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Chromium (VI) adsorption by polymeric PEEK-WC/Aliquat-336 microspheres

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ABSTRACT

Phase inversion process has been successfully applied for polymeric microspheres preparation, based on the use of a modified polyether ether ketone (PEEK-WC) polymer doped with Aliquat-336. The modified microspheres were characterized by several techniques such as the Rheometer for measuring the viscosity of dope solution, scanning electron microscopy (SEM), for morphology analysis BET analysis and porometer for surface area and pore size determination. Meso-porous microspheres were obtained. They presented an asymmetric structure and a diameter of about 1.5 mm. The produced microspheres loaded in a column system have been successfully and efficiently used for chromium (VI) adsorption from aqueous solution.

Keywords: PEEK-WC; Aliquat-336; Phase inversion; Microspheres; Chromium(VI)

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1. Introduction

Microspheres (MS) are a solid material of micrometer/millimeter size, with large specific area and widely used in adsorption, biomedical treatment, instrument calibration, chromatography, molecular imprinted materials, biomedical drugs carrier and template for synthesis of porous materials [1–13]. As benefits, microspheres present bulk total surface area, large inner volume and spherical shape. For this reason, much more attention has been devoted to polymeric microspheres due to their widespread application in biomedical and biochemical field. However, microspheres for any application in metal ions separation, as an ion exchange adsorbent, lack of functional groups and needs to be functionalized with hydroxyl, amine, carboxyl and aldehyde using copolymerization and grafting method [2,14–19]. All over these techniques, phase inversion technique has been widely used for microspheres preparation and functionalization due to the simplicity of the process. To our knowledge, just few works have been done in functionalization of polymeric microspheres by phase inversion technique for chromium (VI) adsorption [20–23].

Chromium (VI) is a highly toxic element, which can affect human physiology, accumulate in food chains and cause intensive health problems ranging from simple skin irritation to lung cancer [24] and it can be widely used in various industries such metal plating, steel manufacturing and tanning leather [25]. Several techniques have been developed for the removal of Cr(VI) from aqueous solution including chemical precipitation, reverse osmosis, ion exchange, liquid/liquid membrane contractors, flotation and adsorption [26]. Precipitation and adsorption are the two commonly practiced non-membrane methods used for the removal of chromium (VI) using chelating agent and different adsorbents. Among many types of natural and synthetic adsorbents of Cr(VI), polymeric microspheres, have been studied as an alternative technology. Senar et al. [27] reported the adsorption of Cr(VI) by polysulfone

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microcapsules containing Cyanex-923 prepared by solvent evaporation. The produced microspheres were used more than three cycles and showed a high extractant selectively against various metals, including Cr(III), Ni(II), Pb(II), Cu(II) and Zn(II). The adsorption kinetics were well described by pseudo-second order model and the equilibrium well presented by Redlich-Peterson and Langmuir models. Ochoa et al. [28] investigated the extraction of Cr(VI) by polysulfone microspheres using Aliquat-336 as extractant prepared by phase inversion and emulsion cross-linking techniques. Yang et al. [29] reported in their work the preparation of polystyrene microcapsule containing Aliquat-336 using the solvent evaporation technique. The results showed the high separation factor of Cr(VI) /Cd(II) and Cr(VI) /Zn(II).

The present work deals with the adsorption of chromium (VI) by using the modified polyether ether ketone (PEEKWC) microspheres containing Aliquat-336. PEEKWC has been selected since it is a hydrophilic amorphous polymer presenting a high chemical, thermal and mechanical stability. Aliquat-336, a quaternary ammonium chloride, has been chosen as ions carrier, thanks to the chelating characteristics of its functional groups (quaternary ammonium) with the chromium mono-oxyanions in the pH range 4.5–6. The effect of different content of Aliquat-336 on microsphere properties (morphology, pore size, porosity, etc) and the adsorption capacity of chromium (VI) has been investigated.

2. Experimental

2.1. Chemical and reagents

Aliquat-336 (methyl trioctyl amine chloride) was supplied by Sigma-Aldrich. Dimethyl formamide (DMF) and ethanol were supplied by Pancreac (Italy) and dodecane from Carlo Erba. Potassium dichromate was purchased from Sigma-Aldrich (Italy). Sodium chloride (NaCl) and sodium oxide (NaOH) were purchased from Sigma-Aldrich (Italy).

As basic material, modified polyether ether ketone (PEEK-WC) (from institute of Applied Chemistry, CHANG CHUN, PR China) was used for microspheres preparation. Polyvinylpyrrolidone (PVP, Luviskol K17, BASF) was purchased by BASF (Germany) and desiccated under vacuum at 50°C overnight before using as pore former agent. All reagents were used without purification.

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, Aliquat-336 was added at different ratio (0, 0.5, 1, 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 (in volume) as shown in Fig. 1. 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

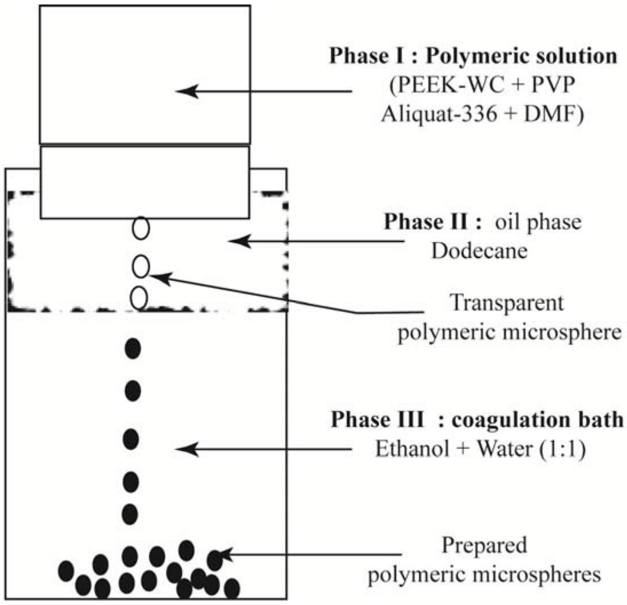

Fig. 1. Schematic representation of the microspheres process.

Table 1
Microspheres preparation conditions and viscosity measurements

Polymer	Additives	Type	Ratio PEEK-WC/Aliquat-336	Coagulation bath	Viscosity (cP)	(*)
PEEK-WC % (w/w)	PVP % (w/w)			Ethanol /water % (V/V)		
10	2	A	1/ 0	50/50	116.0	+
		B	1/0.5		101.5	+
		C	1/1		108.0	+
		D	1/1.5		96.0	+
		E	1/2		84.0	+
		F	1/3		40.3	-

(*): + : Formation of microspheres; – : No formation of microspheres employedis reported by Figoli et al. [30]. These droplets retained their spherical shape during the drop formation. Then, when in contact with the non-solvent (phase (III)), the polymer/DMF/Aliquat-336 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 Aliquat-336 from the surface. Microspheres were dried overnight at 50°C for further characterization.

2.3. Chromium (VI) extraction

In the column, 0.4 g of functionalized microspheres was packed into a column of 10 mm of diameter and 130 mm in height. A second column, having 20 mm diameter, was also used for studying the bed height effect on the extraction. The experiments for chromium(VI) adsorption by prepared microspheres were carried out by using 100 ml of the aqueous feed solutions containing 20, 50 and 100 ppm of Cr(VI) at pH = 4.5 with a flow rate of 0.6 ml/min were tested in re-circulating mode during 8 h in order to determine equilibrium time.

The adsorption capacity and the efficiency of extraction were calculated by the following equation:

$$Q\left(\frac{mg}{g}\right)=\frac{\left(C_0-C_e\right)\times V}{W} \tag{1}$$

$$E(\%)=\frac{C_0-C_t}{C_0}\times 100 \tag{2}$$

where Q is adsorption capacity (mg/g), (C_0) and (C_e) are the initial and the equilibrium concentration of metal ion (mg/l) respectively W, is the weight of the dried microspheres (g), (V) is the volume of the feed solution (l) and (C_t) is the chromium concentration in the aqueous solution at extraction time (t). The analysis of Chromium(VI) was carried out colorimetrically with 1.5 diphenylcarbazide method by using a UV-Visible spectrophotometer (Schimadzu UV-1700) at 540 nm.

For the stability and reusability of the produced microspheres, tests were performed in the column system in the same conditions as before. Three consecutive cycles were carried out where each cycle was performed as a single Cr(VI) extraction and re-extraction process. The stripping tests were performed with a solution of 0.1 M of NaOH and 1 M of NaCl. After each cycle, the system was washed with the distilled water, for 20 min, to remove the residual stripping solution.

3. Results and discussion

3.1. Microspheres formation

Functionalized polymeric PEEK-WC microspheres were successfully produced using immersion precipitation process, based on the exchange rate (DMF) between the solvent and the non-solvent (water/ethanol). In our system, the microsphere formation was strong dependent on the viscosity of the casting solution. The viscosities of the polymeric solution are shown in Table 1. The latter decreases drastically by increasing the Aliquat-336 content in the casting solution, from 116 cP to 40.3 cP, for the ratio (PEEK-WC/Aliquat-336) 1/0 (microspheres A) and 1/3 (microspheres F) respectively. As a result, the microsphere formation, with the lowest viscosity (40.3 cP), was not attainable. This could be explained by the excess of the Aliquat-336 which induced a reduction in viscosity and also did not allow to keep the spherical shape. The same results were reported by Lakshmi et al. [20] using ionic liquid as additive. The use of low polymeric solution viscosity makes the microspheres formation difficult.

3.2. Microspheres characterization

3.2.1. Microsphere size distribution

Size distribution of the PEEK-WC microspheres, without and with Aliquat-336, was calculated by measuring with a digital micrometer the diameter of 100 particles formed. The distribution of the diameter of the produced microspheres is represented in Fig. 2.

For the pristine polymer (without Aliquat-336), the diameter size is ranged from 0.78 mm to 1.38 mm with a maximum of particles number at 1.05 mm. The addition of Aliquat-336 brings to an increase of the diameter size distribution in the range from 0.9 mm to 1.8 mm with a maximum at 1.38 mm (Fig. 2). The presence of Aliquat-336 in the dope solution increases the microspheres diameter and it is in a complete agreement with SEM pictures (Fig. 3). However, the addition of Aliquat-336 at different ratio has a minor influence on particle size of the microspheres formed.

3.2.2. Microspheres morphology

PEEK-WC microspheres morphology was examined using scanning electron microscopy (SEM). From SEM pictures, as shown in Fig. 3, spherical microspheres with a small tail and irregular rough outer surface were obtained. All the microspheres, by analyzing their cross

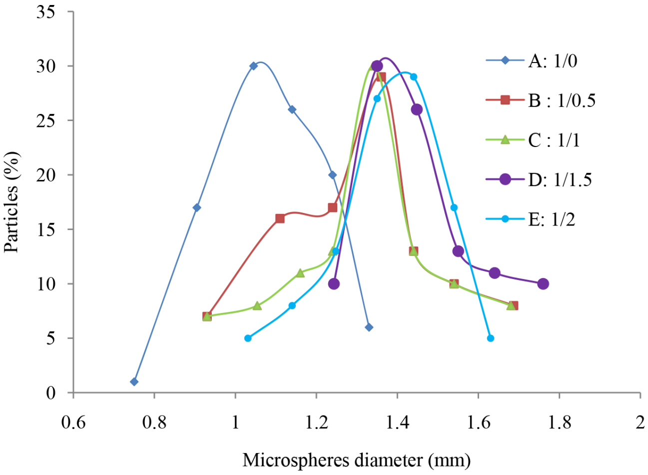

Fig. 2. Size distribution of PEEK-WC microsphere with and without Aliquat-336.

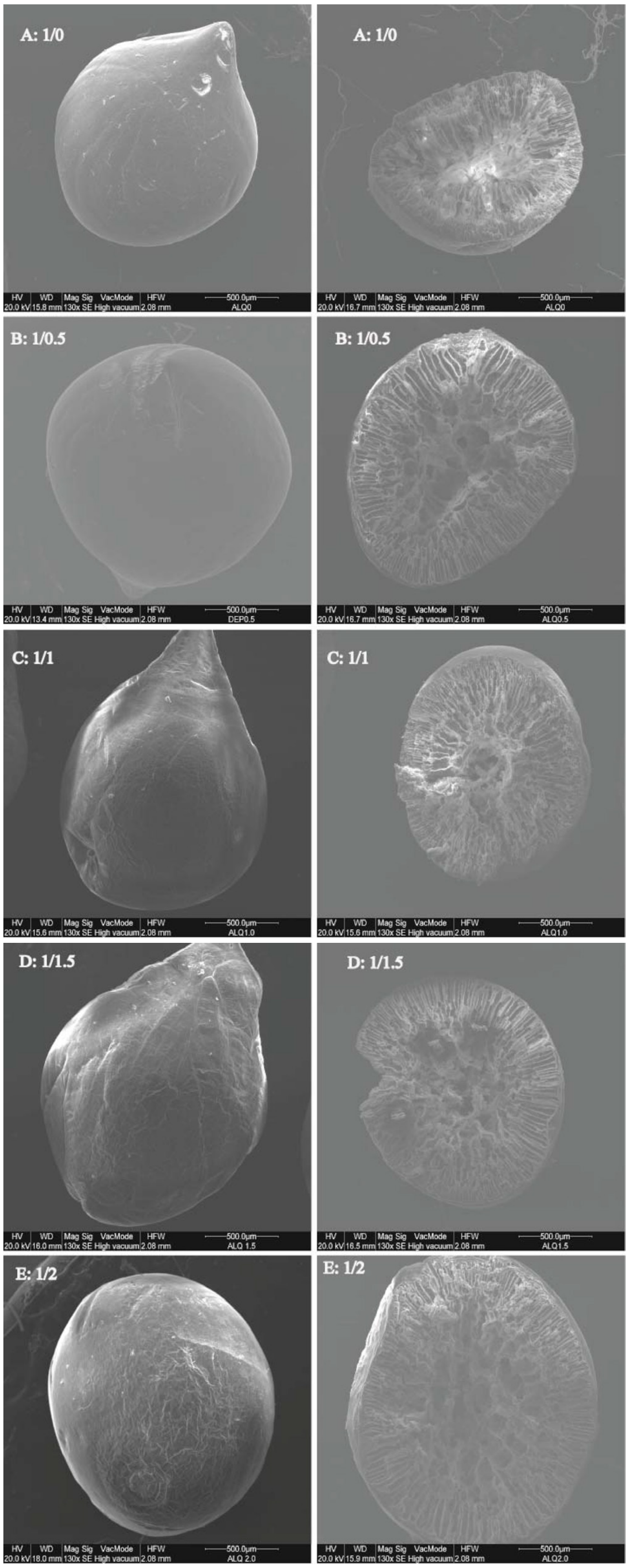

Fig. 3. SEM micrographs of PEEK-WCwith and without Aliquat-336.

section, present an asymmetric structure characterized by a micro-porous 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 content of Aliquat-336 has a minor effect on the morphology of the microspheres.

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 [25]. In our case, the dispersion of Aliquat-336 affects drastically the specific surface. In fact, the BET surface area of the microspheres decreases from 9.709 m^2/g to 1.796 m^2/g without and with Aliquat-336 (1/3), respectively. For the microspheres containing Aliquat-336, the specific surface increases at higher content of Aliquat-336, from 2.618 m^2/g to 12.27 m^2/g, for the microspheres B(1/0.5) and D (1/1.5), respectively. This is followed by a decrease in specific surface of the microspheres due to the excess of Aliquat-336 which occupied the free volume of the microspheres.

According to BJH results, the average pores surface areas varies from 6.45 m^2/g to 1.75 m^2/g without and with Aliquat-336 (1/3) and the pore size is in the nanometer scale. Thus, it seems that the prepared microspheres have a mesoporous structure [25].

3.2.4. Thermal analysis

The microspheres decomposition patterns show generally two distinct weight losses except for the virgin polymer where simple stage degradation was observed at 400°C, as shown in the Fig. 4. For the microspheres B(1/0.5), it is observed a 11% decrease in mass between 200°C and 290°C and a 40% decrease between 370°C and 600°C. For the microspheres C (1/1), it can be observed a 10% decrease in mass between 180°C and 300°C and a 28% decrease between 360°C and 600°C.

The decomposition patterns for the microspheres D (1/1.5) and E(1/2) resemble each other compared to the

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

Type	Microspheres	BET Surface Area (m^2/g)	BJH desorption analysis	
			Total pores surface area (m^2/g)	Pores radius (Å)
A	1/0	9.71	6.45	15.70
B	1/0.5	2.62	1.39	45.30
C	1/1	2.85	1.09	35.32
D	1/1.5	12.27	7.69	17.97
E	1/2	4.83	3.02	20.70
F	1/3	1.80	1.75	17.50

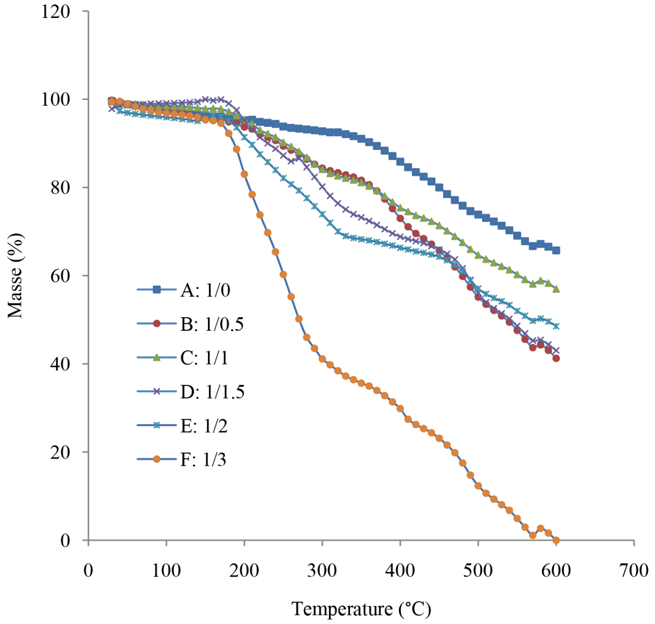

Fig. 4. PEEK-WC/Aliquat-336 TGA plots for different microspheres.

other microspheres. Between 180°C and 320°C, a 25% decrease in mass and a 20% decrease between 460°C and 600°C can be observed too. In fact, the first stage degradation can be attributed to the degradation of Aliquat-336 (boiling point 200°C) and the second between 400°C and 600°C to the decomposition of the polymeric backbone (Fig. 4).

Lakshmi et al. [20] obtained similar curves, but with three distinct weight losses, the first one corresponding to the decomposition of the adsorbed ionic liquid and the other two ones due to the decomposition of the polymeric backbone.

3.3. Column tests for Chromium (VI) adsorption

Chromium was used as an example to preliminary adsorption abilities of the microspheres. For column tests, all the modified microspheres were tested. Fig. 5. shows the obtained results. It can be observed that the adsorption efficiency of Cr(VI) of the produced microspheres increased by increasing the Aliquat-336 content in the microspheres. The minimum is around 20 % obtained with the microspheres B (1/0.5) and a maximum around 75% for the microspheres E (1/2). The results prove that the increase content of Aliquat-336 is an important factor for improving the Cr(VI) adsorption.

Fig. 6 shows that the final adsorption capacity varied with the amount of Aliquat-336 added during the microspheres preparation. The presence of Aliquat-336 caused the adsorption by the presence of the quaternary ammonium groups responsible of the adsorption of Cr(VI). With the increase in microspheres the Aliquat-336 content, the number of the quaternary ammonium groups increased, which enhanced the adsorption capacity and varied from 0.03 mg/g to 22.5 mg/g for the ratios PEEK-WC/Aliquat-336 1/0.5 (microspheres B) and 1/2 (microspheres E) respectively (Fig. 6).

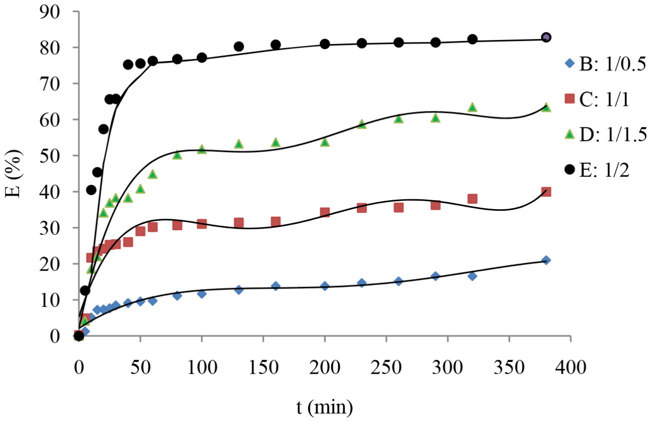

Fig. 5. Cr(VI) recovery (E (%)) vs. time for the prepared microspheres. [Cr(VI)] = 100 ppm; column diameter = 1 cm; bed height = 4.5 cm; Feed solution flow= 0.6 ml/min.

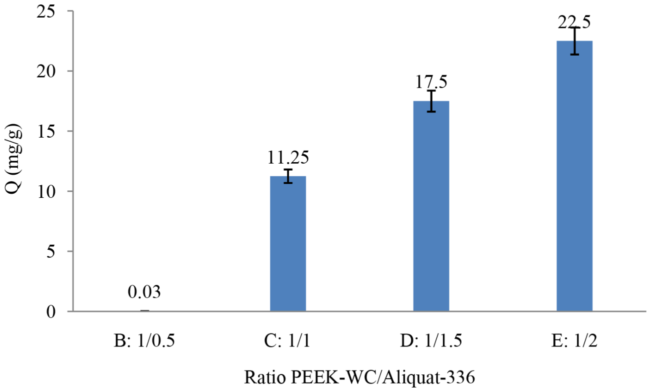

Fig. 6. Adsorption capacity of the modified microspheres. [Cr(VI)] = 100 ppm; column diameter = 1 cm; bed height = 4.5 cm; Feed solution flow= 0.6 ml/min.

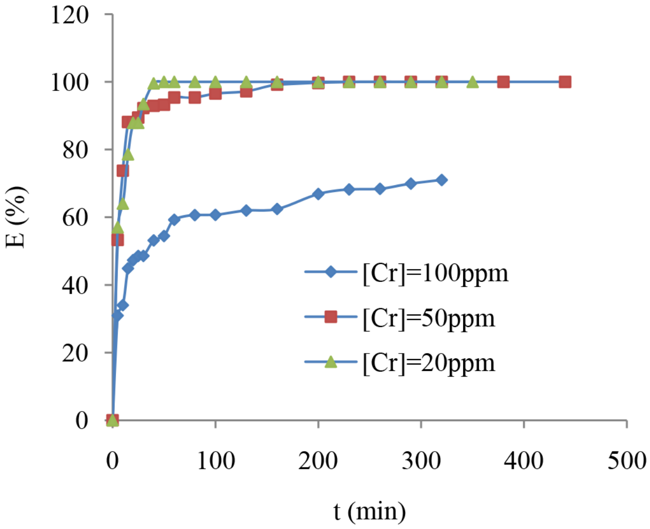

Fig. 7. Effect of the initial Cr(VI) on recovery (E (%)) for the prepared microspheres. [Cr(VI)] = 20, 50 and 100 ppm; PEEK-WC/Aliquat-336 (microspheres D):1/1.5; column diameter = 1 cm; bed height = 4.5 cm; Feed solution flow= 0.6 ml/min.

It can be noticed that at low concentration of Cr(VI) in aqueous solution, 20 ppm and 50 ppm, using the microspheres PEEK-WC/Aliquat-336 1/1.5 (microspheres D) the capacity was higher and the efficiency could reach 100%, as demonstrated in Fig. 7.

By varying the column diameter, the capacity of adsorption was influenced too, as shown in. Fig. 8. This could be explained by the contact time of Cr(VI) ions with the microspheres. For the same quantity of the microspheres (0.4 g), by using a larger column (2 cm in diameter), the height bed was around 2.5 cm, less higher than the first column, not enough for the chromium ions to be in contact for longer time with quaternary ammonium groups (Fig. 8) inducing the decrease of the efficiency of the extraction. It has been also noticed that at a lower initial concentration (20 and 50 ppm) of chromium (VI) no effect of the bed height was observed.

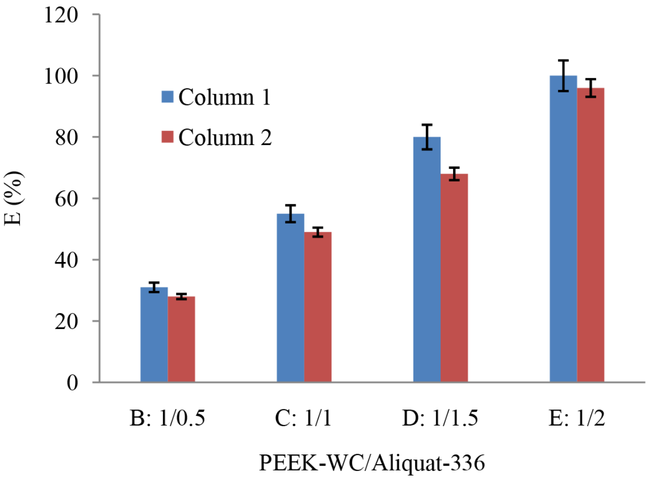

Fig. 8. Effect of the column diameter the extraction of Cr(/VI) for the prepared microspheres. [Cr(VI)] = 100 ppm; column1 diameter = 1 cm; bed height = 4.5 cm; column2 diameter = 2 cm; bed height = 2.5 cm; Feed solution flow= 0.6 ml/min.

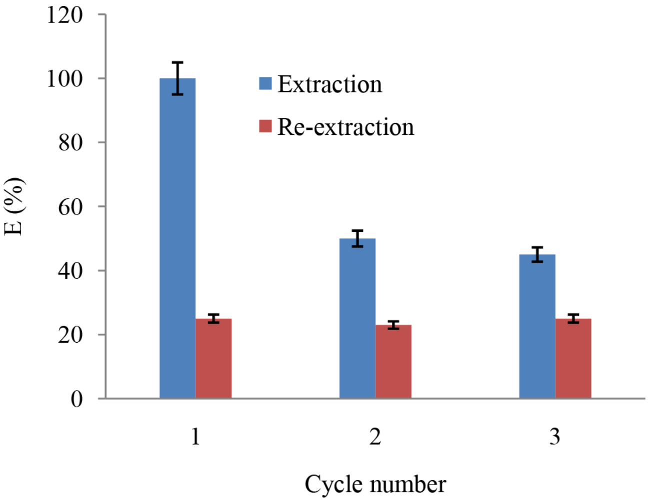

Fig. 9. Adsorption-desorption values of Cr(VI) ions with the prepared microspheres. [Cr(VI)] = 100 ppm; PEEK-WC/ALIQUAT-336(Microspheres D): 1/1.5; column1 diameter = 1 cm; bed height = 2.5 cm; Feed solution flow= 0.6 ml/min.

Table 3
Comparison of adsorption capacities of PEEK-WC/Aliquat-336 microspheres and other adsorbents for adsorption of Cr(VI)

Adsorbent	*Q* (mg/g)	Reference
Mesoporous NiO nano particles	4.73	[25]
Ethylenediamine modified chitosane microsphere	28.81	[30]
Ehtylenediamine modified crosslinkedmagnétiquechitosane resin	51.8	[31]
Chitosane modified with cellulose	13.8	[32]
Chitosane modified with PVA	12.4	[33]
Fe-Montmorillonite	13.48	[34]
Montmorillonite support magnetique	13.88	[35]
Chitosanemontmorillonite	9.36	[36]
PEGMA-co-VI microspheres	8	[37]
PEEK-WC/Aliquat-336 microspheres	22.5	This study

3.4. Desorption and reusability of the produced microspheres

From a practical point of view, the regeneration of the sorbent materials from the target is an important step to be evaluated. In this study, desorption tests were performed with a solution of 0.1 M NaOH and 1 M NaCl.The results indicate that the Cr(VI) extraction performance decrease after each cycle as shown in Fig. 9 and that the microspheres could not be regenerate completely. This could be explained by the microspheres structure and the stability of the complex formed between Aliquat-336 and chromium (VI).

4. Comparison with adsorbents reported in literature

In Table 3, a comparison of the results obtained in the present study for Cr(VI) adsorption with the ones reported in the literature [25,31–38] is reported. As it can be seen, the produced microspheres are promising adsorbents for Cr(VI) from aqueous solution. In fact, the results show the very interesting performance of the prepared adsorbents with respect to the adsorption capacity (*Q*, mg/g) and also rapidness. Moreover, the new adsorbents present also a rapid and efficient adsorption.

5. Conclusion

Asymmetric polymeric microspheres based on PEEK-WC containing Aliquat-336 in different concentrations were successfully prepared by phase inversion and applied for Cr(VI) adsorption. Asymmetric structures were obtained with mesopores for the different content in the dope polymeric solution except for the ratio 1/3 where the viscosity was too low (40 cP) for inducing the formation of the microspheres. The highest extraction Cr(VI) efficiency was obtained with the microspheres PEEK-WC/Aliquat-336 (1/1.5 ; 1/2),reaching 100% for the concentration of Cr(VI) below 50 ppm. However, the adsorption capacity of the modified microspheres depended on the initial concentration of Cr(VI) and the highest capacity was obtained for the ratio 1/2 (PEEK-WC/Aliquat-336). The results show as the PEEKWC-ALIQUAT-336 microspheres could be successfully applied as alternative adsorption material in Cr(VI) removal from aqueous solutions.

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