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SORPTION OF METAL COMPLEX DYES ONTO ION EXCHANGE RESINS

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The scientific work was carried out in 2006-2011 at the Center for Physical Sciences and Technology, Institute of Chemistry, Department of Environmental Chemistry.

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CHEMIJOS INSTITUTAS

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1. INTRODUCTION

Relevance of the work. Metal complex dyes are a problematic group of substances, that presents the negatively charged anion form in mixed industrial wastewater that should be removed. Environmental concerns arise from the carcinogenic properties of metals (Cr, Cu), from amines formed by reductive cleavage of azo groups of organics and color. Therefore, a complete removal of these hazardous dyes from wastewaters is necessary to prevent them from release into the environment. Adsorption on activated carbon of dyes has been investigated widely. However some disadvantages using activated carbon in practice were observed, e.g. high regeneration costs and production of fines due to the brittle nature. Since their adsorption capacities, mechanical strength, and other properties need further improvement for wider application, the polymeric sorbents are still under development as a potential alternative to activated carbons.

On the one hand, the dye removal is based on dye-adsorbent interaction that dependence on the number and type of functional groups or the chemical and physical structures of matrix and on the structure of dye, the related performance of adsorbent should be intensively evaluated in the particular case. From the practical point of view, the investigated sorption and regeneration characteristics of polymeric sorbent can be used to effective cleaning of wastewater and recovering sorbents that can be usable repeatedly. Creation of the new and perfection usable technologies are necessary not only to economize chemicals, but also to effectively using sorbents and to reuse of process water. And there is very little of information in literature about the removal of metal complex dyes using anion exchangers and hyper-cross-linked polystyrene resins.

The main aim of the present work was to investigate absorption regularity metal complex LanasyI Navy M-DNL and Acid Blue 249 (copper (II) phthalocyanine) dyes on synthetic ion exchangers under static conditions and evaluate facility of ion exchangers to removal dyes from wastewaters by dynamic conditions.

The objectives of the research are the following:

1. To screen most potential ion exchangers depending dyes sorption capacity, dye distribution coefficient and ion exchanger regeneration.

2. To determine and compare anion exchangers sorption capacity dependence from anionic matrix structures, type and functional groups for metal complex dyes.
3. To investigate sorption mechanism, equilibrium and kinetics parameters in dependence from solution pH, concentration, temperatures and interaction time for metal complex dyes on anion exchangers.
4. To estimate suitability theoretical isotherm and kinetics models for analysis of experimental data.
5. To investigate metal complex dyes sorption/desorption under dynamic condition, according environmental standards. Estimating suitability theoretical Wolborska, Bohart-Adams and Juang models for this process.

Scientific novelty and practical value of the work. Determine the interaction mechanism between harmful chromium and copper complex dyes and weak/strong base anion exchangers, also the measurement of the sorption equilibrium and kinetics parameters. The sorption kinetics investigations are supplemented with optic microscopy, determination of metal complex dyes removal mechanism in static and dynamic conditions. The metal complex dyes removal possibility using Macronet sorbent are not investigated at all.

Purolite A847 weak base anion exchanger and nonfunctionalized Macronet MN 200 are able to remove the metal complex dyes from aqua solutions. Possibility to use the sorbents for multifold removal Cr, Cu and organics impurities from water would fulfill the requirements of the environmental standards and water recycling.

The results presented in the dissertation enabled to defend the following most important ***statements***:

- Due to the removal efficiency, sorption capacity and desorption efficiency weak base Purolite A 847 anion exchanger as well as strong base Purolite A 500PS anion exchanger and nonionic Macronet MN 200 were found to be the most suitable for the sorption of metal complex dyes.
- Gel-type anion exchanger with weak base functional groups and acidic medium of the solution are preferable for the sorption of metal complex dye.
- Ion exchange mechanism is involved in the sorption of metal complex dye by weak base Purolite A 847 as well as strong base Purolite A 500PS anion exchangers.

Physical sorption may be considered in the case of nonfunctionalized Macronet MN 200.

- Langmuir as well as Freundlich adsorption models are suitable for the systems Navy-sorbent, although only Freundlich mathematical model could be fitted to the data of the system CuPc-sorbent.
- The data of the equilibrium sorption capacity of the dyes and sorption rate constants shows a good compliance with the pseudo-second – order equation.
- According to the values of ΔG^0 chemisorption seems significant in the system Navy-A 500PS, whereas in the other systems physical sorption prevails. The sorption is endothermic in the case of dyes sorption by strong base A 500PS anion exchanger, and exothermic in the system CuPc-MN 200.
- Purolite A 847 and A 500PS anion exchangers in static conditions are able to effectively remove the ions of chromium and copper as well as organic compounds.
- The presence of two dyes in the solution diminishes the dynamic sorption capacity of Purolite A 847 anion exchanger towards the dyes Navy and CuPc.
- After the regeneration of Purolite A 847 anion exchanger by the mixture of 4% NaOH and ethanol (1:1) the sorption capacity diminishes up to 30%. The regeneration of MN 200 by methanol was 100 %.

Approbation of the research results. The results of the research have been presented in 7 scientific publications including 4 papers in the journals from the ISI Web of Science list. The results of this work have also been reported in 12 conferences.

Structure of the dissertation. The dissertation contains the introduction, three chapters, conclusions, the list of references (91 entries) and the list of original scientific publications. The material of the dissertation is presented in 102 pages including 29 figures, 28 tables and 7 affix.

2. EXPERIMENTS

Main materials. Dyes: acid brown NKM, Lanasyn Navy M-DNL (Navy), Acid Blue 249 (CuPc); Ion exchangers: Purolite A 847, Purolite A 845, Purolite S 108, Purolite A 420S, Purolite A 500PS, Watex W 313, Macronet MN 100, Macronet MN 150, Macronet MN 200); Solutions: 0.05 N, 0.1 N, 0.25 N, 1 N, 5 % or 7 % HCl; 0.05 N

NaOH, 0.1 N NaOH, 1 N NaOH, 4 % NaOH; MeOH; EtOH; EtOH and H₂O (50:50), 4 % NaOH and EtOH (1:1); 4 % NaOH and MeOH (1:1).

Methods. Batch equilibrium experiments were carried out by shaking continuously the mixture of 0.5 g sorbent with 25 ml of a given initial concentration aqueous dyes solution. The concentration of dyes solution in the series ranged from 4 to 500 $\mu\text{mol/l}$. pH values of initial solutions were measured and adjusted with 0.1 N HCl or 0.1N NaOH. After sorption they were rechecked and the change (decrease or increase) pH in solution was estimated. After attaining the adsorption equilibrium, the samples were centrifuged and the residual concentration of dyes was ascertained by UV-Vis Spectrometer Cintra 101 (GBS Scientific Equipment (USA) LLS) at the λ_{max} 616 nm and spectrophotometer KFO at λ_{max} 630 nm. Dyes concentration was calculated from calibration curve. The chemical oxygen demand values (*COD*) of the dye solutions were determined using Spectroquant TR 320 – Spectroquant Picco analyzer. The concentration of chromium and copper was determined using atomic adsorption spectrometry (Perkin Elmer 603, USA). Kinetics values of batch adsorption were determined by analyzing adsorptive uptake of the dyes used from 100 $\mu\text{mol/l}$ dyes solution concentration in different time intervals at 293 and 313 K temperatures. FT-IR spectra were recorded by FT-IR spectrometers Bomem B100 (Hartmann & Braun, Canada) and Perkin Elmer Instruments. Sorbents surface morphology was observed by scanning electron micrograph (SEM) EVO 50EP. Optical microscopy images of sorbents beads were obtained by using MBC optical microscope (Russia) with the Nikon Coolpix 4 500 digital camera at $\times 25$ magnification.

The fixed bed column experiments were performed in order to measure the sorption/desorption curves in a one-centimeter diameter column filled with 10 ml of swollen anion exchanger or MN 200. Then dye solutions were passed through the anion exchanger bed at the volume velocity of 1 $\text{ml/cm}^2 \text{ min}$. At the column outlet the pH value, absorption (D) and electrical conductivity were measured and recorded continuously. Samples were automatically taken from the effluent at pre-set time intervals for determination of effluent's concentration. The dye desorption (regeneration of sorbent capacity) was applied with a dye saturated anion exchanger using a mixture

1:1 (v/v) of 5% NaOH – ethanol, while MN 200 – methanol, keeping the volume velocity of 0.5 ml/cm² min.

3. RESULTS AND DISCUSSION

3.1. Screening of the most potential ion exchangers to the removed metal complex dyes

Screening of the most potential ion exchangers depending on removal fill of the dyes NKM and Navy on static conditions and leading next parameter: 1) highest sorption capacity (q_e) regard dyes; 2) highest dye distribution coefficient (K_d); 3) regeneration of ion exchangers (dyes desorption) (Table 3.1. and 3.2).

Table 3.1. Sorption capacity and dye NKM distribution coefficients. Initial concentration 0.01 mmol/l, pH 5.7.

<i>Sorbents</i>	q_e , μmol/ml	K_d	<i>Desorption</i> , %	<i>Sorbents</i>	q_e , μmol/ml	K_d	<i>Desorption</i> , %
A 847	8.7	495	97	MN 100	7.4	95	80
A 500PS	8.7	495	71	MN 150	7.1	79	82
W 313	8.5	285	90	A 420S	4.6	24	97
S 108	8.2	196	75	MN 200	9.0	116	17

Table 3.2. Sorption capacity and dye Navy distribution coefficients dependence from sorbent type and solution pH. Initial concentration 0.01 mmol/l,

<i>Sorbents</i>	pH 2		pH 6,9		pH 12		pH 6,9
	q_e , μmol/ml	K_d	q_e , μmol/ml	K_d	q_e , μmol/ml	K_d	<i>Desorption</i> , %
A 420S	4.45	250	4.90	400	1.82	186	94
A 845	4.58	375	4.39	136	1.91	117	89
A 847	4.58	375	4.39	136	1.79	226	97
A 500PS	4.17	144	2.93	32	1.79	226	67
W 313	4.58	375	4.39	136	1.85	157	89
S 108	4.58	375	4.39	136	1.82	186	100
MN 100	4.58	375	4.25	111	1.85	157	91
MN 150	4.56	341	0.21	1,05	1.24	78	17
MN 200	3.89	97	4.92	431	1.55	453	59

The dyes often go to wastewaters after various manufacturing processes, then wastewaters pH is not neutral. Therefore the dye sorption dependence from solution pH was also tested (**Table 3.2.**).

Special attention was given to the sorbents matrix structure, type and functional groups influence to dye sorption. The following selectivity sequence for the sorbents, suitable for the removal of dye, was found according to:

- the matrix structure: hypercrosslinked (Macronet) (MN 150, MN 100) < macroporous (Purolite A 500PS) < gel (Purolite A 847);
- the matrix type: polystyrene matrix (Purolite A 500PS) < polyacrylic matrix anion and the functional groups: nonfunctionalized < strong base ≤ weak base.

As a whole, according to the physical-chemical characteristics of the sorbents and established dye removal parameters (sorption capacity, dye distribution coefficient (K_d) and sorbent regeneration) more detailed investigations were performed with: weak basic Purolite A 847 (A 845), strong basic Purolite A 500PS and nonfunctionalized Macronet MN 200.

3.2. Equilibrium studies under static conditions

3.2.1. Dyes sorption onto anion exchangers

The removal of the dyes from aqueous solution by adsorption is related to pH of the solution, which affects the surface charge of the sorbent, degree of ionisation and speciation of dyes.

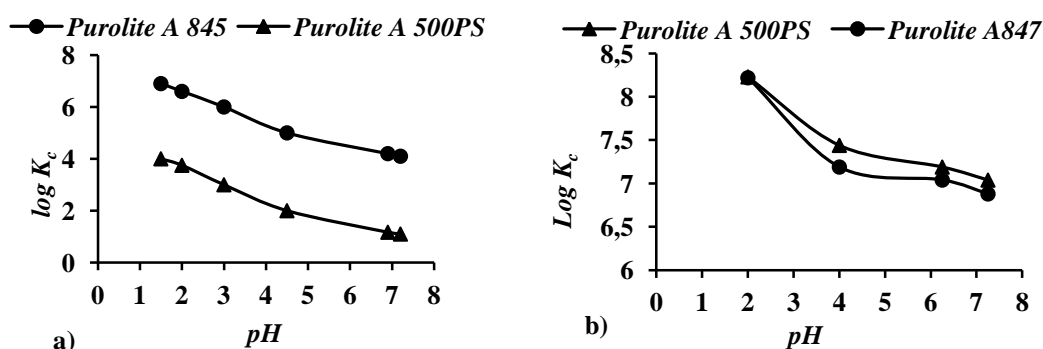


Fig.3.1. Sorption Navy (a) and CuPc (b) on anion exchangers equilibrium constant K_c dependence from solution pH. The initial concentration of dyes 0.1 mmol/l, temperature 293 K, amount of anion exchangers – 0.5 g, interaction time – 1 h.

The dyes removal for both anion exchangers during the investigation were higher in acidic (pH 1.5-4.0) than in neutral solution (**Fig.3.1**). This can be explained by anion exchanger's basicity functional degree. The dissociation constant pK_a describes acidity or basicity properties of anion exchangers and corresponds to pH value, when 50% of functional groups are protonated. Determinate dissociation constant pK_a and capacity of salt decomposition (**COSD**) for functional groups in anion exchangers A 847 and A 500PS are shown in table **3.3**. In the A 847 dominate weak tertiary amine functional groups, and sorption is preferred in acidic solution. The strong base anion exchanger A 500PS has only a quaternary of amine functional groups.

Table 3.3. Dissociation constant pK_a and capacity of salt decomposition (COSD) for functional groups in anion exchangers

<i>Anion exchangers</i>	<i>Functional groups</i>	<i>pK_a</i>	<i>COSD</i> (mg-ekv/ml)	Sorption capacity according 1 N HCl standart, mg-ekv/ml
A 847	$-\text{NH}^+(\text{CH}_3)_2$	5,5	0,0074	1,6
A 500PS	$-\text{N}(\text{CH}_3)_3$	10,8*	0,613	0,8

*-value from literature

In aqueous solutions, the dye was dissolved and the strongly sulfonated group of the chromium or copper complex dye was dissociated and converted to anionic dye ions $-\text{R}'(\text{SO}_3)_x^{x-}$. The sorption proceeded due to the formation a stable ion pair $(\text{R}'_2(\text{SO}_3)_2\text{R}')$ between the anion of dyes $(\text{R}'(\text{SO}_3)_2^{2-})$ and the functional groups of anion exchanger in OH^- form (ROH). The aromatic ring (styrene, divinylbenzene) in Purolite A 500PS, aromatic ring (divinylbenzene) and $-\text{C}=\text{O}$ groups in Purolite A 845 and groups $-\text{SO}_3\text{Na}$, $-\text{N}=\text{N}-$, aromatic rings in the dye structure can also participate in covalent, coulombic, hydrogen or weak Van der Waals forces. The physical sorption and π - π dispersion forces can also result from the aromatic nature of the anion exchanger and chromium complex dye. So, the amount of the sorbed dye is the summation of sorption on all sites.

FT-IR spectrum was recorded for both of the anion exchangers: dye Navy and CuPc loaded and dye unloaded. The changes of intensity or position specific peaks of loaded anion exchangers matrix and position peaks of dyes functional groups ($-\text{SO}_3^-$), compared with FT-IR spectra unloaded anion exchangers and single dye, proves

participation of covalent, coulombic, hydrogen or weak Van der Waals forces. The effect of dyes solution concentration is shown in **Fig. 3.2**.

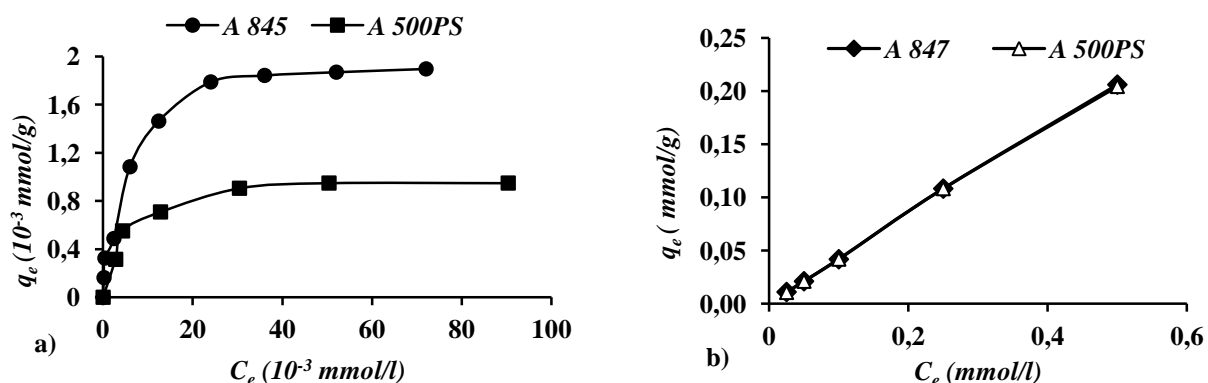


Fig.3.2. Experimental isotherms for Navy (a) and CuPc (b) dyes sorption on A 847 and A 500PS. Initial pH 2, amount of sorbent (a) – 0.38 g, (b) – 0.1 g, temperature 293 K, the interaction time 1 h.

The anion exchangers investigated effective removable of the dye Navy at low initial concentrations; at higher concentrations the isotherms reach a maximum capacity as indicated by the plateau of the data. The dye CuPc equilibrium sorption capacity (q_e) increases in proportion with initial solution concentration.

Experimental data fitted to *Langmuir* and *Freundlich* isotherms models. *Langmuir* isotherms model parameters are: q_m ($\mu\text{mol/g}$) the amount of dye adsorbed at complete monolayer coverage; K_L ($\text{g}/\mu\text{mol}$) the affinity parameter. The values of K_L and q_m evaluated from the slope and intercept of the plot of $1/q_e$ vs $1/C_e$. The correlation of dye Navy adsorption data with Langmuir isotherm model was high, with R^2 values for Purolite A 845 as Purolite A 500P of 0.9613 and 0.9317, respectively.

The Freundlich isotherm is a specific case of the Langmuir model that describes adsorption based on heterogeneous surface energy. The Freundlich constant K_F is an approximate indicator of the adsorption capacity ($\mu\text{mol/g}$) and $1/n$ is related to the adsorption intensity. A linear form of the Freundlich equation yields the constant K_f and $1/n$ from intercept and slope of a plot $\ln(a)$ versus $\ln(c)$. The obtained model parameters values, which indicate that correlation of the sorption dye Navy data with the Freundlich isotherm model, are good for low initial concentration, with $R^2 = 0.949$ (A 845) and $R^2 = 0.843$ (A 500PS). A weak basic anion exchanger Purolite A 845, which $K_F = 1.765$

$\mu\text{mol/g}$, sorption is better in about seven times than strong basic anion exchanger Purolite A 500PS, which $K_F = 0.30 \mu\text{mol/g}$.

The Freundlich constant K_F for both anion exchanger according dye CuPc adsorption are the same: $K_F = 1.35 \text{ mmol/g}$, $1/n = 1$ and correlation of dye CuPc adsorption $R^2 = 1$.

3.2.2. Dyes sorption onto Macronet MN 200

The removal of dyes using Macronet MN 200 is more effective at pH 2 than that at pH 7 (Fig. 3.3).

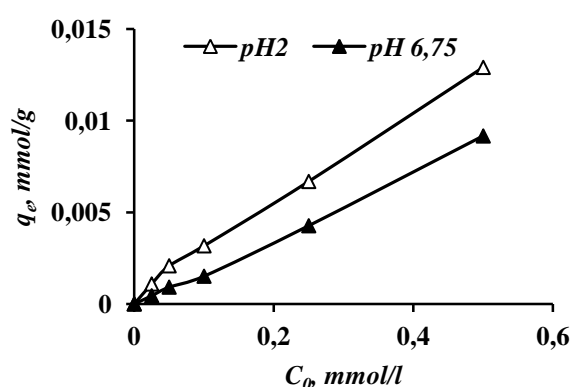


Fig. 3.3. Initial solution concentration and pH effects on the equilibrium sorption capacity (q_e) for dye CuPc sorption onto MN 200. The amount of sorbent – 0.1 g, temperature – 293 K, interaction time 1 h.

Depending on solution pH, protonation and deprotonation of surface functional groups create an electrical charge and hence a potential on the surfaces of adsorbents, that may further facilitate or complicate the adsorption of metallic complex dyes. The Macronet MN 200 total surface charges measured as points of zero charge (pH_{pzc}) was determined comprehensively by all the functional groups. Neutral Macronet MN 200 showed a $\text{pH}_{\text{pzc}} = 3.60$. These results are received by the Boehm titration. It was a due apparently a phenolic group concentration of the Macronet MN 200. The pH_{pzc} values of MN 200 are higher than the equilibrium solution pH, indicating the occurrence of a positive charge in whole net of sorbent in acidic solution favourable for dye anion adsorption.

FT-IR spectra were record for MN 200 before and after dyes Navy and CuPc sorption. The light changes in peeks positions, whose characterizations phenolic groups in MN 200 matrix, were observed. However, new peeks, corresponding to the dye matrix

(-NH, N-N, C-N) and functional groups ($-\text{SO}_3^-$) were recorded. Therefore, dye sorption onto MN 200 proceeded due diffusion dye molecule on positively charged surface and, in consequence, formation hydrogen bonds or weak Van der Waals forces.

Experimental data fitted to *Langmuir* and *Freundlich* isotherms models. *Langmuir* isotherms model parameters (**Fig. 3.4.**).

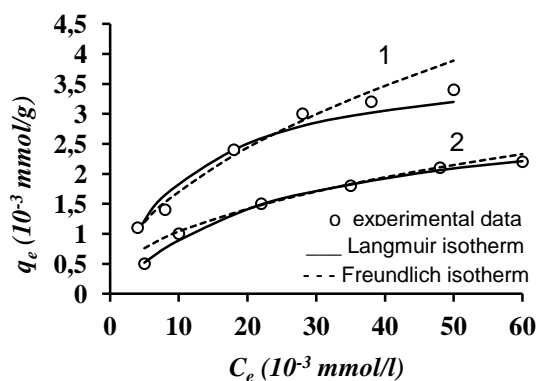


Fig. 3.4. Adsorption isotherms for dye by Macronet MN 200 adsorbent at pH 2 (1) and pH 7 (2): experimental data and comparison of isotherm models. The amount of sorbent – 0.5 g, temperature 293 K, interaction time 24 h.

The shape of the experimental isotherms (**Fig. 3.4.**) indicates L2-behavior accordingly to Giles and Smith classification and is usually associated with ionic solute adsorption at weak competition with the solvent molecules. Experimental data fitted to Langmuir isotherm model and correlation of Navy dye adsorption data with Langmuir isotherm model were high for Macronet MN 200, the R^2 values was 0.9626 at pH 2 and 0.9976 at pH 7. A comparison of the K_L values shows, that solution pH 2 was twice favorable as pH 7 for Navy dye adsorption on Macronet MN 200 (at pH 2 $K_L = 0.093$ g/ μmol , at pH 7 $K_L = 0.040$ g/ μmol).

The Freundlich model empirical equation is used to describe heterogeneous systems and is not restricted to the formation of the monolayer. The model equation can become linear and fit to the experimental data: on system CuPc-MN 200 (**Fig. 3.4.**) and on system Navy-MN 200 at low concentration (under 30 $\mu\text{mol/l}$) (**Fig. 3.4.**). The correlation coefficient of dyes adsorption data with the Freundlich was high, the R^2 values for Navy being 0.9848 – 0.9926, and the R^2 values for CuPc being 0.9666 – 0.9625.

The solution pH 2 is favorable as pH 7 for both dyes adsorption on Macronet MN 200, like show **Fig. 3.4**.

3.3. Kinetics studies under static conditions

3.3.1. Dyes sorption on anion exchanger

For the sorption of the dyes kinetics is very important the contact time between the adsorbent and the dye solution and the temperature of initial dyes solution. When sorbents are using in water circulation systems, it is very important not to limit efficiency work of all water circulation systems, that's mean the maximum of sorption could be touched as soon – no longer than 15 min.

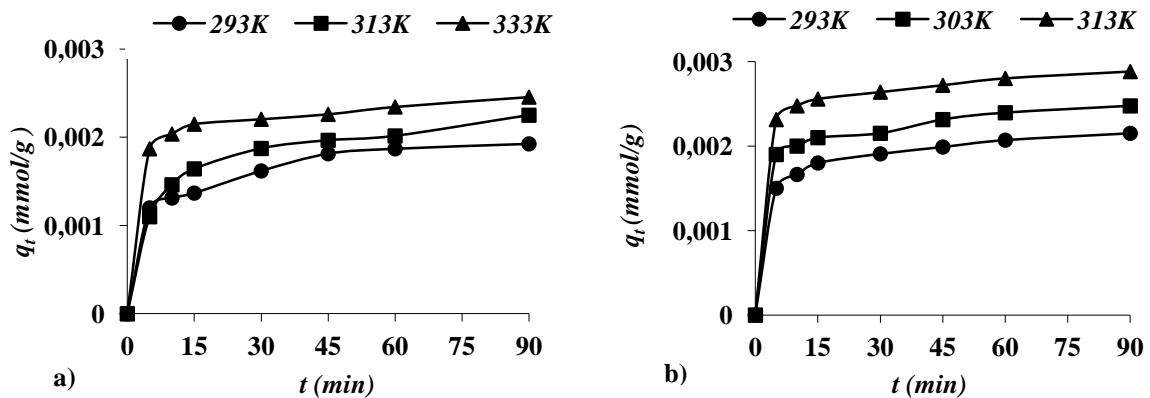


Fig. 3.5. Kinetic curves for Navy dye sorption on anion exchanger: a) Purolite A 845; b) Purolite A 500PS. Initial concentration of dye 0.1 mmol/l, pH 2.

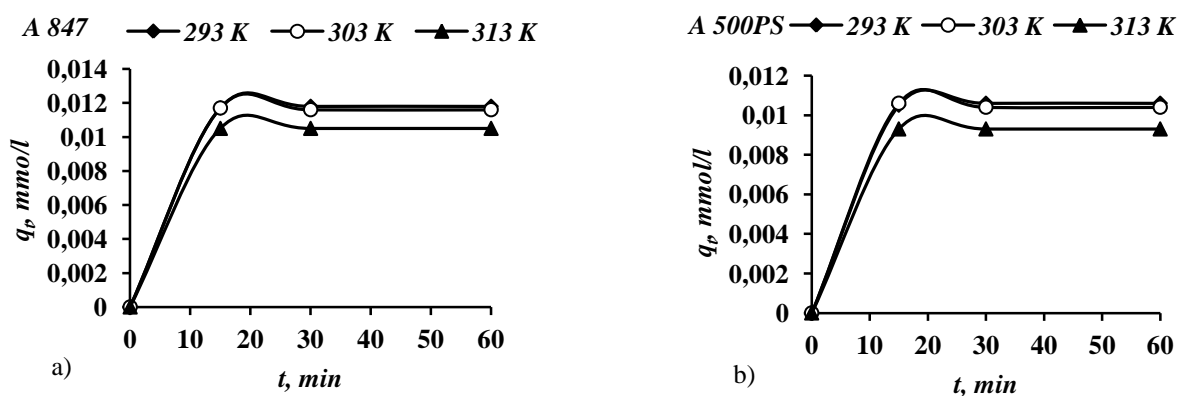


Fig. 3.6. Kinetic curves for CuPc dye sorption on anion exchanger: a) Purolite A 845; b) Purolite A 500PS. Initial concentration of dye 0.1 mmol/l, pH 2.

After the sorption Navy dye on anion exchangers A 845 and A 500PS we can see, that the sorption capacity of dye Navy q_t grows till 30 min contact time, later it slowly

comes to the equilibrium values (**Fig. 3.5.**). The sorption CuPc dye on anion exchangers A 845 and A 500PS sorption capacity of dye CuPc q_t approach to the equilibrium values over 15 min. (**Fig. 3.6.**).

Highest temperatures are more favorable for the sorption of dye Navy, and lowest temperatures – for the sorption of dye CuPc.

Two theoretical models (pseudo-second-order-reaction and intraparticle diffusion) were used to describe the sorption kinetics, also to determine the constants of sorption rate (k_2), intraparticle (k_i) and film diffusion (k_s).

The rate constant of sorption was determined using the pseudo-second order equation. This model is the correct one to describe chemisorption, physical sorption or ion exchange mechanism. The rate constant of sorption was calculated from plot of t/q_t vs t a linear relationship for Purolite A 845 and Purolite A 500P and is shown in the table **3.4.**

Table 3.4. Pseudo-second order rate constants and equilibrium sorption capacity values for Navy and CuPc dyes sorption on A 845 and A 500PS obtained at various temperatures.

Anion exchangers	Temperature (K)	Parameters of pseudo-second order model		
		k_2 (g/mmol min)	q_e (mmol/g)	R^2
Navy				
A 845	293	0.1608	1.6526	0.9959
	313	0.1217	2.067	0.9950
A 500PS	293	0.8202	0.8239	0.9862
	313	0.3038	1.3947	0.9915
CuPc				
A 847	293	0.0687	2,8645	0.9861
	303	0.1108	2,8361	0.9811
	313	0.2842	1,8857	0.9893
A 500PS	293	0.0234	3.9841	0.9894
	303	0.0355	2.9455	0.9857
	313	0,1644	1.8769	0.9902

Two steps appear to control the sorption rate: mass transfer in either the bead (intraparticle diffusion) or the liquid (film diffusion), which of them is slower. The pseudo-second order kinetic model cannot identify the diffusion mechanism and the kinetic results were analyzed by using the Moris-Weber intraparticle diffusion model. According to this model, the plot of amount of dye on the surface of the sorbent (q_t) vs square root of time ($t^{0.5}$) should be linear if intraparticle diffusion is involved in adsorption and if these lines pass through the origin, then the intraparticle diffusion is the rate-controlling step.

The correlation coefficients (R^2) are high, in the range of 0.9383 – 0.9963, confirm a good agreement with the experimental data for both dyes.

In our case, the plots for dyes Navy and CuPc sorption on anion exchangers are multilinear and did not pass to the origin, that indicated that the sorption process consist two or more steps. The parameters of intraparticle diffusion are presented in the table 3.5.

Table 3.5. Parameters of intraparticle diffusion for Navy and CuPc dyes sorption on A 845 and A 500PS obtained at various temperatures.

Anion exchangers	T (K)	Parameters of intraparticle diffusion		
		k_i (mmol/g min ^{0.5})	A (boundary layer thickness) (mmol/g)	R^2
Navy				
A 845	293	0.112	0.759	0.9842
	313	0.134	0.964	0.9417
A 500PS	293	0.066	0.439	0.9621
	313	0.110	0.548	0.9326
CuPc				
A 847	293	0.0046	0.0272	0.9771
	303	0.0049	0.0272	0.9383
	313	0.0057	0.0182	0.9963
A 500PS	293	0.0046	0.0363	0.9939
	303	0.0034	0.0272	0.9560
	313	0.0033	0.0182	0.9963

The values of the intercept A represent, indirectly, the boundary layer thickness, which formed around sorbent beads, thus the larger intercept then greater the boundary layer effect is.

The boundary layer thickness is major for sorption Navy dye on weak base anion exchanger than on strong base anion exchanger (Table 3.5). The small boundary layer consists (from 0.0182 till 0.0363 mmol/g) of sorption CuPc on anion exchangers.

The correlation of the coefficients (R^2) are high for systems: Purolite A 845-Navy are 0.9417 – 0.9842 and Purolite A 500PS-Navy are 0.9326-0.9621, Purolite A 847-CuPc are 0.9383 - 0.9963 and Purolite A 500PS-CuPc are 0.9560-0.9963.

3.3.2. Dyes sorption onto Macronet MN 200

The dependence amount of Navy and CuPc dyes sorption on Macronet MN 200 at different initial pH values from contact time between the adsorbent and the dye solution and from temperature is present in Fig. 3.7.

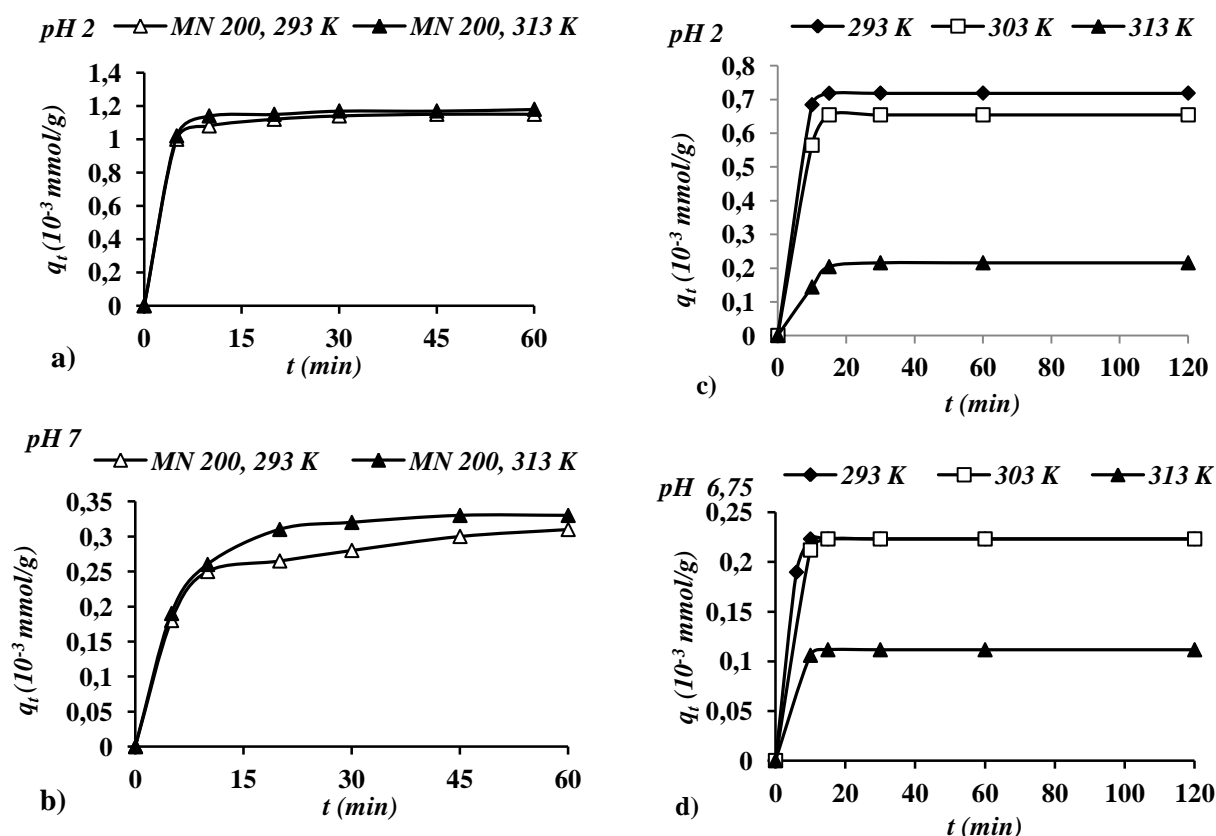


Fig. 3.7. Kinetic curves for Navy (a, b) and CuPc (c, d) dyes sorption on Macronet MN 200 at different initial pH values and temperatures. Initial concentration of dyes 0.1 mmol/l.

The calculated rate constant k_2 and equilibrium capacity q_e values of sorption using the pseudo-second order equation is presented on table 3.7. The correlation coefficients (R^2) are high, in the range of 0.9914 – 0.9998, confirming a good agreement with the experimental data for both dyes.

The rate constant k_2 values obtained for Navy decrease from 1.07 to 0.88 g/($\mu\text{mol min}$) with increase in temperature from 293K to 313K at pH 2 and from 0.59 to 0.47 g/($\mu\text{mol min}$) at pH 7, but equilibrium sorption capacity increased (Table 3.6). This indicates that, the sorption of chromium complex dye onto Macronet MN 200 not completely obey the physical sorption mechanism, but proceeds others processes involving diffusion.

Table 3.6. Pseudo-second order rate constants and equilibrium sorption capacity values for Navy and CuPc dyes sorption on MN 200 obtained at various temperatures and initial pH.

T (K)	pH	Macronet MN 200		
		k_2 (g / $\mu\text{mol min}$)	q_e ($\mu\text{mol/g}$)	R^2
Navy				
293	2	1.07	1.17	0.9998
	7	0.59	0.04	0.9929
313	2	0.88	1.21	0.9996
	7	0.47	0.36	0.9914
CuPc				
293	2	0.59	0.21	0.9919
	6,75	6.03	0.23	0.9988
313	2	2.25	0.22	0.9920
	6,75	9.40	0.11	0.9988

The rate constant k_2 values obtained for CuPc increase from 0.59 to 2.25 g/($\mu\text{mol min}$) with increase in temperature from 293 to 313 K at pH 2 and from 6,03 to 9.40 g/($\mu\text{mol min}$) at pH 7, whereas, the equilibrium sorption capacities q_e decrease (Table 3.6.). This means that the sorption of copper complex dye on Macronet MN 200 proceeds according to physics sorption mechanism.

The kinetic results were analyzed using the Weber - Moris intraparticle diffusion model. The calculated parameter of diffusion model was presented on table 3.6.

For the dye Navy sorption on Macronet MN 200 the calculated correlation coefficients (R^2) are high, in the range of 0.7910-0.9692. The boundary layer thickness effect is major in acidic media and it increases with increase in temperature (Table 3.7).

For the dye CuPc sorption on Macronet MN 200 the calculated correlation coefficients (R^2) are low (Table 3.7). This mean, that intraparticle diffusion model is not correct for describing kinetics sorption CuPc dye on Macronet MN 200, and, talking of it, better proceeds at low temperature.

Table 3.7. Parameters of intraparticle diffusion for Navy and CuPc dyes sorption on MN 200 obtained at various temperatures and initial pH values.

T (K)	pH	Macronet MN 200		
		k_i ($\mu\text{mol/g min}^{0.5}$)	A ($\mu\text{mol/g}$)	R^2
Navy				
293	2	0.025	0.0098	0.7910
	7	0.022	0.0016	0.8888
313	2	0.023	0.0103	0.8548
	7	0.026	0.0014	0.9692
CuPc				
293	2	0.0069	0.5929	0.2954
	6,75	0.0020	0.2062	0.2299
313	2	0.0062	0.1602	0.3944
	6,75	0.0016	0.0979	0.3404

3.4. Sorption thermodynamics

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what process will occur spontaneously. Determine thermodynamic parameters for sorption Navy and CuPc dyes on anion exchangers A 847 (A 845), A 500PS and on Macronet MN 200.

Physics sorption is typical for all dye-sorbent systems at 303 - 313 K temperature investigated, except system Navy-A 500PS, where Gibb's free energy (ΔG^0) is in the

range of -20 to 0 kJ/mol. Only at high temperature in the system Navy-A 500PS revealed chemical sorption, because ΔG^0 is -123.61 kJ/mol at 303 K and -126.37 kJ/mol at 313 K.

The positive enthalpy (ΔH^0) values present endothermic nature of process and more prevails for sorption Navy and CuPc dyes on strong basic anion exchanger Purolite A 500PS. The negative enthalpy (ΔH^0) values present exothermic nature of process and is crucial in system CuPc – Macronet MN 200.

Entropy ΔS^0 has been defined as the degree of chaos of a system. The positive values of ΔS^0 show an increased disorder at the solid/solution interface during the sorption of Navy dye onto both anion exchangers and Macronet MN 200. The negative values of ΔS^0 show a decreased disorder at the solid/solution interface during the adsorption of CuPc dye onto both anion exchangers Macronet MN 200.

The most positive entropy (311.74 J/mol K) determine for sorption dye Navy on strong basic anion exchanger Purolite A 500PS, whereas, the most negative entropy (-68.2 J/mol K) determine for sorption CuPc dye on strong basic anion exchanger Purolite A 500PS.

3.5. The removal efficiency of Cr, Cu and organic substances from modeling solution under static condition

The residual concentration of Cr or Cu, chemical oxygen demand (COD) in the dye solutions after interaction with sorbents under static conditions can be used tentatively for the characterizing the dye removal efficiency to the requirements of the environmental standards. The extent of removal depends on the dye concentration, solution pH and temperature. The removal efficiency of color as well as hazardous components such as Cr, Cu and organic substances (COD), increases at low concentrations, whereas it decreases at high concentrations.

The residual concentration of Cr and COD values in solution after the dye Navy interaction with A 847 is equal 0, and removal efficiency was 100%. Whereas, pH values in acidic media (from 2 to 3.2) increases smoothly but sharply increase in neutral solution (from 7 to 9.2).

The residual concentration of Cr and COD values after interaction dye Navy solution with MN 200 was less at pH 2 neither pH 7. When Cr concentration in initial solution was low (till 3.08 mg/l), at pH 2 dye removal efficiency reached 100%.

Cu residual concentration in solutions after interaction CuPc dye with sorbents is low in acidic solutions neither neutral (pH 6.75), whereas the removal efficiency obtained better for A 847 than for the A 500PS. The lowest value of COD (185 mg/l O₂) of dye solution was recorded after interaction with A 500PS at pH 2.

In summary, high metal complex dyes removal efficiency (Cr 36 – 100 %, Cu 86-94 %) was obtained for dye Navy interaction with A 847 (A 845) at initial solution pH 2 and with Macronet MN 200 (only at low initial dye concentration < 3.08 mg/l) and can satisfy the environmental requirement for chromium concentration less than 0,1 mg/l.

3.6. The sorption/desorption study under dynamic condition

The column dynamics of the sorption of dye Navy and dye CuPc by A 847 and Macronet MN 200 was studied. The breakthrough curves illustrating the column operation were obtained from experimental data, considering to the requirements of permitted concentration of copper and/or chromium both in discharged into land disposal treated wastewaters and in reused as process waters. The estimated parameters of the sorbent performance such as the breakthrough capacity (*BC*) of the column depended on the dye solution composition and on content of the sulpho groups in the dye molecule chemical structure and were lower for CuPc (the four-sulpho groups) as compared to those for the Navy (the two-sulphonate groups). The breakthrough of the column expressed in *BV* of effluents until dye concentration in effluent reached $C=0.5 C_0$ at actual value of pH 7 and the breakthrough capacity of the column with anion exchanger are presented in table **3.8**.

The possible competition is for effects of different the sulphonate group concentration in dyes are taken in to account in this work. The sorption capacity of A 847 decreased for removal dye Navy or dye CuPc from their mixture (0.05 mmol/l Navy and 0.05 mmol/l CuPc).

Table 3.8. Column performance of the Purolite A 847 for the removal of chromium or copper complex dye from one-component solutions and from their mixture: Bed volumes treated before breakthrough point (BV) and breakthrough capacity (BC)

<i>Dye solution composition</i>	<i>BV</i>	<i>BC</i> (mmol/l)
One-component Navy	45	4,5
One-component CuPc	10	0,2
Navy in equimolar mixture with CuPc	35	1,75
CuPc in equimolar mixture with Navy	2,5	0,125

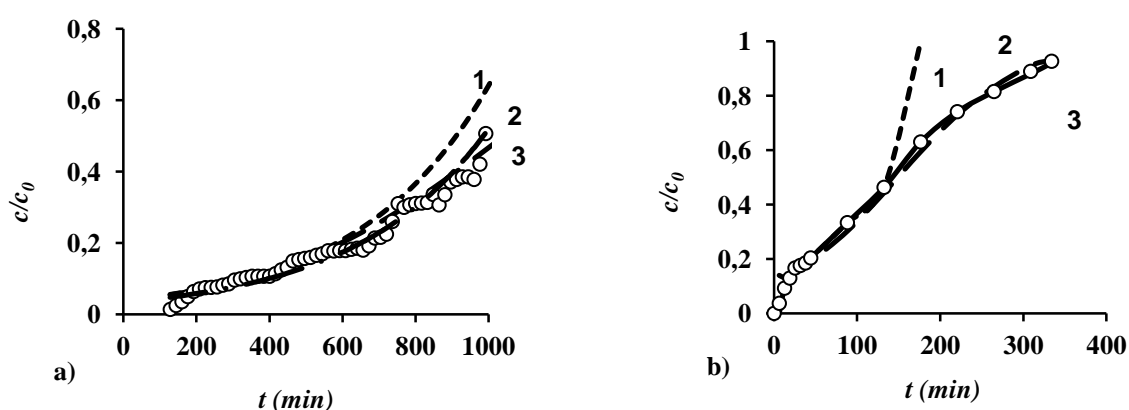


Fig. 3.8. Comparison of the experimental (cycle symbols) and the predicted column effluent concentrations for Cr complex dye sorption from one-component solution (a) and from mixture with Cu complex dye (b) using theoretical models: 1). Wolborska model, 2) Bohart-Adams, 3) Juang model.

The Wolborska, Bohard-Adams and Juang models were applied to experimental data (**Fig. 3.8.**) to predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design. All models are found suitable for the describing the whole or a definite part of the dynamic behavior of the column with respect to the dye solution composition and chemical structure of the dye. The simulation of the whole breakthrough curve was effective with the Bohard-Adams and the Juang model (R^2 is range 0.9468-0.9999 for Bohard-Adams model and range 0.9556-0.9939 for Juang model.) for sorption Navy and CuPc onto Purolite A 847.

Recovery of the dye as well as the regeneration of anion exchanger was an important process in wastewater treatment. The high amount of removed dye was achieved using mixture of ethanol and 4% NaOH (1:1) (**Fig. 3.9.**).

The first aliquot of three bed volumes elutes about 50% of the adsorbed chromium complex dye (**Fig. 3.9.**). The rest of dye was desorbed in next increments of one bed volume each. The percentage recovery was 70% for anion exchanger column. After desorption, the column of anion exchanger was washed with 100 ml deionised water and again loaded with the dye solution to check the sorption efficiency of anion exchanger during subsequent cycles.

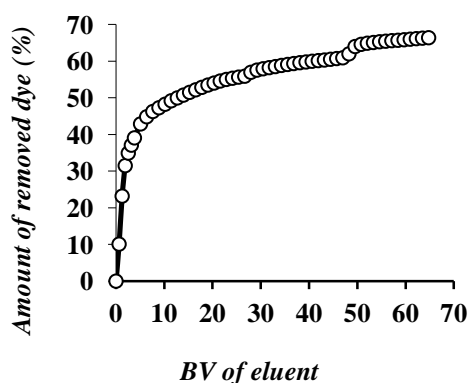


Fig. 3.9. Dependence amount desorbed dye (%) from bed volumes of eluant 4% NaOH and ethanol (1:1).

The for chromium complex dye-Purolite A 845 system fall in 30% when compared the sorption capacity in the first and in the fourth cycles. A significant fall in the sorption capacity was quite apparent. Therefore, the regeneration should be done after each cycle. The data might be helpful in designing a fixed-bed sorbent for the treatment of known concentrations of dye.

The methanol was fixed as the best eluant for regeneration of Macronet MN 200. The concentration of dye Navy in eluate after regenetrating of MN 200 using methanol is presented on **Fig. 3.10.**

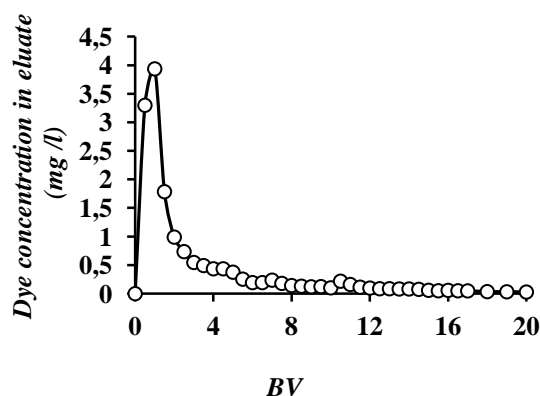


Fig. 3.10. Navy dye concentration in eluate (mg /l) from bed volumes of eluant methanol.

Desorption of dye Navy from MN 200 was fast and effective process. The most amount of dye was removable using 2 eluate volumes. Because the regeneration of MN 200 was perfect (100 %), this sorbent should be perspective using it in columns to repeatedly removal dyes from solutions.

CONCLUSIONS

1. Screening with chromium-complex dye (acid brown NKM, LanasyN Navy M-DNL) solutions wide range sorbents, according to the physical-chemical characteristics of the sorbents and established dyes removal parameters (sorption capacity, distribution coefficient and sorbent regeneration) shows that the polyacrylic, gel type, weakly basic anion exchanger Purolite A 847 (A 845); polystyrene, macroporous, strongly basic anion exchanger Purolite A 500 PS and nonfunctionalized Macronet MN 200 are the most promising sorbents for the metal complex dye removal.

2. The sorption of dyes Navy and CuPc proceeded: 1) on the weak basic Purolite A 847(A 845) and strong basis Purolite A 500PS anion exchangers according to the ion exchange mechanism in the presence of additional hydrogen, coulombic or weak Van der Waals forces; 2) on the nonfunctionalized sorbent Macronet MN 200 according to the physical sorption mechanism including diffusion process following formation hydrogen bonds or weak Van der Waals forces. The mechanism of sorption was confirmed by analyzing the recorded of FT-IR spectra of sorbents, dye unloaded and loaded.

3. The sorption capacity for anion exchangers and MN 200 strongly depends on solution pH, with higher values at acidic pH. With an increase temperature from 293 to 333 K in the solution the dye Navy sorption capacity on both anion exchanger and on MN 200 increases, whereas the dye CuPc decreases.

4. The experimental data showed a good correlation with Langmuir (correlation coefficients R^2 are from 0.9317 till 0.9789) and Freundlich (correlation coefficients R^2 are from 0.8430 till 0.9848) theoretical isotherm models for all system Navy-sorbent. Whereas, the data of the systems CuPc-sorbent satisfies only Freundlich mathematical model (correlation coefficients R^2 are from 0.9995 till 1).

5. Pseudo-second order kinetic model (the correlation coefficients R^2 are from 0.9811 till 0.9959 for anion exchangers and from 0.9914 till 0.9998 for nonfunctionalized MN 200) is suitable to determination of equilibrium sorption capacity and rate constant according to the dye Navy and dye CuPc. The Weber-Morris intraparticle diffusion model was used for calculation the intraparticle diffusion coefficient (k_i) and for indirect evaluation of the influence of boundary layer, which was formed about the sorbent bead. Determinate boundary layer thickness for sorption dye Navy on both anion exchangers was biggest neither for dye CuPc sorption, and it was lesser for sorption dye Navy on MN 200 neither for dye CuPc sorption. Thermodynamic parameter was determination for all system dye-sorbent.

6. High metal complex dyes removal efficiency (Cr 36 – 100 %, Cu 86-94 %) was obtained for dye Navy interaction with A 847 (A 845) at initial solution pH 2 and with Macronet MN 200 (only at low initial dye concentration (<3.08 mg/l) in solution) and can satisfy the environmental requirement for chromium concentration less than 0.1 mg/l and COD less than 150 mg/l O_2 .

7. The mass transfer in the system anion exchanger and one-component dye solution depended on the concentration of the sulphonate groups in the chemical structure of dye molecule and was lower for the dye with four-sulpho groups (C.I. Acid Blue 249) than that for the dye containing two-sulphonate groups (Lanasyn Navy M-DNL).

8. Several models were applied to the experimental data obtained from dynamic studies performed on fixed bed columns to predict the breakthrough curves and to determine the column kinetic parameters. The simulation of the whole breakthrough

curve is effective with Bohart-Adams and Juang models for sorption dye Navy and dye CuPc onto Purolite A 847 and with the Bohard-Adams for sorption dye Navy onto nonionic MN 200. A linear relationship between $\ln(c/c_0)$ and the time at a given bed height and flow rate was obtained in the initial region of effluent concentration ($c < 0.5 c_0$), suggesting that this segment of the breakthrough curve fit Wolborska model, and allows estimating the kinetic mass transfer coefficient in the fixed bed.

9. The column capacity for Purolite A 845 and MN 200 was found to be higher than the batch capacity. It is possible to regenerate the anion exchanger quantitatively (70%) recovering the dye with mixture of 4% NaOH and ethanol (1:1). Whereas MN 200 regeneration with methanol is perfect (100 %).

LIST OF ORIGINAL PUBLICATIONS

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METALO KOMPLEKSINIŲ DAŽIKLIŲ SORBCIJA JONIT AIS

Santrauka

Pagrindinis aplinkosauginės politikos bruožas yra taršos metalo dažikliais mažinimas gamybos metu ir efektyvių šalinimo iš nuotekų metodų paieška. Regeneruojami, mechaniškai atsparūs ir nekenksmingi gamtai polimeriniai sorbentai naudojami dažikliams valyti yra pranašesni už plačiai paplitusias aktyvintąsias anglis. Ištyrus polimerinių sorbentų sorbcines ir regeneracines savybes, nustatius palankias darbinės sąlygas, sorbentai gali būti pritaikomi nuotekų valymui, o išvalytas vanduo grąžinamas atgal į gamybinius procesus. Tokiu būdu, vandens išteklių gali būti apsaugoti nuo taršos sunkiaisiais metalais ir organiniais junginiais, sumažinti gamybos kaštai, nes regeneruoti sorbentai naudojami pakartotinai.

Šiame darbe tiriama metalo kompleksinių dažiklių Navy M-DNL (1:2 chromo monoazo kompleksas) (Navy) ir Acid Blue 249 (Vario (II) ftalocianino tetrasulforūgšties tetranatrio druska) (CuPc) sorbcijos sintetiniais jonitais dėsningumus statinėmis sąlygomis ir įvertinti jonitų galimybes valyti nuotekas nuo dažiklių dinaminėmis sąlygomis.

Geriausiai iš vandeninių tirpalų šalinantys dažiklius sorbentai atrinkti pagal geriausią sorbcinę gebą ir regeneraciją, dažiklio pasiskirstymo tirpale koeficientą yra: silpnai baziniai anijonitai Purolite A 847 (A 845), stipriai bazinis anijonitas Purolite A

500PS, nejoninis makrotinklinis sorbentas Macronet MN 200. Statinėmis sąlygomis nustatyta dažiklių (Navy ir CuPc) sorbcijai palankiausia terpė (pH 2) ir temperatūra atitinkamai dažikliui Navy aukštesnės – 303-313 K, dažikliui CuPc – 293 K. Sorbcijos pusiausvyros ir kinetikos eksperimentiniai rezultatai analizuoti remiantis optine mikroskopija ir FT-IR. Įvertinti dažiklių sorbcijos termodinaminiai parametrai (ΔG^0 , ΔH^0 and ΔS^0). Nustatytas dažiklių Navy ir CuPc sorbcijos mechanizmas. Atlikti FT-IR tyrimai sorbcijos mechanizmus patvirtina. Nustatyta, kad tirtų sistemų „Navy-sorbentas“ izotermoms analizuoti tinka Langmiuro ir Froindlichio matematiniai modeliai. Tačiau sistemoms „CuPc-sorbentas“ analizuoti tinka tik Froindlichio matematinis modelis.

Dažiklių sorbcijos anijonitais ir nejoniniu MN 200 kinetika paklūsta pseudo-antrojo laipsnio ir vidinės difuzijos (Veberio-Moriso) modeliams. Dažiklio Navy sorbcijai abiem anijonitais ir Macronet MN 200 apskaičiuotos vidinės difuzijos koeficiento ir ribinio sluoksnio vertės yra didesnės nei sorbuojant dažiklį CuPc.

Nustatyta dažiklių šalinimo iš vandeninių tirpalų dinaminėmis sąlygomis ypatumai. Vykdam kartotinę dažiklio Navy sorbciją anijonitu Purolite A 847 ir jo regeneraciją 4% NaOH ir etanolio (1:1) mišiniu, anijonito sorbcinė geba po 4 ciklų sumažėja apie 30 %, nejoninio MN 200 regeneracija metanolio yra 100 %. Kolonos sorbcinės gebos ir darbinio režimo parametrams įvertinti taikyti teoriniai modeliai: Volborskos, Boharto-Adamso ir Jungo.