



## Research Paper

## Preparation and Characterization of Modified PEEK-WC: DEHPA Microspheres for Rhodamine B Adsorption. Kinetics Studies

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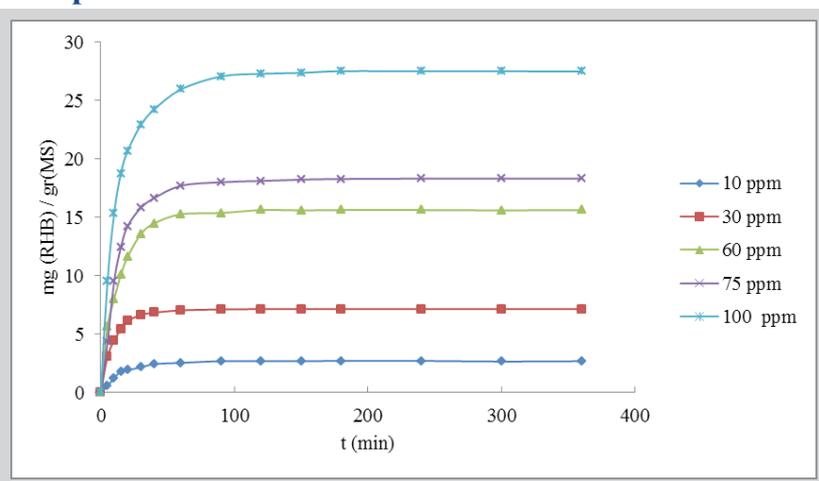
## Keywords

Microsphere preparation  
 PEEKWC  
 Rhodamine B removal  
 Beads preparation

## Highlights

- Asymmetric spherical PEEK-WC: DEHPA microspheres were prepared by phase inversion method.
- The prepared microspheres were successfully used for Rhodamine B adsorption and reused at least 09 cycles.
- The pseudo second order and intra-particle models describe well the adsorption kinetics of Rhodamine B by the modified microspheres.

## Graphical abstract



## Abstract

Functionalized polymeric microspheres based on a modified polyether ether ketone (PEEK-WC) using immersion precipitation techniques were successfully prepared by doping initial polymeric solutions with DEHPA. The viscosity of the doping solution was measured for determining the optimal value for obtaining reproducible capsules. The modified microspheres were characterized by several techniques such as SEM, BET and porometer. From the results, meso-porous microspheres with a small tail were obtained characterized by an asymmetric structure and a diameter varying from 50  $\mu\text{m}$  to around 1400  $\mu\text{m}$ . The produced microspheres have been used efficiently for Rhodamine B adsorption in a column system with extraction efficiency of 99%. Moreover, the modified microspheres could be regenerated with high efficiency and a good reusability after 9 cycles of sorption and desorption. The adsorption kinetics, of Rhodamine B by the produced microspheres, was best represented by the pseudo-second-order kinetics model which confirms a chemisorption mechanism. However, the results of the intra-particle model reveal that the sorption of Rhodamine B onto the microspheres is a combination between the chemisorption and intra-particle diffusion. The findings of this study provide novel information for the development of new polymeric microspheres adsorbents towards dyes for potential applications for example in wastewater textile treatment.

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## 1. Introduction

Nowadays, water pollution by toxic industrial waste is one of the most serious social and ecological issues in particular the expanding use of dyes in different industries such as textile, polymers, food and pharmaceuticals generating a huge volume of dyeing effluent. Thus, the majority of these dyes are synthetic

containing aromatic rings in their structure and non-biodegradable when discharge into waste stream. As a result, they affect equally the human health and the aquatic ecosystem. Even in very small quantities, dyes lead to changes in salinity and visible coloration of the water,

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reducing sunlight penetration and thus hindering the process of photosynthesis, while some of them are toxic and carcinogenic [1–5]. For that reason, several techniques have been investigated for the removal of dyes from aqueous solution including the flocculation [6], flotation [7], precipitation [8], coagulation [9], ion exchange [10], membranes [11–12], electrolysis [13], photo-degradation [14], extraction [15], radiation [16], oxidation [17], biological treatment [18] and sorption [19]. Despite the large number of methods, most of them are either too expensive to be applied in small plants or inefficient [20].

Traditionally, sorption process is recommended to be an effective process for the removal of pollutants from wastewaters in particular dyes due to their resistance toward oxidation and biodegradation.

Recently, various adsorbents have been used to remove pollutants from aqueous solution such as chitin [21], silica gel [22], wood [23], natural clay [22], bagasse pith fibers, and polymeric adsorbents [24].

Rhodamine B, a synthetically prepared carcinogenic xanthine dye is widely used for paper painting, textile dyeing, leather and paint industries. Its discharge and presence in the effluent can cause environmental degradation inducing low transparency of light and high content of organic load; irritate skin, eyes and respiratory tract and it is carcinogenic and toxic to nervous system too [25]. Besides all the sorbents and the techniques cited, sorption on activated carbon is the most widely used for this purpose thanks to its high adsorption capacity of organic matter. However, its use is limited due to its high initial and regeneration cost [26]. Consequently, many researchers have evaluated the possibility of using low-cost substances for the removal of various dyes and pollutants from wastewater. Recently, polymeric microspheres has been also successful presented as an alternative technology for the adsorption of toxic metal ions such as chromium (VI), arsenic (V), nickel [28–34]. However, to our best knowledge, no studies on the adsorption of Rhodamine B by the polymeric microspheres, based on a modified polyether ether ketone (PEEKWC) doped by di-ethyl hexyl phosphoric acid (DEHPA), have been reported. For that reason, we reported in this study, the preparation and characterization of PEEKWC polymeric microspheres doped with different content of di-ethyl hexyl phosphoric acid (DEHPA) as adsorbent has been applied. The efficiency of the prepared microspheres has been evaluated for removal of Rhodamine B from aqueous solutions.

## 2. Experimental

### 2.1. Chemical and reagents

Diethyl hexyl phosphoric acid (DEHPA) was supplied by SIGMA-ALDRICH. Dimethyl formamide (DMF) and ethanol were supplied by PANCREAC and dodecane from CARLO ERBA. Rhodamine B (RHB) was purchased from Sigma-Aldrich. As basic material, modified polyether ether ketone (PEEK-WC) (from institute of applied chemistry, CHANG CHUN, PR China) was used for microspheres preparation. Chemical formulas of specific products are presented in Figure 1. All the reagents were used without purification and analytical grade.

### 2.2. Microspheres preparation

Homogeneous polymeric solutions were prepared based on PEEK-WC 10 % (w/w) in DMF doped with 2 % (w/w) of PVP –K17 as pore former. After complete dissolution of polymer, DEHPA was added at different ratio

with a polymer at: 0, 0.5, 1.5, 2 and 3 % in weight. Table 1 summarized the microspheres preparation conditions. Each solution was used as phase (I) for microspheres preparation. Dodecane was chosen as oil phase (phase (II)) whereas the coagulation bath (phase (III)) contained a mixture of ethanol and water at 1:1 ratio (V/V) (Figure 2). The viscosity of the polymeric solution was measured by BROOKFIELD DV III-ULTRA Rheometer at 25 °C.

In this experimental work, the polymeric solution was poured in the module containing a polyethylene film (PE) mono-pore of size 600–800 µm. The casting solution, moved slowly down through the mono-pore film by gravitational forces, forming a spherical droplets at the pore borders of dodecane (phase (II)). The detailed description of the set-up employed has been deeply described by Figoli et al. [35]. These droplets retained their spherical shape during the drop formation. Then, when in contact with the non-solvent (phase (III)), the polymer /DMF/DEHPA solution immediately coagulated by phase inversion. The obtained microspheres were filtered and washed with the distilled water in order to remove the excess solvent and DEHPA from the surface. Microspheres were dried overnight at 50 °C for further characterization (SEM, BET, TGA, microspheres size).

### 2.3. Rhodamine B extraction

In the column, a quantity of functionalized microspheres was packed into a column of 1 cm of diameter and 130 mm in height. A second column, having 2 cm in diameter, was also used for studying the bed height effect on the extraction. The aqueous feed solutions containing 10, 30, 60, 75 ad 100 ppm of Rhodamine B (RHB) at pH = 4.5 with a flow rate of 0.145 ml/s were tested. Moreover, the effect of the microspheres dosage, temperature and the DEHPA content on the adsorption of RHB was investigated.

The adsorption capacity (Q) and the efficiency of extraction (E) were calculated by the following equation:

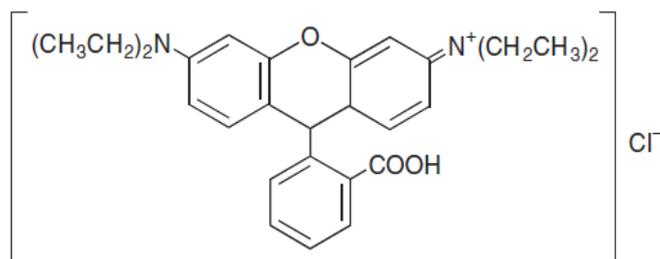
$$Q(\text{mg/g}) = ((C_0 - C_e) * 0.1) / W \quad (1)$$

$$E(\%) = ((C_0 - C_t) / C_0) * 100 \quad (2)$$

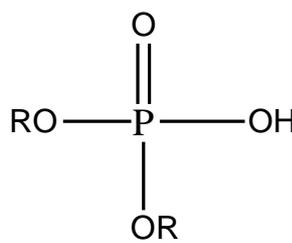
where Q is adsorption capacity (mg/g), (C<sub>0</sub>) and (C<sub>e</sub>) are the initial and the equilibrium concentration of metal ion (mg/l) respectively, W is the weight of the dried microspheres (g), (C<sub>t</sub>) is the Rhodamine B concentration in the aqueous solution at extraction time (t).

**Table 1**  
Microspheres preparation conditions and viscosity measurements.

Polymer	Additive	Ratio	Coagulation bath	Viscosity
PEEK-WC	PVP	PEEK-WC/DEHPA	Ethanol /water	(cP)
% (w/w)	% (w/w)		% (V/V)	
		1:0		116
		1:0.5		106
10	2	1:1	50/50	100
		1:1.5		90.5
		1:2		//
		1:3		//



Rhodamine B (RHB)



Diethyl hexyl phosphoric acid (DEHPA)

**Fig. 1.** Chemical formulas of specific products.

#### 2.4. Desorption studies

Desorption studies can elucidate the nature of adsorption and recycling of the adsorbent and the dye. For that, in the same system used for the adsorption, desorption experiments were carried out with nitric acid at 3N. At least 9 cycles of extraction and re-extraction were carried out for proving the potentiality of the system in long operation conditions.

### 3. Results and discussion

#### 3.1. Microspheres formation

Functionalized polymeric PEEK-WC microspheres were successfully produced using immersion precipitation process based on the exchange between the solvent and the non-solvent. In our system, the microsphere formation was strong dependent on the viscosity of the casting solution. This latter drastically decreases by increasing the DEHPA content in the casting solution, from 116 cP to 90.5 cP, for the ratio (PEEK-WC/DEHPA) 1:0 and 1:1.5 respectively. As a result of adding DEHPA, below the ratio 1:1.5, the microsphere formation was not possible due to the low viscosity of the polymeric solution. Moreover, for the ratio 1:2 and 1:3, the polymeric solutions resulted turbid, even increasing the temperature (60 °C) and time (48h), indicating that DEHPA at high concentration was not soluble in the dope mixture. The different polymeric solutions are reported in Figure 3.

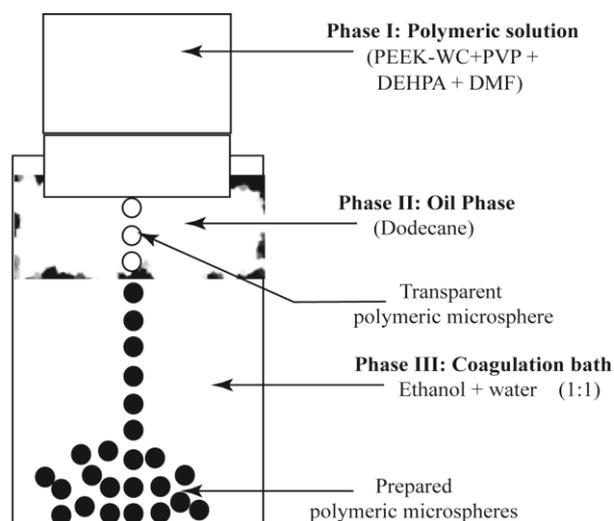


Fig. 2. Schematic representation of the microspheres process [35].

#### 3.2. Microspheres characterization

##### 3.2.1. Microsphere size distribution

Size distribution of the PEEK-WC microspheres, without and with DEHPA, was calculated by measuring the diameter of 100 microspheres produced by means of a digital micrometer.

For the pristine polymer microbeads (without DEHPA), the diameter size ranged from 0.78 mm to 1.38 mm with a maximum of particles number at 1.05 mm. The addition of DEHPA brings to an increase of the diameter size distribution, in the range from 0.9 mm to 1.7 mm, with a maximum at 1.38 mm at 0.5 wt% content of DEHPA (Figure 4). However, an unexpected result is obtained at the ratio 1:1 and 1:1.5 of PEEK-WC: DEHPA where the particle size drastically decreased from 0.035 mm to 0.057 mm with a maximum at 0.04 mm and 0.045 mm, respectively. This could be explained by the decrease in viscosity of the polymeric solution inducing a rapid formation of the droplet through the film mono-pore.

##### 3.2.2. Microspheres morphology

PEEK-WC microspheres morphology was examined using Scanning Electron Microscopy (SEM). From SEM pictures (Figure 5), microspheres present a small tail and irregular rough outer surface. The cross-section of the microspheres presents an asymmetric structure characterized by a microporous skin layer and finger like structure from the external surface to the center of microspheres, which is characteristic of an instantaneous phase separation during the process formation. However, the higher content of DEHPA, up to a ratio to 1:1.5, retards the solubility in water making microspheres with a roughness surface and a suppression of macro-voids as visible in the section of the microspheres. The increasing of the content of DEHPA at high concentration affects considerably the morphology and the structure of the microspheres.

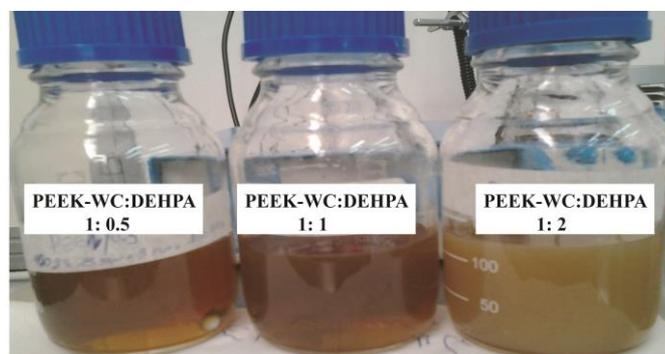


Fig. 3. Polymeric solutions at different ratio PEEK-WC:DEHPA.

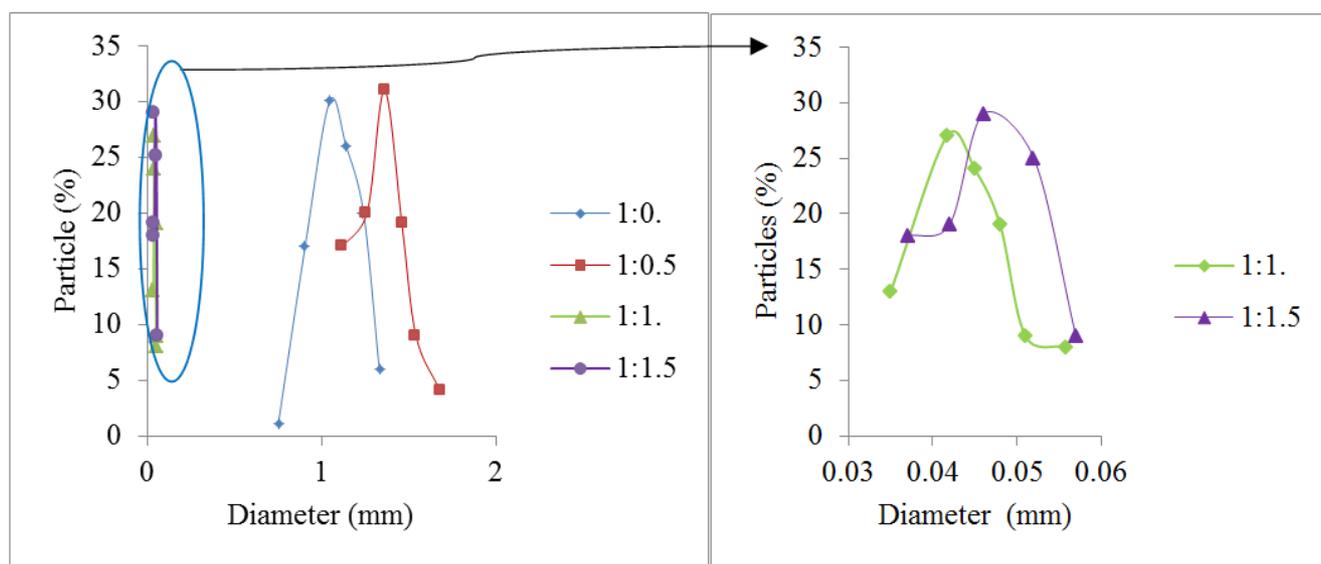


Fig. 4. Size distribution of PEEK-WC microsphere with and without DEHPA.

### 3.2.3. BET analysis

In Table 2, BET surface area, pores radius and total pores surface area of microspheres were reported.

In general, the low BET surface area is in agreement with those reported for polymeric materials [36]. In our case, the presence of DEHPA affects drastically the specific surface. In fact, the BET surface area of the microspheres decreases from 9.70 m<sup>2</sup>/g to 0.474 m<sup>2</sup>/g and 0.349 m<sup>2</sup>/g for the ratios 1:0, 1:1.5 and 1:1.5, respectively; which can be explained by the excess of the DEHPA and its low solubility in the aqueous solution reducing the penetration of the coagulant inside the polymer matrix and occupied the free volume in the microspheres.

According to BJH results, the average pores surface areas vary from 6.45 m<sup>2</sup>/g to 1.426 m<sup>2</sup>/g and the pore size is in the nanometer scale. Thus, it seems that the prepared microspheres have a meso-porous structure [36].

**Table 2**  
BET surface area, pores radius and total pores surface area of the prepared microspheres.

Type	Microspheres	BET Surface Area (m <sup>2</sup> /g)	BJH desorption analysis	
			Total pores surface area (m <sup>2</sup> /g)	Pores radius (Å)
A	1:0	9.71	6.453	15.68
B	1:0.5	9.139	6.185	17.67
C	1:1	0.474	4.182	15.63
D	1:1.5	0.349	1.426	17.52

### 3.2.4. Thermal analysis

The decomposition patterns for the microspheres shows generally two distinct weight losses except for the virgin polymer where simple stage degradation was observed at 400 °C. For all the microspheres, a first degradation stage was observed around 200°C which can be attributed to decomposition of DEHPA and the residual PVPK-17, with different mass losses depending on the content of the DEHPA in the microspheres. However, the second stage degradation observed between 400 °C and 600°C is due to the decomposition of polymeric backbone (Figure 6).

Lakshmi et al. [37] obtained similar curves, but with two distinct weight losses, the first one corresponding to the decomposition of the adsorbed ionic liquid and the other two one due to the decomposition of the polymeric backbone.

## 4. Column tests for Rhodamine B adsorption

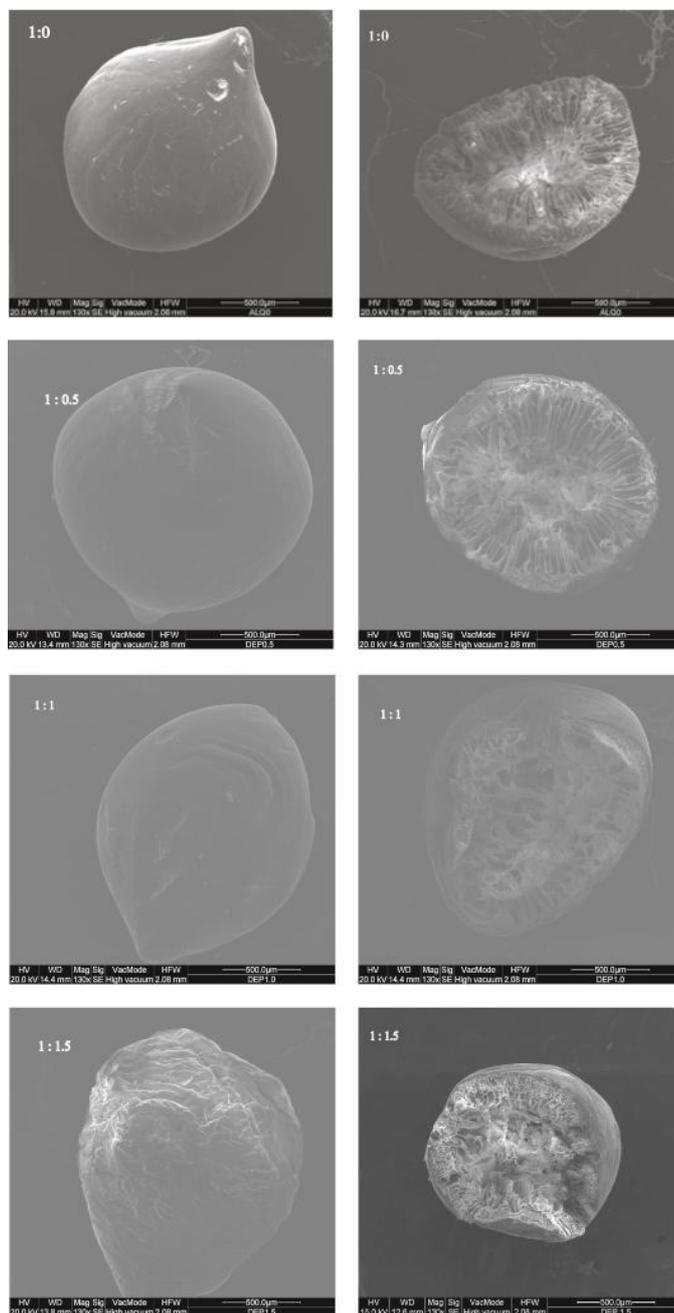
### 4.1. Effect of DEHPA and PEEK-WC ratio on RHB sorption

For column tests, all the modified microspheres were tested. Figure 7 shows the results.

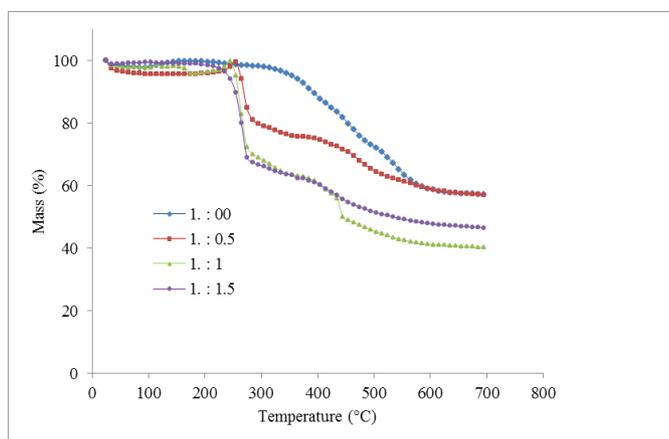
The obtained results are represented in Figure 7. The efficiency (E%) of the adsorption of microspheres increases at higher DEHPA content by keeping a constant amount of PEEK-WC. This is expected due to the increase of the amount of DEHPA, which enhances the formation of complex between RHB and DEHPA thanks to the presence of more free active sites. However, an unexpected result, related to the loss of efficiency, was observed for the microspheres D (1:1.5) which can be explained by the low specific surface (0.349 m<sup>2</sup>/g) and pore total surface (1.426 m<sup>2</sup>/g). Based on these results, further experiments have been conducted using the optimum ratio of PEEK-WC: DEHPA at C (1:1).

### 4.2. Effect of RHB initial concentration

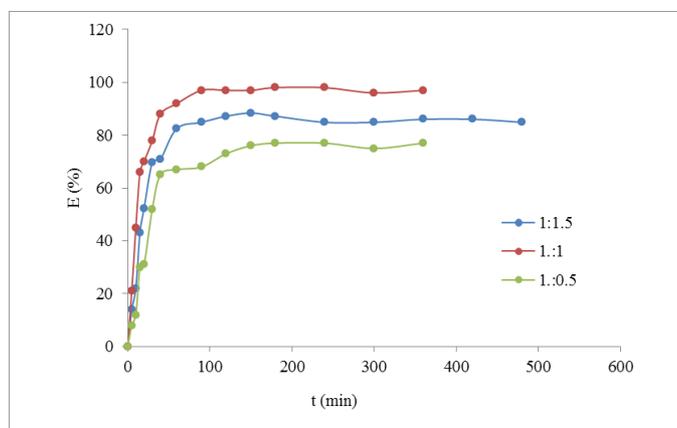
The influence of initial concentration of RHB on its removal was examined by varying the initial RHB concentration from 10 ppm to 100 ppm at pH 4.58. The results, represented in Figure 8, demonstrated that increasing the initial concentration improved the amount of RHB adsorbed. In fact, the amount of RHB adsorbed varied from 2.68 mg (RHB)/g (MS) to 27.5 mg (RHB)/g (MS) for the initial concentration of RHB of 10 ppm and 100 ppm, respectively. This could be explained by the increasing of driving force for mass transfer with the concentration of RHB. Moreover, all the adsorption process was very fast at the beginning and reached a steady state at low RHB concentration after 50 min (Figure 8). The equilibrium time increased with increasing initial concentration of RHB and reached 60min for 100ppm.



**Fig. 5.** SEM micrographs of PEEK-WC for different ratio PEEK-WC : DEHPA (1:0; 1:0.5; 1:1; 1:1.5).



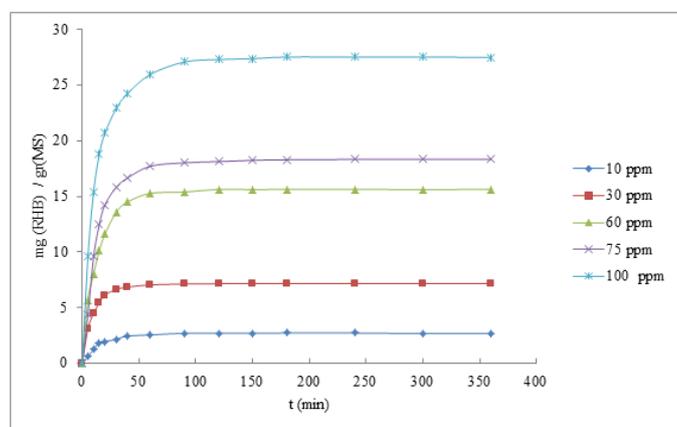
**Fig. 6.** PEEK-WC/DEHPA TGA plots for different microspheres.



**Fig. 7.** Effect of DEHPA content on the efficiency (E%) of RHB removal;  $Q_e=0.145$  ml/s.  $m(MS)=0.4$  g.  $D$  (column)=1 cm.  $H=3.3$  cm.  $[RHB]=10$  ppm.  $pH_i=4.58$ ;  $pH_f=3.62$ ;  $T=20$  °C.

#### 4.3. Effect of dosage sorbent (microspheres)

In order to maximize the interaction between the RHB and the desorption site of the modified microspheres, it is important to study the effect of the dosage of the microspheres on RHB adsorption by varying the quantity of microspheres from 0.2 g to 0.8 g. The results are shown in Figure 9. It is found that the removal efficiencies increased as much as possible with the increase of the dosage of adsorbents and reached a steady state at the adsorbent dosage over 0.6 g. This can be explained by the increase in the availability of more active adsorption sites and an increase in surface area of the microspheres. Moreover, at higher sorbents dosage, the high of the fixed bed is increased inducing the increase in the contact time between the RHB and the microspheres improving the efficiencies of the system. This is in agreement with the expectation that at a higher sorbent dosage results in a lower  $Q_e$  values. In fact, the content of DEHPA is related to the PEEK-WC:DEHPA concentration through surface site density. Hence, the removal increases at higher microspheres dosage, while  $Q_e$  decreases. Similar results were found by Arivoli et al. [38] by using the activated carbon. In the same logic, M.H.Beyki et al. [39] reported the possibility of RHB removal by melamine-base dendronized magnetic polymer nanoparticles with high capacity of sorption by increasing the dosage of the sorbent.

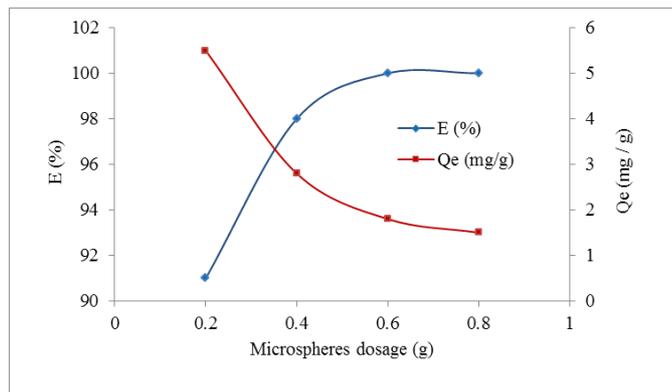


**Fig. 8.** Effect of Rhodamine B initial concentration on the sorption capacity of the modified microspheres.  $Q_e=0.145$  ml/s.  $m(MS)=0.4$  g.  $MS$  (1:1).  $D$  (column)=1 cm.  $H=3.3$  cm.  $pH_i=4.56$ ;  $pH_f=3.12$  at  $T=20$  °C.

#### 4.4. Effect of temperature

Figure 10 shows the effects of systems temperature on RHB adsorption by the modified microspheres. It can be seen that the extraction rate decreases slightly with increasing temperature. This phenomenon indicates that the extractive reaction is exothermic. In other word, the effect of temperature on the removal of RHB is not significant. For this reason, the best solution is to work at room temperature instead of cooling the solution for adsorption

system. In the literature, similar results, which refer to the extraction of acidic colorants, were reported by Hu et al. [40]. In another work, Arivoli et al. [38] reported that the adsorption of RHB on the activated carbon was also favorable and spontaneous.



**Fig. 9.** Effect of microspheres dosage on the sorption capacity of RHB by the modified microspheres.  $Q_e=0.145$  ml/s.  $MS$  (1:1).  $D$  (column)=1 cm.  $H=3.3$  cm.  $pH_i=4.56$ ;  $pH_f=3.12$  at  $T=20$  °C.

#### 4.5. Adsorption kinetics

Adsorption kinetics studies are important for choosing operating conditions for design purpose. For that, in order to investigate the mechanism of adsorption and potential rate controlling steps such as chemical reaction, diffusion control and mass transport process, kinetics models have been used to test experimental data from the adsorption of RHB onto the produced microspheres. In order to understand well the adsorption behaviors of RHB onto the prepared microspheres, pseudo-first order, pseudo-second order and intra-particle models were used.

##### 4.5.1. Pseudo-first and pseudo-second order equations

The pseudo-first-order equation is expressed as follows:

$$\left(\frac{dq_t}{dt}\right) = k_1(q_e - q_t) \quad (3)$$

$$\left(\frac{dq_t}{dt}\right) = k_2(q_e - q_t)^2 \quad (4)$$

Integration equations (3) and (4) for the boundary conditions:  $q_i=0$  to  $q_t=q_t$  at  $t=0$  to  $t=t$ , the equation can be given as:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

$$\left(\frac{t}{q_t}\right) = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) * t \quad (6)$$

where  $q_e$  (mg/g) and  $q_t$  (mg/g) are the amount of solute adsorbed by adsorbent at equilibrium and at time (t) respectively;  $k_1$  (1/min) and  $k_2$  (g/mg.min) are the rate constants pseudo-first and pseudo-second order models, respectively.

The intercepts and the slope of the plots of  $\log(q_e - q_t)$  versus time gives the values of  $q_e$  and  $k_1$ . However, in the case of the pseudo-second-order, the value of  $q_e$  and  $k_2$  were obtained from the intercepts and the slopes of the plot  $(t/q_t)$  versus time.

The binding of RHB to PEEK-WC: DEHPA microspheres were analyzed by pseudo-first-order and pseudo-second-order kinetics models and described in Figure 11a and Figure 11b respectively. The theoretical and experimental values of the adsorbed amount of RHB are summarized in Table 3 with the corresponding correlation coefficients.

From the results, the value of  $R^2$  for pseudo-second-order model ( $R^2=0.998$ ) is higher than that for the first-pseudo-order ( $R^2=0.903$ ). The pseudo-second-order kinetics model described correctly the adsorption of RHB on the prepared microspheres. Moreover, the value of  $q_e$  obtained from the linear form of pseudo-second order expression was approximately the same to the experimental value. These results suggest that the overall rate of RHB adsorption process was controlled by chemi-sorption which involves the ion exchange between the DEHPA and the RHB adsorbed. Similar results were reported by many researchers using the activated carbon as sorbent media [5, 25, 39, 41-43].

**Table 3**

First and second - order kinetics parameters for adsorption of RHB onto the produced microspheres. [RHB] = 10ppm; Q=0.145ml/s. MS C (1:1). D (column)=1cm. H=3.3cm. pH<sub>i</sub>=4.56; pH<sub>f</sub>=3.12.

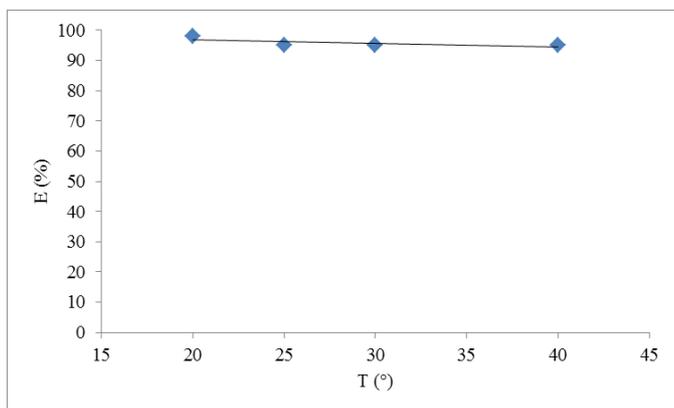
Parameters	Rate constant K		R <sup>2</sup>	q <sub>e</sub> (from the model) (mg/g)	q <sub>e</sub> experimental (mg/g)	
Pseudo-first-order (k <sub>1</sub> )	0.02 min <sup>-1</sup>		0.903	1.45		
Pseudo-second-order (k <sub>2</sub> )	0.45 g.mg <sup>-1</sup> min <sup>-1</sup>		0.998	2.78		
Diffusion intra-particle (k <sub>int</sub> )	k <sub>1</sub>	0.759	R <sub>1</sub> <sup>2</sup>	0.998	C1	2.71
	k <sub>2</sub>	0.191	R <sub>2</sub> <sup>2</sup>	0.930	C2	
	k <sub>3</sub>	0.000	R <sub>3</sub> <sup>2</sup>	0.028	C3	

**Table 4**

Comparison of RHB adsorption property of the prepared microspheres with some sorbents.

Adsorbent	Capacity (*) (q <sub>e</sub> ) (mg/g)	Equilibrium time (min)	Reusability (cycle)	Reference
Fe-Montmorillonite	170.89	150	03	[42]
Magnetic BaFe <sub>2</sub> O <sub>4</sub>	124	5	5	[39]
Fe <sub>3</sub> O <sub>4</sub> /MIL-100 (Fe)	28.36	30	none	[5]
PDTpc	578.2	200	10	[47]
PDBpc	328.7	150	none	
<b>Activated carbon :</b>				
- <i>Lythrumsalicaria</i>	223.5-293.4	100	none	[25]
- <i>Industrial solid waste</i>	16.1	150	5	[48]
- <i>Coir pith</i>	2.6	150	none	[49]
PEEK-WC : DEHPA	2.7	30	10	This work

(\*) :experimental adsorption capacity of each adsorbent.



**Fig.10.** The effect of the extraction temperature on RHB removal. Q=0.145ml/s. MS C (1 :1). D (column)=1cm. H=3.3cm. pH<sub>i</sub>=4.56; pH<sub>f</sub>=3.12.

#### 4.5.2. Intra-particle diffusion

In order to identify the diffusion mechanism, the intra-particle diffusion model was used to evaluate the rate-controlling step, then the adsorption data can be presented by the following equation:

$$q_t = k_{int}t^{1/2} + C \quad (7)$$

where  $k_{int}$  is the intra-particle diffusion rate constant (mg/g.min<sup>1/2</sup>) and C the intercept, which represent the thickness of boundary layer. A large C value means a greater effect of the boundary layer [25, 41].

Figure 11c illustrates the variation of the amount of RHB adsorbed versus  $t^{1/2}$  by the microspheres. The plot is multi-linear and there are three different portions, indicating the different stages in the process of adsorption. Wu et al. and Ho [44, 46] depicted the different portion of the plots. They reported that the first portion of the plot represents the external mass transfer. The second portion describes the gradual adsorption stage, where the intra-particle diffusion is rate controlled. The third part indicates the equilibrium state of the process.

The results, presented in Figure 11c shows that the plot does not pass through the origin, which indicate that the intra-particle diffusion is not the only rate step and boundary layer control may be involved in the process [46]. The intra-particle diffusion model parameters, values of  $K_{int}$ ,  $q_e$  and  $R^2$ , are presented in Table 3.

#### 4.6. Desorption and reusability of the prepared microspheres

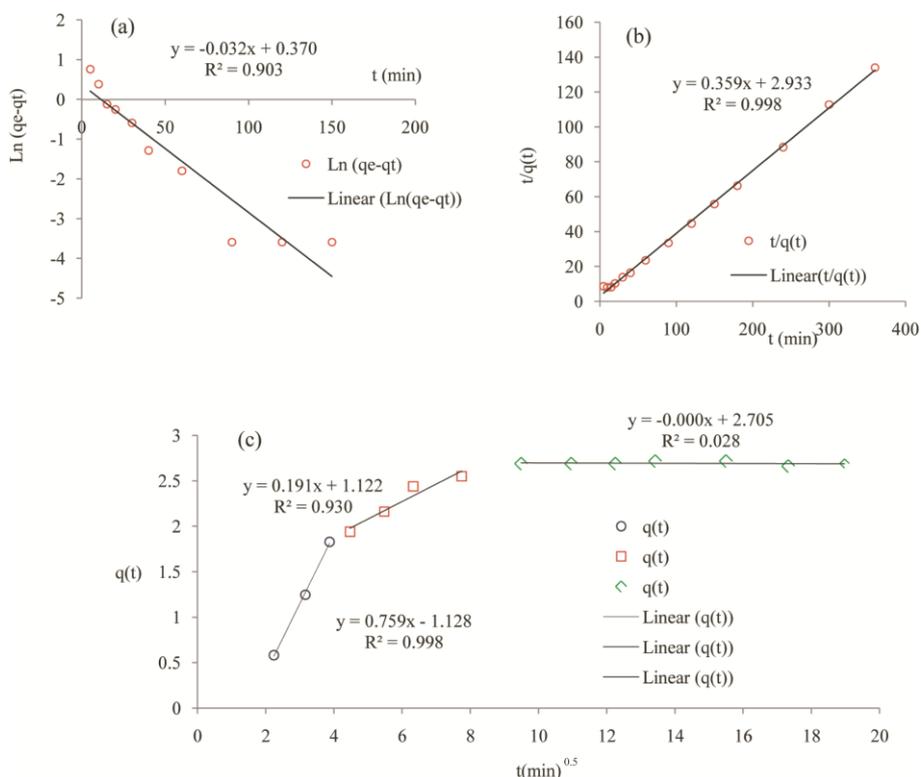
For practical point of view, regeneration or desorbs of target analytes from the sorbent materials make the sorption process more economical. According to the results, desorption were examined using acidic solution of HNO<sub>3</sub> at 3N. It was observed that the acidic solution can release more than 97% of the adsorbed RHB. Moreover, in order to evaluate the reusability of the modified microspheres, they were subjected to several cycle of extraction and re-extraction. The obtained results are represented in Figure 12. It was found that the prepared microspheres can be used for more than 9cycles. This confirms the good stability of the prepared sorbents.

#### 4.8. Comparison with literature

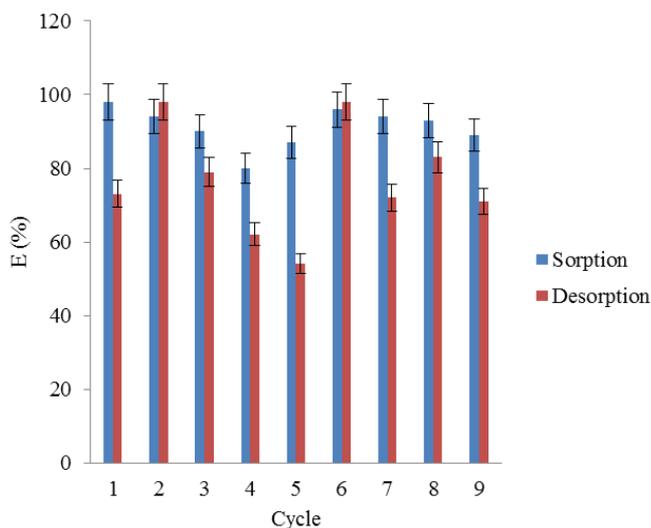
A comparative study for RHB adsorption using the PEEK-WC:DEHPA with a ratio of 1:1 tested in this study and others sorbents, which have been reported in the literature, is presented in Table 4. The prepared microspheres show fast adsorption rate and in particular, the microspheres (Type C) appear to be a promising sorbent for the removal of RHB from aqueous solution.

## 5. Conclusions

In this work, novel asymmetric polymeric microspheres were prepared by immersion -precipitation technique based on PEEK-WC doped with DEHPA and employed for Rhodamine B adsorption. The results indicate that polymeric microspheres based on PEEK-WC: DEHPA are a very promising adsorbents for the removal of RHB from aqueous solution in particular at the ratio 1:1 of PEEK-WC:DEHPA. The adsorption of RHB follows the pseudo-second order model with an intra-particle diffusion as one of the rate-limiting steps. The recycling ability of PEEK-WC: DEHPA microspheres and their stability can be presented as an interesting economically and environmentally sorbent for adsorption of Rhodamine B from aqueous solutions.



**Fig. 11.** Plots of pseudo-first order (a), pseudo-second order (b) and intra-particle (c) kinetics for adsorption of RHB onto the prepared microspheres. [RHB] = 10ppm, Q=0.145ml/s. MS C (1:1). D (column)=1cm. H=3.3cm. pH=4.56; pH=3.12.



**Fig. 12:** Adsorption and desorption efficiency by nitric acid of the adsorbed RHB. Q=0.145ml/s. [HNO<sub>3</sub>] = 3N; microspheres: C (1:1). D (column)=1cm. H=3.3cm. pH=4.56; pH=3.12 at T = 20 °C.

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