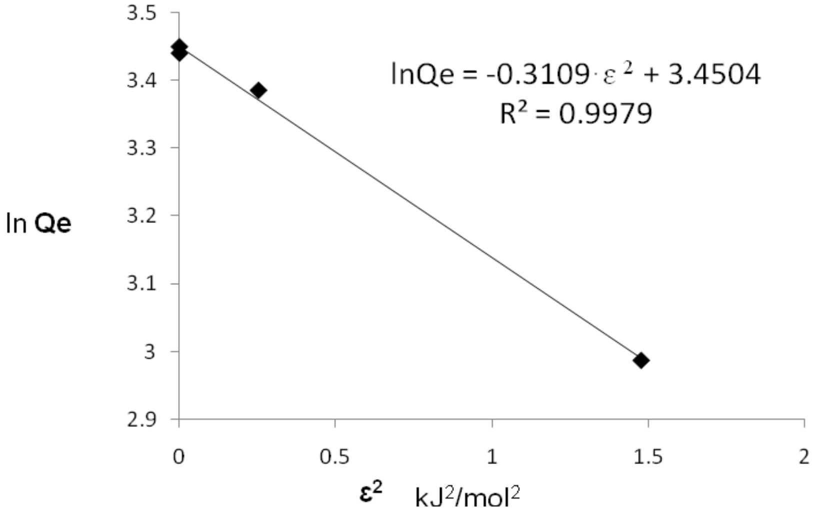


Fig. 5.10b: Linearized form of Dubinin-Radushkevich isotherm for TB on Dowex 1 (Cl^-), 50 mesh at 20°C.

V.3.4. Temkin-Pyzhev isotherm model

The Temkin-Pyzhev isotherm model suggested that, due to the adsorbent- adsorbate interactions, the heat of adsorption of all molecules in the layer decreased linearly with coverage and that the adsorption mechanism is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy.

The applicability of the Temkin-Phyzev isotherm was studied by plotting Q_e vs. C_e (Fig. 10). The correlation coefficient ($r^2 = 0.632$) showed that this model did not fit well to ***R***-dye's adsorption data on Dowex 1. The heat of sorption, b_T , and the isotherm constant, *A,* (the equilibrium binding constant corresponding to the maximum binding energy) were found to be 1539.78 J/mol and 14.40 L/g respectively.

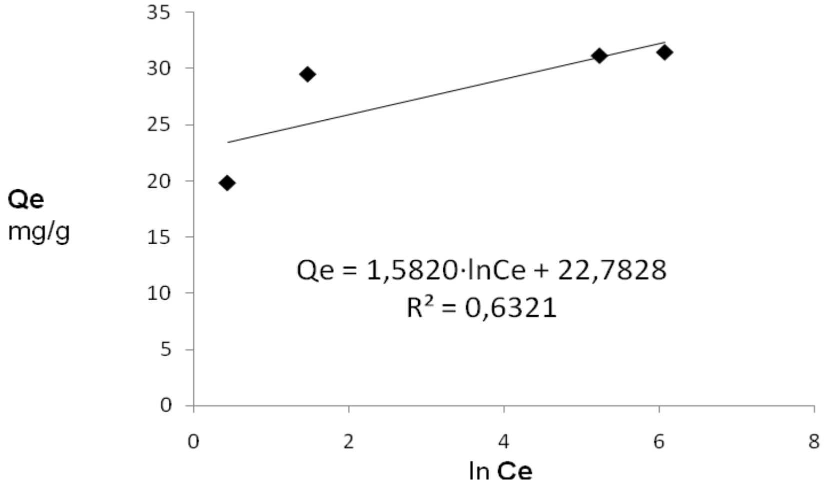


Fig. 5.11: Linearized form of Temkin-Pyzhev isotherm for TB on Dowex 1 (Cl^-), 50 mesh at 20°C.

V.4. Kinetic studies

The Lagergren pseudo-first order model the pseudo-second order model as well as the Weber and Morris intraparticle diffusion model were fitted to the experimental data of TB sorption on Dowex 1 (Cl^-) [Ada, 2009; Wawrzkiewicz, 2010a; Wawrzkiewicz, 2010b; Dorfner, 1991; Menr, 2009].

The conformity between the experimental data and the model predicted values was expressed by the correlation coefficients. From the slopes and intercepts of plots $log(Q_e – Q_t)$ vs. t (fig. 5.12) obtained at the initial concentrations of 200, 300, 500 şi 750 mg/L mg/L at 20°C, the first-order rate constants k_1 and the calculated adsorption capacities $Q_{1,cal}$ were determined. The correlation coefficients r^2 determined for tartrazine sorption using the Lagergren model obtained at all studied initial concentrations were relatively high, ranging from 0.962-0.994.

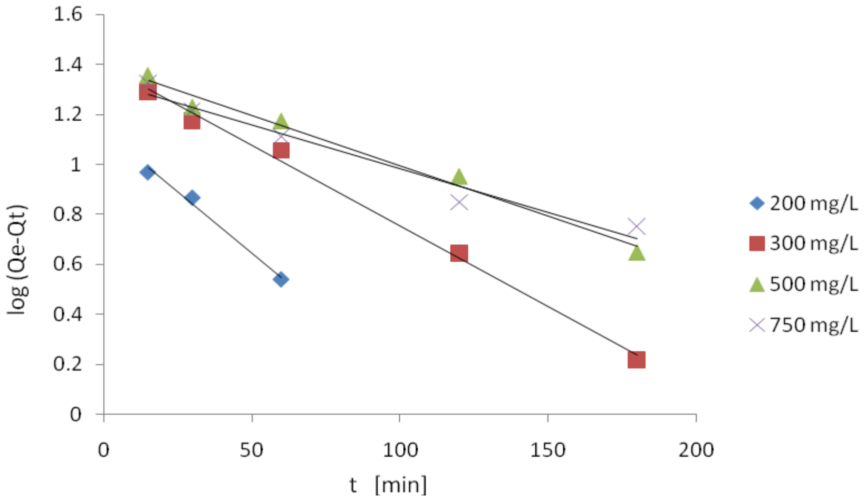


Fig. 5.12: Fitting of sorption kinetics of Telon Brown 3G at different initial dye concentrations on Dowex 1 (Cl^-), by means of the Lagergren model at 20 °C.

In order to calculate the pseudo-second order rate constant k_2 and the adsorption capacity $Q_{2,cal}$ from the slope and intercept, respectively, t/Q_t was plotted against t (fig. 5.13) ranging the initial dye concentrations. It was found that the Q_2,cal values determined for TB increased from 22.3 to 33.9 mg/g with the increase in the initial concentration from 200 to 750 mg/L, respectively. The correlation coefficients r^2 were high (from 0.979 to 0.996).

The intraparticle diffusion step controls the sorption when the graph of Q_t against $t^{0.5}$ is a straight line passing through the origin. As shown in Fig. 5.14, the results do not pass through the origin, indicating that intraparticle diffusion is not the only rate-limiting mechanism. The intercept C_i gives information about the boundary layer thickness, the larger the intercept, the greater is the boundary layer effect [Wawrzkiewicz, 2010a]. The values of C_i increase with the increasing concentration from 2.78- 5.49 mg/g. The values of intraparticle diffusion rates constants k_{id} calculated from the second portion of the plot Q_t vs. $t^{0.5}$ for TB increased from 1.35-1.87 mg/g min$^{0.5}$ with the increase in the initial concentrations from 200 to 750 mg/L. The values of r^2 were in the range 0.962- 0.991.

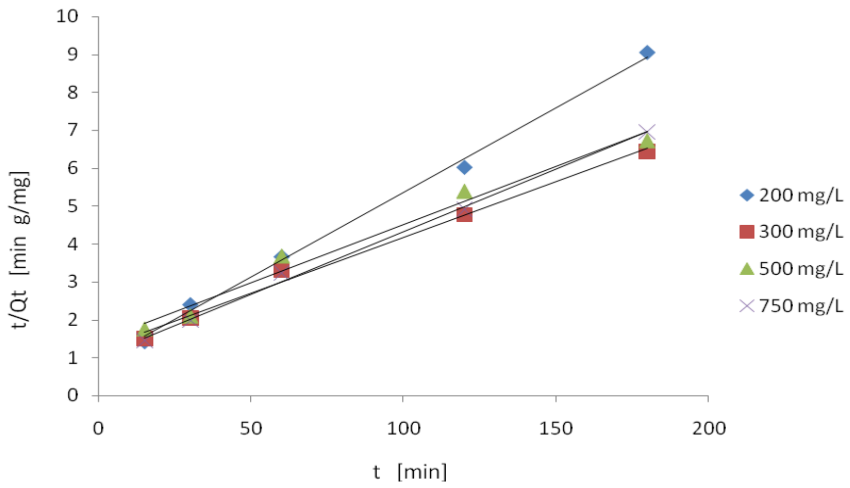


Fig. 5.13: Fitting of sorption kinetics of Telon Brown 3G at different initial dye concentrations on Dowex 1 (Cl^-), by means of the pseudo second-order model at 20 °C.

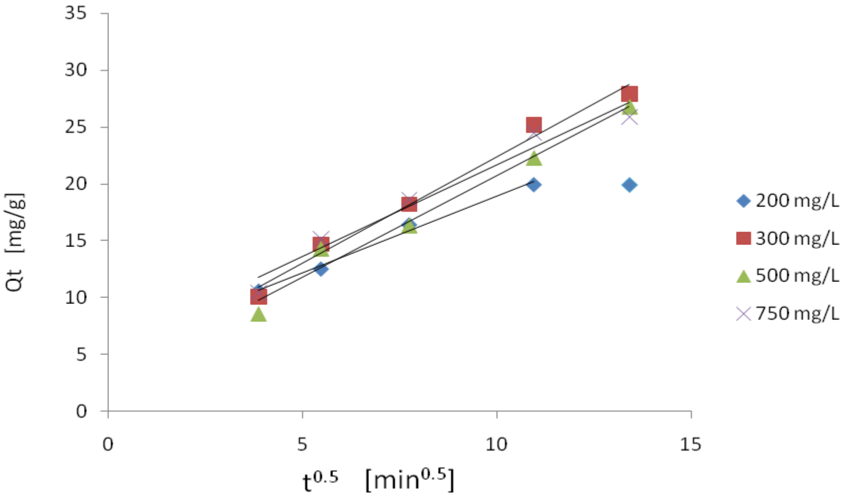


Fig. 5.14: Weber and Morris intraparticle diffusion kinetics for Telon Brown 3G sorption from aqueous solutions of different initial concentrations by Dowex 1 (Cl^-), at 20◦C (C_0 = 200–750 mg/L, agitation speed 175 min^{-1}).

Conclusions

Thesis objectives are related to obtaining, through ion exchange processes, and characterization of ion exchange resins with complexes forming functional groups that can be used for selective separation and concentration of the cations, and also to study organic dyes retention in anion exchange resins to remove them from the water.

The first step towards realizing the experimental part of the thesis has been to conduct a spectrometric study on the interactions between cations Fe^{3+}, Cu^{2+} şi UO_2^{2+} and disodium salt of 2-hydroxy-5-[(4-sulfophenyl) azo]-benzoic acid (referred to as Acidic yellow chromate or Solocrom Yellow 2GS). Thus, fast methods have been developed for direct determination of ions Fe^{3+}, Cu^{2+} şi UO_2^{2+} with organic reagent Solocrom Yellow 2GS (GAC). The spectrometric determination methods developed in the study were then used to obtain a new ion exchange resin with complexes forming functional groups that can be used for separation and concentration of heavy metal ions.

In the next stage of the study the optimum operating conditions to remove the Solocrom Yellow 2GS from water were determined and ion exchange experiments have been conducted on obtaining anion exchange resins functionalized with GAC reagent, its stability in HCl solutions of different concentrations and its use for fixing of Fe (III) ions from aqueous solutions.

Also ion exchange experiments have been performed for obtaining and characterization of a resin functionalized by an organic azopirazolonic reagent derived from sulphanilic acid. The influence of reagent amount, of mixing time and the degree of crosslinking effect on fixation of the reagent in resin were studied and also the effect of pH solution on the reagent desorption from resin.

The last phase of the study in the development of the doctoral thesis work aimed to establish optimal conditions for recovery 3G Brown Telon dye from aqueous solutions, and also experiments to obtain an anion exchange resins functionalized with organic reagent Telon Brown 3G. Sorption capacity of Dowex 1 anion exchange resins having different degrees of crosslinking and particle sizes was evaluated for Telon Brown 3G dye. The obtained experimental data were compared with Langmuir, Freundlich, Dublin - Radushkevich and Temkin - Phyzev isotherms models and kinetic studies were performed.

Chapter I contains literature data involving obtaining and characterization of ion exchange resins having complex-forming groups. Common anion exchange resins can be converted into different types of functionalized resins either by synthesis or just by shaking with aqueous reagent soluutions. Several authors have discussed the mechanisms for ligand loading into the resins. From these studies it can be concluded that the retention of chelating reagents on polymer substrate in order to obtain complexing resins generally involves ion exchange mechanisms and /or adsorption.

Based on literature data, the sorption potential of some anion exchange resins for the recovery of dyes from aqueous solutions was evaluated. Sorption is affected by different parameters such as contact time, initial dye concentration, stirring rate, temperature, pH, resin particle size and degree of crosslinking of the resin. Amount of reagent retained in the resin grows with increasing contact time of phases, with increasing concentration of the reagent in solution and with decreasing resin particle size. Sorption capacity increases with temperature of the reagent solution. Acid dyes sorption is favored by increasing temperature due to increased mobility of reactive molecules with temperature. It was studied the relationship between initial pH of the solution and the resin loading (a dye or organic reagent). Based on the solution pH influence on resin sorption, it can be said that ion exchange mechanism is predominant. Other mechanisms, such as interaction forces between reagent molecules and/or between the resin matrix and reagent play an important role in reagents sorption in/on sorbents. Effects of initial concentration of the reagent and of the contact time were taken into account when assessing the sorption capacity of the anion exchanger. The equilibrium data obtained were processed according to the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models. Kinetic data obtained at different reagent concentrations were processed according to Lagergren and Weber-Morris models to determine the adsorption dominant phase and sorption capacity at equilibrium. Kinetic data obtained at different reagent concentrations were processed according to Lagergren and Weber-Morris models to determine the adsorption dominant phase and sorption capacity at equilibrium.

In *Chapter II* of the thesis are presented the results of a spectrometric study on the interactions between cations Fe^{3+}, Cu^{2+} şi UO_2^{2+} and disodium salt of 2-hydroxy-5-[(4-

sulfophenyl) azo]-benzoic acid (referred to as Acidic yellow chromate or Solocrom Yellow 2GS).

A rapid, reliable and inexpensive method for the direct determination of Fe (III) with the organic reagent Solochrome Yellow 2GS (disodium salt of 2-hydroxy-5-[(4-sulfophenyl)azo]-benzoic acid) is reported. In a 5-fold excess over Fe(III) concentration the organic reagent, **R** form with Fe (III) within pH range 2,79-3,00 a 1:2 (Fe: GAC) stable complex. The value of the total stability constant βs = $3{,}023 \cdot 10^5 \pm 1{,}55 \cdot 10^5$ $L^2 \cdot mol^{-2}$ was determined, which indicates the formation of a rather stable complex. On this basis a spectrometric method for the quantitative determination of traces of iron (III) was proposed. The method is sensitive, accurate and reproducible, being characterized by a detection limit of 0,11 $mg \cdot L^{-1}$, a linearity range between 0,3-5,0 μg·mL-1, a recovery of 98,45 % ± 1,38 %, as well as a good repeatability and reproducibility, characterized by relative standard deviations of 1,537% and 1,365%, respectively. This method was applied in order to determine the iron contents in samples of drinking water and natural mineral water.

On the same principle a rapid, reliable and inexpensive method for the direct determination of Cu (II) with the organic reagent Solochrome Yellow 2GS (disodium salt of 2-hydroxy-5-[(4-sulfophenyl)azo]-benzoic acid) is reported. In a 4-fold excess over Cu (II) concentration the organic reagent form with Cu (II) within pH range 6,30 – 9,43 an 1:2 (Cu: GAC) stable complex. The value of the total stability constant βs = $1{,}58 \cdot 10^6 \pm 0.4 \cdot 10^6$ $L^2 \cdot mol^{-2}$ was determined, which indicates the formation of a rather stable complex. On this basis a spectrometric method for the quantitative determination of copper (II) at traces level was proposed. The method is sensitive, accurate and reproducible, being characterized by a detection limit of 0,10 mg·L-1, a linearity range between 0,12 – 5,12 $\mu g \cdot mL^{-1}$, a recovery between 93,27% and 95,49% as well as a good repeatability and reproducibility, characterized by relative standard deviations of 3,333% and 1,392%, respectively. The method was applied in order to determine the copper contents in samples of drinking water and wine.

Based on a spectrometry study was developed also a rapid, reliable and inexpensive method for the direct determination of U (VI) with the organic reagent Solochrome Yellow 2GS (disodium salt of 2-hydroxy-5-[(4-sulfophenyl)azo]-benzoic acid) is reported. In a 4-fold excess over U (VI) concentration the organic reagent, R form with U (VI) within pH range 4.40 – 4.83

an 1:2 (U:GAC) stable complex. The value of the total stability constant $\beta s = 1{,}72 \cdot 10^9 \pm 1{,}68 \cdot 10^9$ $L^2 \cdot mol^{-2}$ was determined, which indicates the formation of a rather stable complex. On this basis a spectrometric method for the quantitative determination of copper U (VI) at traces level was proposed. The method is sensitive, accurate and reproducible, being characterized by a detection limit of 3,3 $mg \cdot L^{-1}$, a linearity range between 5,0 - 50,0 $\mu g \cdot mL^{-1}$, a recovery between 95,33 % and 97,11 % as well as a good repeatability and reproducibility, characterized by relative standard deviations of 1,294 % and 2,380 %, respectively.

The aim of the study presented in *Chapter III* was to get a new ion exchange resin having complex-forming groups (functionalized with Solochrome Yellow 2GS reagent) that can be used for separation and concentration of heavy metal ions, but also to establish optimum operating conditions to remove the acidic dye from water.

Based on the results obtained in the ion exchange experiments for obtaining an anion exchange resin functionalized with Solochrome Yellow 2GS (GAC) reagent, its stability in HCl solutions of different concentrations and its use for fixing of Fe (III) ions from aqueous solutions, the following conclusions were drawn. The results indicated that the amount of dye adsorbed per mass unit of the anion exchanger increased with time and initial GAC concentration. After 15 minutes of stirring, the entire amount of GAC-dye in aqueous solution was bound to the anion, when the initial concentration of the aqueous solution was 366 mg/L. After 30 min of phase contact time, the resin loading changed insignificantly for all the concentrations in the initial solutions. For reagent concentrations greater than 1647 mg / L in the initial solution, the amount of reagent incorporated in resin vary slightly, which leads to the conclusion that for the working conditions, it was achieved the maximum sorption capacity of the resin, determined as of 0.745 mmol/g dry resin.

In order to examine the stability of the GAC –loaded resin in acidic solutions, this study used aqueous solutions of HCl in different concentrations. A decrease in the amount of dye from the resin while the concentration of HCl increases can be observed. At 0.10 M concentration of the HCl solution, the GAC -loaded resin was stable and, thus it can be used for separation and concentration of cations. The GAC -dye can be removed from the resin by prolonged exposure to a 0,10 M solution of HCl.

The experiments conducted in order to determine the effect of acidity on the desorption of Fe(III) from the GAC -loaded resin, showed an increase in the amount of iron that leaves the resin with the increase in the concentrations of HCl solutions mixed with the resin. When the concentration of aqueous solution of HCl was less than 0,10 M, no iron was desorbed from the resin.

The equilibrium data fitted well with the Langmuir isotherm model so the sorption of acidic dye in the anion exchangers was deemed as monolayer sorption of dye molecules/ anions in/ on the homogeneous internal and external surfaces of the anion exchanger.

Of the four sorption isotherm models applied, the values obtained for Langmuir and Dubinin-Radushkevich models were very close together; however, comparison of their maximum monolayer capacity showed that Langmuir isotherm model had a better agreement with experimental data. The value of maximum monolayer capacity Q_0 for sorption of the dye was 320,51 mg/g (i.e. 0,876 mmol/g) which is closer to the experimental capacity of 294,50 mg/g (or 0,842 mmol/g) in comparison with the corresponding Dubinin-Radushkevich parameter X_m = 242,74 mg/g. The Langmuir isotherm model better explained the experimental data of the acidic dye sorption than the Dubinin-Radushkevich model. The fitting of the data, obtained from the sorption of the acid dye in/on anion exchange resin, to the four isotherm models showed that the linearity of the Langmuir isotherm models (r = 0,998) was higher than that of the other isotherm models. This showed that the sorption of the acid dye was rather a monolayer sorption than a sorption on a surface with heterogeneous energy distribution.

The sorption is also well described by the Freundlich isotherm model (r^2= 0,972). The measured value K_F = 43,95 mg/g showed an easy uptake of the acidic dye with a high adsorptive capacity of the anion exchanger. The value of $1/n$ = 0,31 for the sorption system is less than unity which reflects the favorable adsorption of GAC - dye over the entire concentration range used in this study, indicating a strong bond between the acidic dye absorbed and the anion exchanger.

The Dubinin-Radushkevich constants are calculated and given for the uptake of GAC by the anion exchanger Amberlite IRA 400. The value of coefficient of determination (r^2 = 0,651) indicate that the Dubinin-Radushkevich isotherm model does not fit with the equilibrium data as compared with the other models considered. The constants A and b_T, according to the Temkin equation were also calculated. The correlation coefficient was equal to 0,943.

It can be concluded that the Langmuir isotherm provided the best model of the sorption system taking r^2 value into account.

In *Chapter IV* are presented the results obtained in ion exchange experiments performed to obtain a new resin functionalized with an organic azopirazolonic reagent, denoted R, derived from sulphanilic acid and its characterization. The results indicated that the amount of dye adsorbed per mass unit of the anion exchanger increased with time and initial R concentration. After 120 min of phase contact time, the resin loading changed insignificantly for all the concentrations in the initial solutions. For reagent concentrations greater than 1584 mg / L in the initial solution, the amount of reagent incorporated in resin vary slightly, which leads to the conclusion that for the working conditions, it was achieved the maximum sorption capacity of the resin, determined as of 0,195 mmol/g dry resin.

The influence of the degree of cross-linking on the sorption of TB dye was studied and the results indicate an increase in the amount of dye retained in the ion exchanger with the decrease in the degree of cross-linking.

In order to examine the stability of the R –loaded resin in acidic solutions, this study used aqueous solutions of HCl in different concentrations. A decrease in the amount of dye from the resin while the concentration of HCl increases can be observed. At 1 M concentration of the HCl solution, the R -loaded resin was stable and, thus it can be used for separation and concentration of cations. The R -dye can be removed from the resin by prolonged exposure to a 4 M solution of HCl. To examine the stability of the R –loaded resin in alkaline solutions, this study used aqueous solutions of NaOH in different concentrations. At 0,50 M concentration of the NaOH solution, the R -loaded resin was stable and, thus it can be used for separation and concentration of cations.

In *the fifth chapter* of the thesis are shown the results obtained by ion exchange experiences on establishing optimal working conditions for recovery of Telon Brown 3G dye from aqueous solutions, process by which it is obtained an anion exchange resins functionalized with the organic reagent Telon Brown 3G.

The sorption process took place in two distinct phases: in the beginning, there is a marked increase in dye sorption with increasing the phase contact time, after which, the concentration of TB-dye remains constant, or increases slowly. After 120 minutes of phase contact time, the resin loading changed insignificantly, except for the big concentrations of dye in the initial solutions (for 500 mg/L and 750 mg/L).

The influence of resin bead size on the sorption process was studied A fost studiat efectul dimensiunilor particulelor de răşină asupra sorbţiei colorantului and the data indicate that the amount of dye retained in the resin increases with the decrease in resin bead size. The influence of the degree of cross-linking on the sorption of Telon Brown 3G dye was also studied and results indicate an increase in the amount of dye retained in the ion exchanger with the decrease in the degree of cross-linking.

In order to examine the stability of the TB–loaded resin, this study used HCl aqueous solutions of of different concentrations. Data indicate that exposing the TB-loaded resin to HCl solutions of 0,1 – 0,5 M concentrations results in a decrease in the dye amount onto the resin as the concentration of HCl increases. Up to a 4 M concentration of HCl and 60 min of phase time contact, the TB-loaded resin is relatively stable, with the dye retained in the ion exchanger.

In this study, the potential of the strongly basic anion exchange resin Dowex 1 for the removal of Telon Brown 3G dye from aqueous solutions was evaluated. Dowex 1 shows a sorption capacities towards Telon Brown 3G dye, ranging from 10.02 to 32.35 mg/g when the initial concentration of the dye changed from 100 to 750 mg/L. The equilibrium sorption capacity of the anion exchanger increased with the time of contact between the resin and the dye solution, as well as with the dye concentration. The Langmuir isotherm described the sorption of Telon Brown 3G on Dowex 1 with high correlation coefficients. The adsorption kinetics was found to follow both the pseudo-second order and the Weber and Morris intra-particle diffusion model. This study highlighted that the strongly basic anion exchanger Dowex 1 can have practical application in the removal of Telon Brown 3G dye from industrial effluents and surface water.

The aim of the studies in this thesis was to gain new ion exchange resins with complex forming functional groups that can be used for separation and concentration of heavy metal ions, but also to determine the optimal working conditions for removal of organic dyes from water. Ion exchange experiments were conducted (by batch method) in systems: ion exchange resin - reagent/dye solution using strongly basic anion exchange resins Amberlite IRA 400 and Dowex1 type and acid Solochrome Yellow 2GS, Telon Brown 3G and the organic azopirazolonic reagent, derived from sulphanilic acid. The experimental data were fitted to those obtained using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin-Phyzev isotherm models. Also, Lagergren and Ho kinetic models and Weber-Morris intraparticle diffusion model were compared with experimental data obtained from sorption of studied dyes in the anion exchange resin.

PhD thesis has 208 pages and contains: 58 tables, 98 figures and 210 references.

References (selection)

Ada, K., A. Ergene, S. Tan, E. Yalcin, **2009**. Adsorption of Remazol Brilliant Blue R using ZnO fine powder: Equilibrium, kinetic and thermodynamic modeling studies, J. Hazard. Mater., 165 (1-3), p. 637-644.

Bekci, Z., C. Ozveri, I. Seki, K. Iurdakoc, **2008**. Sorption of malachite green on chitosan bead, J. Hazard.Mater., 154(1-3), p. 254-261.

Dizge, N., B. Keskinler, H. Barlas, **2009**. Sorption of Ni(II) ions from aqueous solution by Lewatit cation-exchange resin, J. Hazard. Mater., 167, p. 915–926.

Dorfner, K., Ed., **1991**. Ion Exchangers, Walter de Gruyter, Berlin.

Greluk, M., Z. Hubicki, **2009**. Sorption of SPADNS azo dye on polystyrene anion exchangers: Equilibrium and kinetic studies, J. Hazard. Mater., 172, p. 289-297.

Hameed, B.H., **2009**. Spent tea leaves: a new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions, J. Hazard.Mater., 161(2), p. 753-759.

Khaled, A., El Nemr, A., El-Sikaily, A., Abdewahab, O., **2009**. Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: Adsorption isotherm and kinetic studies, J.Hazard. Mater., 165, p.100-110.

Lata, H., V.K. Garg, R.K. Gupta, **2008**. Adsorptive removal of basic dye by chemically activated parthenium biomass: equilibrium and kinetic modeling, Desalinisation, 219 (1-3), p. 250-261.

Menr, A.E., O. Abdelwahab, A. El-Sikaily, A. Khaled, **2009**. Removal of direct blue-86, from aqueous solution by new activated carbon developed from orange peel. J. HAzard. Mater. 161, p. 102-110.

Mittal, A., D.Kaur, J. Mittal, **2009**. Batch and bulk removal of a triarylmethane dye, Fast Green FCF, from wastewater by adsorption over waste materials**,** J. Hazard.Mater., 163(2-3), p. 568-577.

Olbrych-Sleszynska, E, Brajter, K., Staskiewicz, M., **1988**. Preconcentration and separation of metal ions by means of amberlite XAD-2 loaded with pyrocatechol violet, Talanta, 35, p. 65-67.

Radu, C., Vlădescu, L., **2009**. Solochrom yellow 2 GS as organic reagent for spectrometric determination of iron (III), Rev. Roumaine Chim., 54(1), 85–92.

Radu, C., Vlădescu, L., **2012a**. Equilibrium studies on the sorption of the acidic dye Telon Brown 3G by a strong basic anion exchanger, Solvent Extraction and Ion Exchange (trimis la revistă).

Radu, C., Vlădescu, L., **2012b**. Preparation, characterization and iron sorption studies of a dye-loaded anion exchange resin, J. Hazard. Mater. (trimis la revistă).

Radu, **C.**, Vlădescu, L. **2013**. Solochrome Yellow 2GS as organic reagent for spectrometric determination of uranium (VI), Rev. Chim. (Buc.), 64 (2) (în curs de publicare).

Tan, I.A.W., A.L.Ahmad, B.H. Hameed, **2008**. Adsorption of basic dye on high-surface area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater., 154, p. 337–346.

Vlădescu, L., **Radu, C.**, **2012**. Spectrometric method for copper (II) determination at trace level, Rev. Chim. (Buc.), 63 (2), 131–135.

Wawrzkiewicz, M., **2010a**. Application of Weak Base Anion Exchanger in Sorption of Tartrazine from Aqueous Medium, Solvent Extr. Ion Exc., 28, p. 845-863.

Wawrzkiewicz, M., Hubicki, Z., **2010b**. Equilibrium and kinetic studies on the sorption of acidic dye by macroporous anion exchanger, Chem. Eng. J., 157, p. 29-34.