Equilibrium and Kinetics Studies of 4-nitrophenol Adsorption Onto Porous Crosslinked Beads

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Batch adsorption of 4-nitrophenol (4-NP) from aqueous solutions on some non-ionic porous copolymers based on the styrene and divinylbenzene was investigated. The adsorption studies were performed as a function of various parameters: contact time, initial concentration of 4-NP solution and adsorbent/adsorbate ratio. Equilibrium and kinetics studies were investigated. Also, from the adsorption data the specific surface area of the polymeric adsorbents has been determined. The results showed that the porous beads prepared in presence of porogen mixture (toluene:gasoline) could have potential applications in the treatment of environmental pollution caused by 4-NP.

Keywords: adsorption, 4-nitrophenol, styrene-divinylbenzene copolymer, isotherm models

Water is an important factor in ecological equilibrium and its pollution is a current problem with serious effects on the human health. The hazardous water pollutants include a wide spectrum of substances like oil, detergents, dye, dangerous chemicals, fertilizers and pesticides, heavy metals, organic compounds, pathogenic microbes (bacteria and viruses) and suspended particles that are toxic at low concentrations, carcinogenic, mutagenic and can be bioaccumulated [1-4].

The phenolic derivative 4-nitrophenol (4-NP) is an important raw material and/or product of many industries like petrochemicals, plastics, leather, paint, steel, pesticides, rubber and pharmaceutical [5, 6]. 4-NP is a toxic pollutant that irritates the eyes, skin and respiratory tract and cause the inflammation of these parts. The water purification and removal of phenolic compounds can be achieved by destruction method (chemical oxidation, electrolysis, photodegradation, ozonation, photo-Fenton degradation, catalytic wet oxidation, electrochemical treatment and biodegradation) or recovery methods (adsorption, solvent extraction and membrane separation).

Among the various methods, adsorption has been found to be a simple and effective process for treating domestic and industrial effluents because of low initial cost, simplicity and ease of operation [7]. An appreciable amount of work has been done concerning the use of natural or synthetic adsorbents for removal of phenolic compounds from wastewater [8-10].

In the past few decades, the polymeric adsorbents have attracted increasing attention as a potential alternative to activated carbon in water purification due to their greater mechanical strength, higher surface area, porosity, various functionalities and feasible regeneration. Some examples of organic adsorbents found to have an excellent capacity for removing phenolic compounds from water are strong base anion exchanger namely, IRA-420, vinylpyridine-divinylbenzene copolymer, Hyppersol-Macronet resins, molecularly imprinted polymers, the hyper-crosslinked polystyrene beads with bimodal pore size, Amberlite XAD-4 and poly(2-hydroxyethyl methacrylate) beads [11-14].

For designing a suitable adsorbent is necessary to take under consideration two important physico-chemical aspects as follows: the equilibrium and the kinetics of adsorption which depends on the various factors such as, *p*H, temperature, adsorbate/adsorbent ratio, composition of the solution, contact time between adsorbate and adsorbent [15].

The aim of the present work is to study the adsorption properties of a new series of porous styrene-divinylbenzene (St-DVB) copolymers prepared in the presence of gasoline and mixture of gasoline and toluene as porogenic agents. Also, the paper describes the evaluation of the specific surface area for the yielded copolymers using the adsorption data of 4-NP at equilibrium. In order to find potential applications in selective separation with St-DVB copolymers, the four two-parameter isotherm model and two three-parameter adsorption isotherm models has been described.

Experimental part

Materials

Divinylbenzene supplied from Fluka was a technical mixture of isomers (o-DVB, m-DVB and p-DVB) with the residual mainly 3 and 4-ethyl vinylbenzene. The purity of DVB was determined by gas chromatography and was found to be 80%. Styrene supplied from Fluka was purified by vacuum distillation before use. Toluene, gasoline, benzoyl peroxide, NaCl, gelatine, 4-NP, HCl and NaOH were purchased from Fluka.

Synthesis of St-DVB beads

The St-DVB beads were synthesized by aqueous suspension copolymerization of St with DVB using 1.0 wt. % of benzoyl peroxide. DVB content of the copolymers was considered to be equal with those of the monomer mixtures. The mixture of monomers, initiator and porogenic

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agents were added in a flask reactor fitted with a mechanical stirrer with variable rotational speed, thermometer, reflux condenser which already contained 600 mL of aqueous phase at 60°C temperature. The aqueous phase consisted of 3.7 wt. % NaCl, 0.15 wt. % gelatine and 1.0 wt. % ammonium salt of poly(styrene-co-maleic anhydride). The polymerization reactions were performed at 80°C for 14 h with a stirring rate of 200 rpm. The organic: aqueous phase ratio was 1:5 (v/v).

The content of toluene and gasoline used in this study is calculated as follows:

$$f_g = w_m / (w_m + w_p) \qquad (1)$$

where, w_m is weight of monomer (g) and w_p is weight of porogenic agents (g).

After polymerization reaction the yielded beads were extracted with methanol in a Soxhlet apparatus to remove traces of residual monomers, linear oligomers and porogenic agents, then sieved to separate a fraction with at a particle size of 400 – 800 μm and finally, dried under vacuum at 50°C for 48 h.

Characterization of copolymer beads

The specific surface areas of the synthesized beads (S_{BET}, m^2/g) were measured by nitrogen adsorption at the boiling temperature of liquid nitrogen [16] on a Ströhlein Area Meter following the BET method.

The skeletal (ρ_s, g/cm^3) and the apparent (ρ_{ap}, g/cm^3) densities of copolymer beads were measured at 20°C by the picnometric methods with n-heptane and mercury, respectively [17]. The pore volume determined by mercury porosimetry is conducted in the non-swollen state and therefore measures only the fixed pores. Total porosity (% P) and pore volume (PV) were calculated according to the following equations:

$$P = (1 - \rho_{ap}/\rho_s)\cdot 100 \qquad (2)$$

$$PV = 1/\rho_{ap} - 1/\rho_s \qquad (3)$$

The solvent uptake coefficients of copolymer beads were determined at 500 rpm for 20 min by a method developed by Pepper [18]. The samples were put into a stainless steal cylinder with sieves and immersed in the solvent at 25°C for 48 h after which they were centrifuged in order to determine solvent uptake.

Batch adsorption studies

The adsorption of 4-NP onto St-DVB beads was investigated in a batch system. The important parameters that influence adsorption process such as, initial concentration and *p*H were investigated at different temperature. Batch adsorption experiments were carried out by adding a known amount of copolymer beads (0.1g) to a set of 100 mL conical flasks filled with 50 mL 4-NP solution of various concentrations (0.005 - 0.035 mol/L). Also, it was investigated the influence of the 4-NP: beads ratio (g/g). It was observed that the optimal ratio between 4-NP and beads was 1:1. The conical flasks were placed in a thermostated shaker bath (Memmert M00/M01, Germany) and shaken at 180 rpm and 298K until equilibrium was reached. The flasks were than removed from the shaker and the samples were centrifuged at 1000 rpm for 10 min. The concentrations of 4-NP in the supernatant solution before and after adsorption were determined using a UV-VIS Spectrophotometer (UV-VIS SPEKOL 1300, Analytik Jena) at a wavelength of 315 nm. The amounts of 4-NP at equilibrium, q_e (mol/g) and at any time, q_t (mol/g) was calculated from the following equations [3]:

$$q_e = (C_0 - C_e)\cdot V/W \qquad (4)$$

$$q_t = (C_0 - C_t)\cdot V/W \qquad (5)$$

where, q_e is the equilibrium adsorption capacity, q_t is the amount of 4-NP adsorbed onto copolymer beads at time *t*, C_0 is the initial concentration of 4-NP solution (mol/L), C_t is the concentration of 4-NP solution at any time (mol/L), C_e is the equilibrium 4/NP concentration (mol/L), *V* is the volume of 4-NP solution (L) and *W* is the amount of copolymer beads (g). All the adsorption data were achieved in duplicate and the average values were plotted.

Statistical analysis

Modelling of equilibrium and kinetic data were carried out by a non-linear regression method. Two error functions, i.e., correlation coefficients (R^2) and chi-square statistic (χ^2) were used to measure the degree of fitness of theoretical models with the experimental adsorption data [19]. These errors functions are defined as follows:

$$R^2 = SSR / SST \qquad (6)$$

and

$$\chi^2 = \sum_{i=1}^{n} \frac{(q_{measured} - q_{predicted})^2}{q_{predicted}} \qquad (7)$$

SSR is the sum of square of regression and SST is the sum of square total. Both SSR and SST are given by the experiments and determined from the number of fitted data (n) using the following equations:

$$SSR = \sum_{i=1}^{n} (q_{predicted} - q_{mean})^2 \text{ and } SST = \sum_{i=1}^{n} q_{measured} - q_{mean})^2 \qquad (8)$$

where, $q_{predicted}$ is the adsorption capacity predicted by the fitted model (mol/g).

The values of R^2 vary from 0 (model does not account for the variability) to unity (model accounts for all data variability). Lower values of χ^2 indicate a greater agreement between predicted and experimental adsorption data.

Results and discussions

Crosslinking is a very important process in the formation of the adsorbents structure. Using the suspension polymerization techniques it is possible to obtain porous beads, which could have an optimal morphological structure for various field of application. The properties of the porous crosslinked copolymers are influenced by synthesis parameters, mainly by the thermodynamic quality of a solvent used as porogen as well as by the percentage of monomers and crosslinking degree. Our study was developed on networks with 25% DVB and 45% DVB, respectively. Several characteristic parameters of the synthesized copolymers have been calculated and the values are listed in table 1.

Data from table 1 show the fact that the nature of porogenic agent and DVB content have an important consequence on the porous structure formation. Thus, a porogen mixture used during the monomers copolymerization process favours the formation of porous structure (CR3 sample) with a higher percentages of pores (P = 56.76%). The porous properties in the dry state can be described on the basis of the specific surface area data obtained from the nitrogen sorption. It can be observed that an increase of DVB content from 25 to 45% and the

Table 1
PHYSICO-CHEMICAL CHARACTERISTICS OF St-DVB BEADS

Physico-chemical characteristics	CR1	CR2	CR3
DVB %	25	45	45
Porogenic agent	gasoline	gasoline	toluene : gasoline (1:1)
f_g	0.54	0.54	0.54
S_{BET} (m^2/g)	238	270	421
ρ_S (g/cm^3)	1.141	1.054	1.062
ρ_{ap} (g/cm^3)	0.7830	0.6125	0.4583
PV (mL/g)	0.3317	0.6823	1.2386
P (%)	26.13	42.22	56.76
Uptake coefficient (g/g)			
methanol	0.667	0.716	1.927
cyclohexane	0.518	0.963	1.681
toluene	0.765	1.247	2.509

use of toluene and gasoline mixture lead to the formation of porous networks with high specific surface area (270 and 421 m^2/g). Also, the St-DVB samples regain various solvents (methanol, cyclohexane and toluene) and their quantities depend on the porogen nature and DVB content. The higher uptake coefficients of solvents are observed in case of CR3 sample. This behaviour could be explained by the thermodynamic effect of porogenic agent on the formation of pore structure [20].

Effect of pH on the adsorption process

Adsorption of 4-NP onto three adsorbents was carried out in the pH range 2-12 and the results are shown in figure 1.

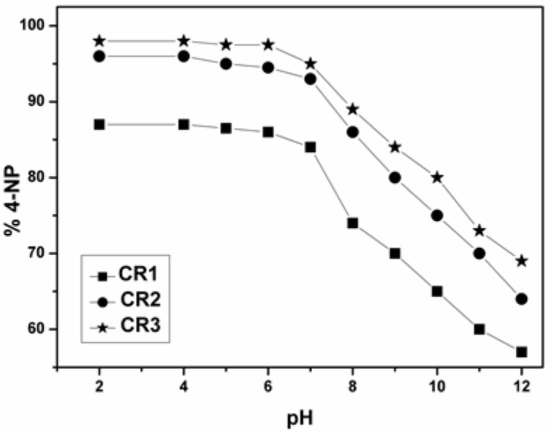

Fig. 1 Effects of *p*H on the adsorption of 4-NP onto St-DVB beads at 298 K

From figure 1 it is observed that, with increasing of *p*H the adsorption capacity of 4-NP did not change in the *p*H range of 2 to 5 and sharply decreased after *p*H = 7. In basic medium 4-NP exists in negative ionic form (phenolate ions). Therefore, the number of hydrophobic interactions decreases and 4-NP is poorly adsorbed on the St-DVB beads. Below *p*H = 7 the 4-NP exists in molecular form and it is adsorbed on the beads by micropore filling mechanism. A similar behaviour was observed for 4-NP adsorption on other adsorbents like: ND-701 and XAD-4 [21].

Effect of initial concentration of 4-NP solution on the adsorption process

In this work, the relationship between the adsorbent and the aqueous concentration of 4-NP at equilibrium has been described by four two-parameter isotherm models: Langmuir [22], Freundlich [23], Temkin [24] and Dubinin-Radushkevich [25], and two three-parameter adsorption isotherm models: Redlich-Peterson [26] and Sips [27].

Two-parameter and three-parameter isotherms

The two and three-parameter isotherm constants, chi-square (χ^2) and correlation coefficients (R^2) are given in table 2.

Analysing the data from table 2 it can be seen that:

- the values of R_L denote the unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($R_L < 1$) or irreversible ($R_L = 0$) process [28]. Values of R_L calculated at 298K for the initial 4-NP concentration values of 0.0005-0.035 mol/L are in range between 0 and 1, which indicate favourable adsorption;

- a small value of K_L indicates a low affinity of CR1 sample for 4-NP and therefore, a small amount of 4-NP has been adsorbed onto the CR1 beads. Higher values of K_L obtained for CR2 and CR3 samples indicate a strong affinity of adsorbate onto the beads and thus a higher amount of 4-NP has been adsorbed. Based on the K_L and q_m values it can be observed that CR3 copolymer is a better adsorbent than CR1 and CR2;

- the *n* values from Freundlich equation (*1/n* is indicative of the energy or intensity of the reaction and suggests the favourability and capacity of the adsorbent-adsorbate system) were calculated as 1.84, 2.24 and 2.63 for CR1, CR2 and CR3 samples, respectively. Since they lie between one and ten, this indicates that 4-NP is adsorbed favourably by all the adsorbents;

- the Temkin adsorption potential, a_T, increases in the following order: CR1 < CR2 < CR3, while the Temkin constant, b_T, decreases in the order: CR1 > CR2 > CR3;

- it is known that the magnitude of E ($E = 1/\sqrt{2 \cdot K_{DR}}$) gives the information about the type of adsorption process: physical (1-8 kJ/mol), ion exchange (9-16 kJ/mol) and chemical (>16 kJ/mol) [29]. The E values were around 2.5 kJ/mol, which is in the range of physical adsorption reactions.

- the β values are close to unity which means that data could preferably be fitted with Langmuir model;

- the exponent (1/n) values are close to unity. This suggested that the 4-NP adsorption data obtained in this study better fit the Langmuir form rather than the Freundlich form.

Based on the high R^2 and low values of χ^2 shown in table 2 the results indicate that the Langmuir and Temkin models represent a better fit of experimental data than Freundlich and Dubinin-Radushkevich models. Similar behaviour was observed in the adsorption process of 4-NP on acid activated jute stick char [30].

The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherm of 4-NP on CR1, CR2 and CR3 beads are shown in figure 2, while in figure 3 are presented the profiles of the three-parameter isotherms.

One of the main objectives of this work was to find another way to calculate the specific surface area of the adsorbents using the adsorption data.

Table 2
TWO AND THREE-PARAMETERS ISOTHERM CONSTANTS

Two-parameter models	Equation*	CR1	CR2	CR3
Langmuir	$q_e = q_m K_L C_e/(1+K_L C_e)$			
q_m (mmol/g)		0.84	1.17	1.75
K_L (L/g)		88.65	142.32	162.83
R_L [$R_L = 1/(1+K_L C_0)$]		0.958-0.244	0.934-0.167	0.925-0.149
R^2 (nonlinear)		0.986	0.992	0.997
χ^2		1.41	0.51	0.48
Freundlich	$q_e = K_f \cdot C_e^{1/n}$			
K_f (L/g)		0.0056	0.0042	0.0049
$1/n$		0.54	0.45	0.38
R^2 (nonlinear)		0.939	0.952	0.963
χ^2		2.07	1.87	1.83
Temkin	$q_e = (RT/b_T)\cdot \ln(a_T C_e)$			
a_T (L/mg)		0.93	1.28	1.87
b_T (J/mol)		2.74	2.54	1.85
R^2 (nonlinear)		0.989	0.991	0.992
χ^2		0.188	0.045	0.014
Dubinin-Radushkevich	$q_e = q_{DR}\cdot \exp(-K_{DR}\cdot \varepsilon^2)$			
q_{DR} (mmol/g)		1.67	1.52	2.13
K_{DR} (mol^2/kJ^2)		0.097	0.078	0.068
E (kJ/mol)		2.28	2.53	2.71
R^2 (nonlinear)		0.964	0.976	0.987
χ^2		2.42	1.95	1.41
Three-parameter model				
Redlich-Peterson	$q_e = K_R C_e/(1+a_R C_e^{\beta})$			
K_R (L/g)		0.063	0.124	0.282
a_R (L/mol)		198.43	180.95	150.12
β		0.81	0.89	0.96
R^2 (nonlinear)		0.994	0.996	0.998
χ^2		0.78	0.81	0.73
Sips	$q_e = q_m a_S C_e^{1/n}/(1+a_S C_e^{1/n})$			
q_m (mmol/g)		0.82	0.90	1.61
a_S (L/g)		926.01	315.78	69.24
$1/n$		0.907	0.943	0.968
R^2 (nonlinear)		0.989	0.992	0.995
χ^2		1.04	0.97	0.94

** q_m is the maximum adsorption capacity, K_L is the Langmuir constant related to the energy of adsorption which reflects the affinity between the adsorbent and adsorbate, R_L is the equilibrium parameter, K_f represents the adsorption capacity at unit concentration while 1/n is indicative of the energy or intensity of the reaction and suggests the favourability and capacity of the adsorbent-adsorbate system, b_T is the Temkin constant related to heat of adsorption, a_T is the equilibrium binding constant corresponding to the maximum binding energy, R is the gas constant (8.314 J/mol K), T is the absolute temperature, q_{DR} is the Dubinin-Radushkevich constant representing the theoretical monolayer saturation capacity, K_{DR} is the constant of the adsorption energy which is related to mean adsorption energy, K_R and a_R are Redlich-Peterson isotherm constants, β is the Redlich-Peterson model exponent, a_S is the Sips model constant and 1/n is the Sips model exponent.*

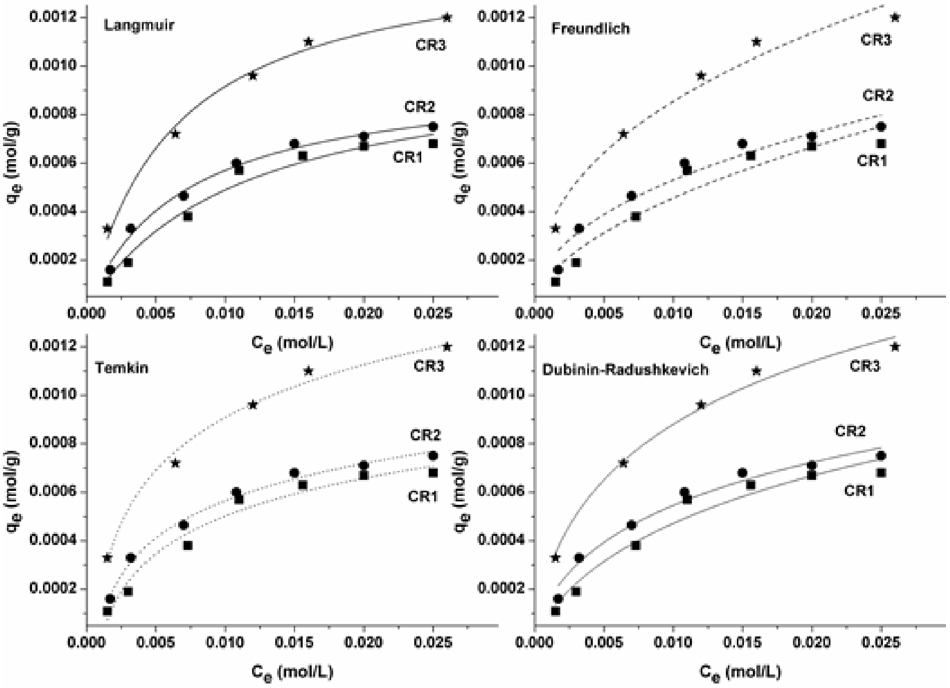

Fig. 2. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich equilibrium isotherms of 4-NP adsorbed onto St-DVB beads

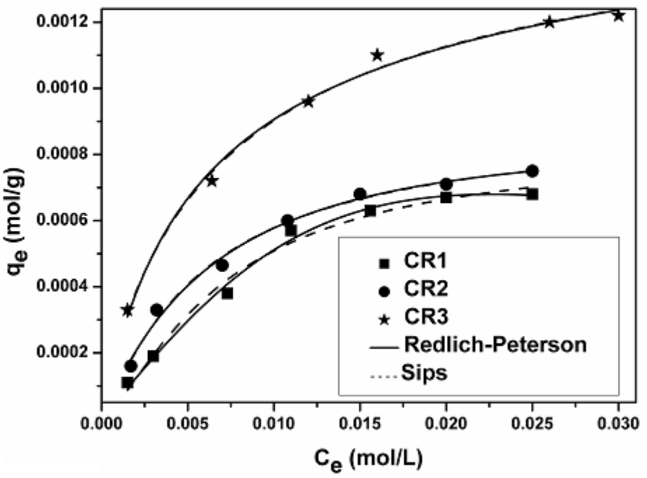

Fig. 3. Three-parameter isotherms for adsorption of 4-NP onto St-DVB beads

The specific surface area occupied by 4-NP was calculated by the following equation:

$$S = q_m \cdot N \cdot A_m \qquad (9)$$

where, S is the specific surface area (m^2/g); q_m is monolayer adsorption capacity (mmol/g); N is Avogadro number (N = 6.023 x 10^{23} molecules per mole) and A_m (A_m = 50.5 Å^2) is the molecular cross-sectional area of the adsorbate, i.e. the area which an adsorbat molecule occupies on the surface of the solid in a completed monolayer.

Therefore the specific surface areas of CR1, CR2 and CR3 samples measured by 4-NP adsorption are 255.49, 295.04, 450.16 m^2/g, respectively. This result is in good agreement with BET surface area measured by the N_2 adsorption method [16] on a Ströhlein Area meter.

Effect of the contact time on the adsorption process

Several models can be used to express the mechanism of solute adsorption onto an adsorbent. In this study the experimental data were interpreted by pseudo-first-order [31], pseudo-second-order [32] and intraparticle diffusion models [33].

The calculated values of adsorption kinetics and their corresponding error function values are shown in table 3.

It is seen from table 3 that the theoretical $q_{e(calc)}$ values calculated from the pseudo-first-order model did not give reasonable values with regard to the experimental uptake ones, $q_{e(exp)}$. Further, the error functions values suggested that the present adsorption system did not follow pseudo-first-order model. The theoretical $q_{e(calc)}$ values agree well with the experimental uptake values, $q_{e(exp)}$ for pseudo-second order. Higher correlation coefficients and lower values of χ^2 indicate that the adsorption of 4-NP on CR1, CR2 and CR3 samples can be more favourably approximated by pseudo-second-order model than the pseudo-first-order one. From table 3 it can be observed that the *h* value obtained for CR1 and CR2 samples was found to be lower than that estimated for CR3 sample. This indicates that the adsorption of 4-NP onto CR3 adsorbent was more rapid and favourable. Also, this result suggests that the rate of adsorption was influenced mainly by the structural properties of the adsorbent such as surface area, porosity and surface morphology.

Figure 4 presents the plots of mass of 4-NP adsorbed per unit mass of adsorbent versus $t^{1/2}$ for all the adsorbents.

It is clear from the figure 4 that the adsorption process was controlled by two stages [34]. The first linear stage (I) could be attributed to the immediate utilization of the most readily available sites on the adsorbent surface. The second stage (II) might be attributed to the very slow diffusion of the adsorbate from the surface inside to the pores. Thus the first stage of 4-NP adsorption could be governed by the intraparticle diffusion whereas the second stage is

Table 3
KINETIC PARAMETERS AND ERROR FUNCTIONS

	Equation*	CR1	CR2	CR3
$q_{e,exp}$ (mmol/g)		0.68	0.75	1.22
Pseudo-first-order	$q_t = q_e \cdot [1 - \exp(-k_1 \cdot t)]$			
q_e (mmol/g)		0.62	0.69	1.13
k_1 (min^{-1})		0.0434	0.0448	0.0444
R^2 (nonlinear)		0.976	0.966	0.956
χ^2		3.72	5.51	8.72
Pseudo-second-order	$q_t = t \cdot k_2 q_e^2 / (1 + t \cdot k_2 q_e)$, $h = k_2 \cdot q_e^2$			
q_e (mmol/g)		0.70	0.74	1.23
k_2 (g/mol·min)		39.37	47.23	50.24
h (mmol/g·min)		0.019	0.026	0.076
R^2 (nonlinear)		0.998	0.994	0.992
χ^2		2.15	1.98	1.83
Intra-particle diffusion model	$q_t = k_{id} \cdot t^{1/2} + C_i$			
$k_{i,1}$ (mmol/g·min$^{1/2}$)		0.060	0.055	0.084
$C_{i,1}$ (mmol/g)		0.097	0.157	0.288
R^2 (nonlinear)		0.986	0.994	0.981
χ^2		0.0053	0.00006	0.0078
$k_{i,2}$ (mmol/g·min$^{1/2}$)		0.006	0.011	0.019
$C_{i,2}$ (mmol/g)		0.547	0.531	0.837
R^2 (nonlinear)		0.988	0.983	0.979
χ^2		0.016	0.019	0.024

**k_1 is the rate constant of the pseudo-first order adsorption process (min^{-1}), k_2 is the rate constant of pseudo-second order adsorption (g/mol×min), h is the initial adsorption rate (mmol/g×min), k_{id} is the intraparticle diffusion rate constant (mmol/g×min$^{1/2}$), C_i is the constant that gives an idea about the thickness of the boundary layer (mmol/g).*

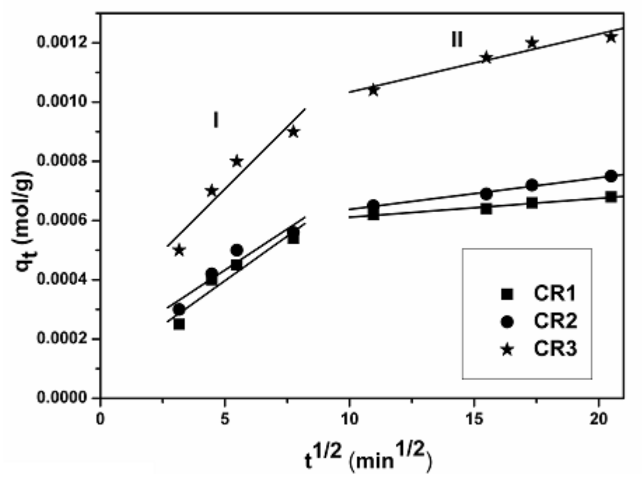

Fig. 4. Weber Morris intra-particle diffusion plots for adsorption of 4-NP onto St-DVB beads

controlled by pore diffusion. The deviation of the straight lines from the origin might be due to the difference in rate of mass transfer in the initial and final stage of adsorption. Further, such deviation of the straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step. The values of the diffusion rate constant $k_{id,2}$ as given in table 3 show the highest value of CR3 sample followed by CR2 and CR1 ones.

Conclusions

The adsorption property of 4-NP onto St-DVB porous samples were investigated. From experimental data result that the adsorption of 4-NP is strongly influenced by the nature of the porogenic agent used in the synthesis of St-DVB samples as well as by the DVB content. The copolymer beads obtained in the presence of the mixture of toluene and gasoline exhibited high specific surface and therefore, high adsorption capacity of 4-NP. The maximum adsorption capacity values of the yielded St-DVB adsorbents increased in the following order: CR1 < CR2 < CR3.

Among of the two-parameter isotherm models, Langmuir and Temkin models gave the best fitting for the adsorption of 4-NP on the St-DVB beads. According to Dubinin-Radushkevich isotherm, the E values indicated the physical adsorption reactions. Kinetic studies demonstrated that the adsorption process of 4-NP on the St-DVB beads obtained in this work follows closely a pseudo-second order kinetic model. Results of the intra-particle diffusion model showed that the pore diffusion is not the only rate limiting step.

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Manuscript received: 16.11.2015