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Preparation and characterization of PVC/Aliqat-336 microspheres for chromium (VI) removal

L. Ouazine, S. Bey, M. Benamor

Laboratory of Membrane Processes and Techniques of Separation and Recovery, Faculty of Technology, Bejaia University, Bejaia 06000, Algeria.

Corresponding author: saidbey06@yahoo.com; said.bey@univ-bejaia.dz; Tel/Fax: +213 34 81 37 27

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ABSTRACT/RESUME

Abstract: *PVC microspheres included with Aliquat-336 as extractant were prepared by phase inversion method. Theirs morphology and structure was determined by scanning electronic microscopy (SEM) and BET analysis. SEM images show an asymmetric structure and different morphologies, obtained by varying the concentration of the polymer. The prepared microspheres were used as adsorbent to the removal of Cr(VI) from an aqueous solution. Various parameters were studied like, the extractant dosage, the microspheres dosage, the agitation speed and the aqueous solution pH. The prepared microspheres were able to remove chromium from aqueous solution and had a maximum adsorption capacity* q_m *more than 35mg/g.*

I. Introduction

Chromium, a highly toxic element, widely used in several industries must be removed from wastewater before their disposal to natural aquatic environment. For that purpose, several techniques were used for Cr(VI) removal such as reduction-precipitation [1,2,3], solvent extraction [4-6], membrane technologies [7,8,9-13], and electrochemical techniques [14] were described in the literature. However, the adsorption seems to be the most efficient techniques in separation, concentration and removal of chromium. Several adsorbents have been studied for chromium removal from aqueous solutions, including activated carbon [15,16], activated alumina [17], metal oxide [18-20], bimetallic nanocomposites [21], Layered double hydroxide [22], zeolite [23], biomass [24-29], chitosane [30,31], silica gel [32,33], and ions exchanger resins [34-38]. Recently, a new adsorbent constitute of a polymer matrix and an active material, microsphere or microcapsule, gained a great interest in the research of removal of chromium ions [39-50]. Microspheres can be presented as an alternative technology as a new class of adsorbent which can be prepared with a wide range of polymers and various technique.

Several studies were done to extract chromium (VI) from aqueous solutions using microspheres. Polysulfone (PSF) microspheres prepared by phase inversion method using polyvinylpyrrolidone (PVP) as additive and silicone microspheres prepared by cross-linking in emulsion were studied by N.A. Ochoa et al. [44]. They analyzed their Cr(VI) extraction capacity after their impregnation with Aliquat-336. They found that for a 80 ml solution of 40 ppm the highest extractive performance of Cr(VI) was obtained from 0.3 g microspheres of PSf–PVP (2:1) (98% of extraction at 90 min) and 0.3 g silicone MS (92% of extraction at 90 min). C.O. Illanes et al. [41] studied the kinetics of Cr(VI) adsorption by polysulfone (PSF) and poly(styrene-acrylenitrile) (SAN) microspheres prepared by phase inversion method and impregnated with Aliquat-336. They found Crank model is more realistic and appropriate to describe Cr(VI) kinetic adsorption results. With Crank model, they concluded that there is a surface diffusion contribution to the overall Cr(VI) mass transport inside the microspheres which becomes more important when the microspheres pore size decreases. The removal of Cr(VI) from acidic aqueous solutions using microcapsules with polymeric matrix of ST-EGDMA and a quaternary ammonium salt as the extractant was studied by G. Barassi et al. [40]. The microcapsules were synthesized by adding the extractant Aliquat-336 during the in situ radical copolymerization of the monomers styrene (ST) and ethylene glycol dimethacrylate (EGDMA). They found that, the adsorption kinetic carried out at different temperatures fits well the pseudo-second-order model with an activation energy of 82.7 kJ mol^{-1}, confirming that the sorption process is controlled by a chemisorption mechanism. The Langmuir's isotherms describe well the adsorption. Finally, from the thermodynamics analysis, they concluded that the chemisorption process is spontaneous and exothermic. S. Ozcan et al. [42] focused their studies on the removal of Cr(VI) from aqueous solution in batch system by using polysulfone microcapsules containing Cyanex 923 as extraction reagent. The microcapsules were prepared by solvent evaporation method. Their results showed that maximum removal of Cr(VI) was obtained by microspheres with Cyanex 923/polysulfone ratio of 1/1. The complex formation between Cr(VI) and Cyanex 923 favoured at initial pH of 1.0. The kinetic adsorption data fits the pseudo second-order kinetic model and the equilibrium time was 30 min. The Redlich Peterson and Langmuir isotherm models describe well the adsorption isotherm data. The Langmuir sorption capacity was 0.430 mmol.g^{-1}. The microspheres preferably adsorbed Cr(VI) against various metal ions, including Cr(III), Ni(II), Pb(II), Cu(II), Zn(II), Cd(II), Co(II). Cellulose microsphere (CMS) adsorbent prepared by radiation-induced grafting of dimethylaminoethyl methacrylate (DMAEMA) onto CMS followed by a protonation process was studied by C. Li et al. [45]. They reported that the adsorption of Cr(VI) onto the resulting adsorbent was very fast; the equilibrium adsorption could be achieved within 15 min. The pH affect strongly the adsorption capacity. A maximum Cr(VI) adsorption (78 mg/g) was obtained at the pH ranging 3.0 to 6.0. The adsorption isotherm data fits the Langmuir isotherm model. Y. Zhang et al. [46] studied the adsorption of Cr(VI) by cellulose microspheres prepared by radiation-induced grafting of styrene onto their surface, followed by acetylation and amination processes. The results showed that adsorption equilibrium could be achieved within 30 min for initial Cr(VI) of 100 mg L^{-1}. The adsorption kinetics was well described by the pseudo-second order model equation, and the adsorption isotherm was better fitted by the Langmuir mode. The maximum theoretical Cr(VI) adsorption capacity was 123.4 mg/g. P. Li et al. [48] prepared polyglycidylmethacrylate (PGMA) microspheres by a dispersion polymerization method and modified by ring-opening reaction to introduce functional hydroxyl groups. Amino groups were grafted to (PGMA) microspheres by cerium initiated surface graft polymerization method and ring-open reaction. They reported that the adsorption of Cr(VI) present a high adsorption capacity (500 mg·g-1).The adsorption isotherm was well fitted with Langmuir isotherm model, and the adsorption process was endothermic and entropy favored in nature. The removal efficiency was optimal at pH1.5. Magnetic poly-(methacrylate-divinyl benzene) microspheres with micron size synthesized by modified suspension polymerization method and surface modified with amino groups were studied by Wang et al. [49]. The adsorption of Cr(VI) from aqueous solution by the prepared magnetic poly-(MA-DVB) microspheres show that the optimum pH was 3, the contact time was 60 min, and the adsorption capacity increased with increasing temperature. C. Hua et al. [50] studied the adsorption of Cr(VI) by quaternized chitosan microspheres (QCMS) prepared by emulsification solvent extraction method. They concluded that the equilibrium Cr(VI) adsorption capacity achieved within 50 minutes at optimal pH 5. The adsorption kinetics was fitted with pseudo second order model, the adsorption isotherm fitted with Langmuir isotherm model and the adsorption thermodynamic was an endothermic and a spontaneous process. Adsorption of Cr(VI) with mesoporous carbon microspheres prepared by a simple and scalable spray drying method was studied by J. Zhou et al. [47]. They found that at pH 3 maximum adsorption capacity is reached (122 mg/g). Adsorption kinetics for Cr(VI) is well fitted by pseudo-second-order kinetic model. The Langmuir isotherm model gives the best fit to equilibrium experimental data (q_m=165.3 mg/g).

The present work focuses on the preparation and characterization of polymeric microspheres based on PVC, by immersion-precipitation technique, doped with Aliquat-336 and applied for Cr(VI) removal from aqueous solution.

II. Experimental procedures

II.1. Reagents and solutions

Polyvinylchloride (PVC) was purchased from PVC Solvin and used as polymer matrix. Aliquat-336 was purchased from ALDRICH and used as extractant. Dimethylformamide (DMF), supplied by ALDRICH was used as solvent. Sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), potassium chromate (K_2CrO_4) and diphynile carbazide (DPC) were all analytical grade reagents.

The initial pH of all these aqueous phases was adjusted, with a sulfuric acid solution and measured with a pH meter (InoLab® pH 720).

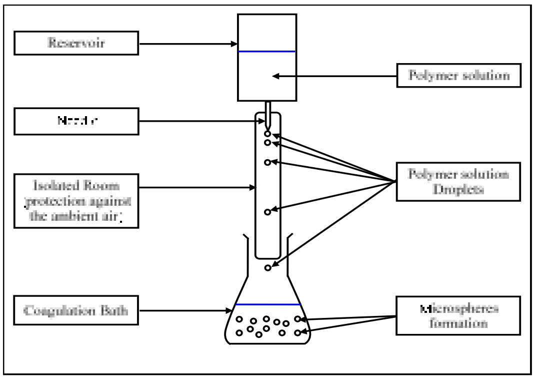

Figure 1. *Schematic representation of microspheres setup preparation.*

Table 1. *polymeric microspheres preparation conditions.*

Microsphere	DMF (%w)	PVC (%w)	Ratio Aliquat-336/PVC (w/w)
MS1	94	6	1/1
MS2	90	10	1/1
MS3	86	14	1/1

II.2. Preparation and characterization of microspheres

The microspheres were prepared by immersion-precipitation technique by dissolving poly(vinyl chloride) (PVC) at 6, 10 and 14 % (w/w) in dimethylformamide (DMF). The prepared solutions were maintained under magnetic agitation during 48 hours for a complete dissolution of polymer. Then, quantities of Aliquat-336 equals to that of PVC were added to the solutions previously prepared to have a PVC/Aliquat-336 ratio equal to 1/1. Agitation was continued during 2h. Finally, the solutions were added drop-wise to a bath containing a non-solvent (figure 1). The non-solvent was distilled water at 25°C. Table (1) summarizes the different solutions used to prepare the different microspheres and their attributed names. After the last drop of polymer solution added, the microspheres were collected and transferred to another bath containing distilled water and kept for a day. Then, the microspheres were washed with distilled water and dried in an oven at 40°C temperature overnight.

The microspheres were observed by scanning electron microscopy (SEM) in a FEI QUANTA 200 apparatus, for the section the microsphere was frozen and fractured in nitrogen liquid. The pore diameter, the void fraction, and the surface area were determined by BET surface area analyzer with a Quantachrome NovaWin2 porosimeter.

II.3. Extraction of Cr(VI) by prepared microspheres

The dried microspheres were used for chromium (VI) adsorption from aqueous solutions, in batch system, using a double wall cell at a well known initial concentration, pH and magnetic agitation speed. For chromium analysis, samples of microliters were diluted by distilled water in 25 ml flasks containing 1 ml of diphenylcabazide solution (DPC) in acetone (0.5 g/100ml) and 0.5 ml of sulfuric acid (5N) and analyzed with UV-Vis spectrophotometer (SCHIMADZU 2101 PC) at 442 nm. Several parameter were investigated such as content of microspheres, initial pH and Cr(VI) concentration and the temperature of the feed soution. The efficiency of adsorption was defined by the following parameters:

The extraction efficiency E (%):

$$E = \left(\frac{C_0 - C_e}{C_0}\right) * 100 \qquad (1)$$

The amount of Cr(VI) adsorbed at any time t, q_t (mg/g):

$$q_t = \frac{(C_0 - C_t) * V}{m_1} \qquad (2)$$

The amount of Cr(VI) adsorbed at equilibrium q_e (mg/g):

$$q_e = \frac{(C_0 - C_e) * V}{m_1} \qquad (3)$$

The microsphere loss of Aliquat-336 L (%):

$$L = \frac{(m_1 - (m_2 - m_{CrO4} + m_{c1}))}{m_1} * 100 \qquad (4)$$

Where:

m_1 : The microspheres weight before extraction (g);
m_2 : The microspheres weight after extraction (g);
m_{CrO4} : The weight of chromate adsorbed (g);
m_{Cl} : The weight of chloride desorbed (g);
C_0 : The Cr(VI) initial concentration (mg/l);
C_t : The Cr(VI) concentration at the time t (mg/l).
C_e : The Cr(VI) concentration at equilibrium (mg/l).

III. Results and discussion

III.1. SEM analysis

Figure 2 shows the SEM images of the microspheres prepared by immersion-precipitation technique. Asymmetric spherical microspheres were obtained. The concentration of polymeric solution affects the external morphology of the microspheres. In fact, the roughness of the surface decreases with the increase of polymer solution concentration. The cross section of the microspheres figure (3), show an asymmetrical structure made of a macro-porous internal layer with the presence of macro-void and a thin macro-porous surface layer.

The increase of polymer solution concentration lead to regular macro-pores directed from the surface to the center of microsphere. With the increase of polymer concentration, the precipitation of PVC will occur more easily and the droplets of polymer-poor phase growth by coarsening decrease, so no large macro-void will form.

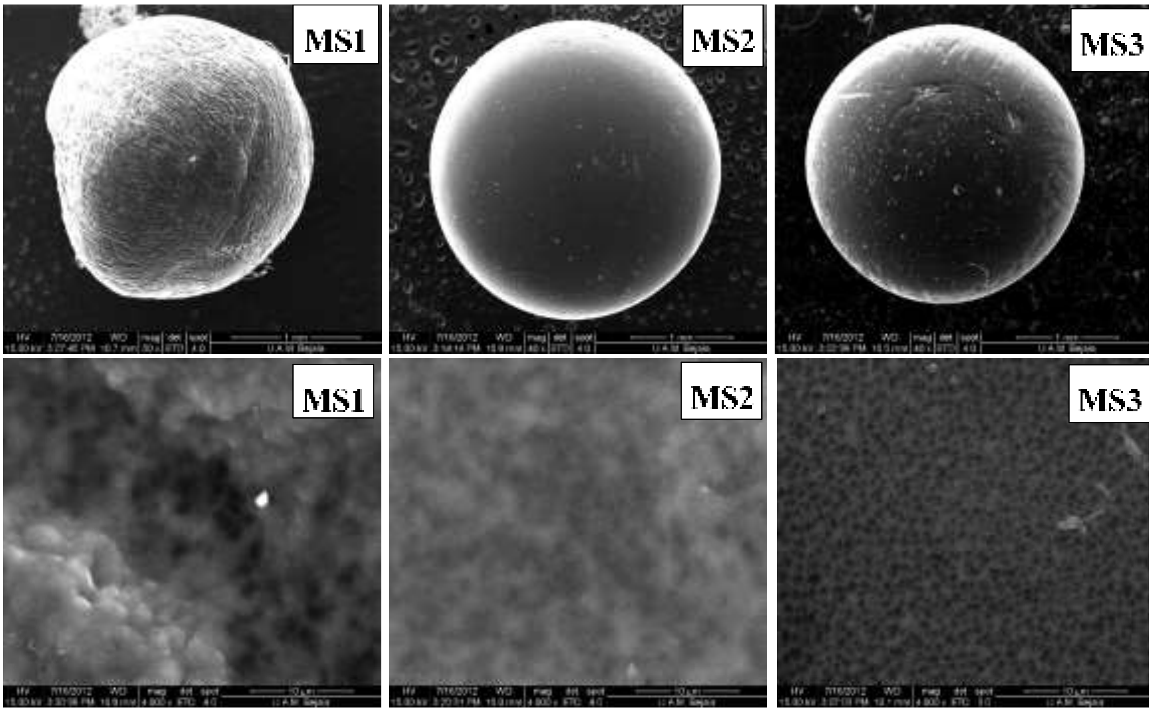

Figure 2. *SEM images of different microspheres surfaces and their magnification*

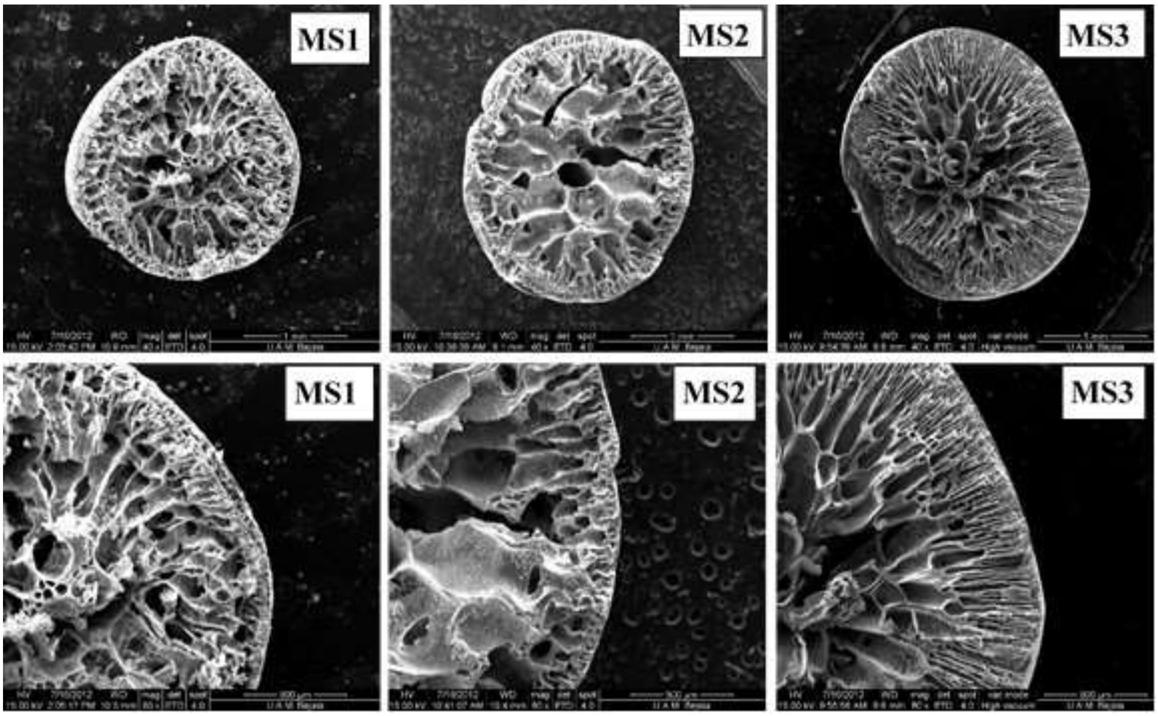

Figure 3. *SEM images of the different microspheres cross-sections*

III.2. Porosity and diameter of microspheres

The average diameter and apparent density of microspheres were determined by measuring a diameter of known number of microspheres, with a FOJU micrometer and taking the average value, and their weights. The apparent density and porosity of microspheres was calculated, considering a perfect spherical shape of microspheres, by following equations:

$$\boldsymbol{\rho_{app}} = \frac{\mathbf{m_n}}{\mathbf{n}.\frac{4}{3}.\boldsymbol{\pi}.\mathbf{r_{avr}^3}} \qquad (5)$$

$$\varepsilon(\%) = \left(1 - \frac{\rho_{app}}{\rho_p}\right) * 100 \qquad (6)$$

Where n, m_n (g), r_{avr} (cm), ρ_{app} (g/cm^3), ε(%) and ρ_p are the number of microspheres, the weight of the n microspheres, the average diameter of the n microspheres, the apparent density, the porosity of microspheres and the density of the polymer respectively.

Table 2 summarizes the results of the different measurement. The microspheres diameter have a high value (around 2.5mm) due to the high diameter of the droplets formed at the end of the module and the instantaneous formation of the skin top layer due to the direct contact with the non-solvent. This could be explained by the system used in this study where the droplet in direct contact with air inducing the enlargement of this latter and formation of microsphere of large diameter. The microspheres had a high porosity (great than 70%) because of the presence of micro-void as can be seen in the SEM pictures. The high porosity of microsphere leads to a low apparent density less than 0.32 g/cm^3. The increase of polymer concentration decrease microsphere porosity from 82.85 to 73.48 %.

Table 2. *Microspheres average diameter, apparent density and porosity*

	Microspheres average diameter (mm)	**Microsphere density (g/cm^3)**	**Microsphere Porosity (%)**
MS 1	2.074	0.2011	82.85
MS 2	2.533	0.2268	80.66
MS 3	2.655	0.3111	73.48

III.3. BET surface area analyses

The microspheres have a small specific surface area and pores volume as shown in table 3. The increase of polymer solution concentration from 6 to 14%, decrease the surface area and the pore volume slightly from 3.561 to 1.857 m^2/g and 0.006991 to 0.00362 cm^3/g respectively. This could be explained by the excess of Aliquat-336 inducing the decrease in the viscosity of the polymeric solution. As a result, the casting solution cannot retain the spherical shape.

Table 3. *Specific surface area and total pores volume of the different microspheres.*

	BET Surface (m^2/g)	**BJH Surface (m^2/g)**	**Total volume of pores (cm^3/g)**
MS1	3.561	2.954	0.006991
MS2	3.431	2.895	0.00594
MS3	1.857	1.028	0.00362

B.J.H: Harett–Joyner–Halenda;

III.4. Adsorption of hexavalent chromium by microspheres

III.4.1. Effect of Aliquat-336 dosage

Figure 4 shows the effect of the Aliquat-336 content in polymeric solution, on the amount of chromium(VI) adsorbed. We notice that for the ratio higher than 1 the droplets of polymeric solution were not formed correctly which can be explained by the excess of Aliquat-336 affecting the formation of microspheres. In fact, the droplet cannot retain the spherical shape induced by a very low viscosity.

The adsorption capacity was zero when no extractant was included in the microspheres. The adsorption started with the addition of extractant and increases with the increase of extractant amount added. Thus, no physisorption is produced and adsorption is controlled only by chemisorption with the formation of the Aliquat-336_Chromates complex according to the following mechanism [11,34]:

$$(R_3(CH_3)N^+Cl^-)_{org} + HCrO_4^- \rightleftharpoons [(R_3(CH_3)N^+)HCrO_4^-]_{org} + Cl^- \quad (\mathbf{1})$$

$$\mathbf{2}(R_3(CH_3)N^+Cl^-)_{org} + CrO_4^{2-} \rightleftharpoons [(\mathbf{R_3(CH_3)N^+})_\mathbf{2}CrO_4^{2-}]_{org} + 2Cl^- \quad (\mathbf{2})$$

As the extractant concentration, increased up to about 0.6 g/g Aliquat-336/PVC ratio the adsorption capacity increases slightly, because of the low extractant content in microspheres. Indeed, the extractant diffuses into the coagulation bath during the formation of the microspheres thus a small amount of extractant remain included in the microspheres after their formations. A further increase in the extractant concentration above 0.6 g/g Aliquat-336/PVC ratio, increase exponentially adsorption capacity. This is due to the increases of the extractant content in the microspheres, thus in spite of the diffusion of extractant into the coagulation bath a significant amount of extractant remains included in the microspheres after their formation. For the farther works, an Aliquat-336/PVC ratio of 1 g/g was chosen to prepare the different microspheres.

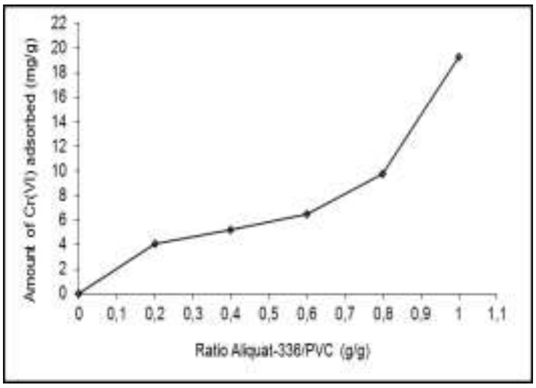

Figure 4. *Effect of microspheres MS1 content of extractant on Cr(VI) adsorption (C_0 : 60 mg/l, pH: 7.4, agitation speed: 300 rpm, PVC concentration on polymer solution 6 wt%, contact time: 48h and microspheres dose=1g/L).*

III.4.2. Effect of microspheres dosage and polymer concentration

The removal of chromium(VI) by the different microspheres at different adsorbent doses (0.5, 1, 1.5, 2 and 2.5 g/L) for the chromium(VI) concentration of 60 mg/L was studied.

Figure 5-a shows the effect of adsorbent dose on adsorption efficiency of Cr(VI). The figure reveals that adsorption efficiency of Cr(VI) increases rapidly with increasing microspheres dosage from 0.5 to 2.5 g/l, due to adsorption sites with increase in adsorbent dose [34,37,38]. The results in figure 5-b show that the amount of Cr(VI) adsorbed decreased slightly with increase of the microspheres dose. This can be attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process; whereas the number of available adsorption sites increases by an increase in adsorbent and this results in an increase in removal efficiency [34,37,38]. In the subsequent studies, the microspheres dose will be fixed at 0.5 g/l.

The figure 5 reveals also that MS2, prepared with a solution of 10 wt% of PVC concentration, is more efficient then MS1 and MS3, prepared respectively with a solutions of 6 and 14 wt% of PVC concentration which can be explained by the low porosity and specific surface in the case of microspheres MS3 and to low active sites (extractant content in microspheres) in the case of microspheres MS1 compared to microspheres MS2.

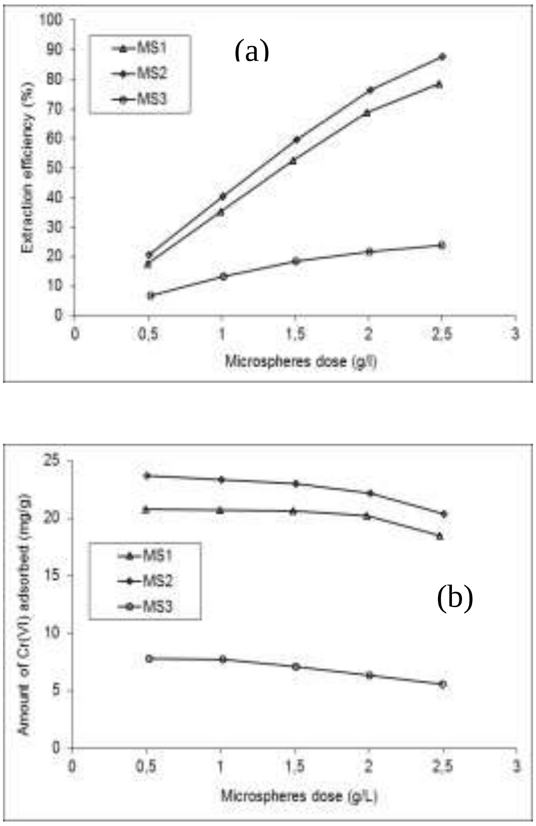

Figure 5. *Effect of adsorbent dose on Cr(VI) adsorption efficiency (a) and adsorption amount (b) (C_0 : 60 mg/l, pH: 7.4, agitation speed: 300 rpm and contact time: 48h).*

III.4.3. Effect of agitation speed

Agitation speed is an important parameter in sorption phenomena, which has a serious action on the distribution of the solute in the bulk solution and the formation of the external boundary film. The effect of agitation on the uptake of Cr(VI) by the different microspheres was studied at different agitation speeds (200-600 rpm). From figure 6 it can be observed that the increase of agitation speed from 200 to 300 rpm significantly increases the adsorption capacity of Cr(VI) because of best dispersion of microsphere in the aqueous solution and reduction of the diffusion film. The microspheres had a small density below 0.32 kg/l and were hydrophobic so they float on the surface of the aqueous solution at low agitations speeds. Above agitation speed of 300 rpm the adsorption capacity increases slightly because of the increase of the microspheres loss of Aliquat-336 as can be seen on the figure 7 . For the further studies, we chose an agitation speed of 300 rpm.

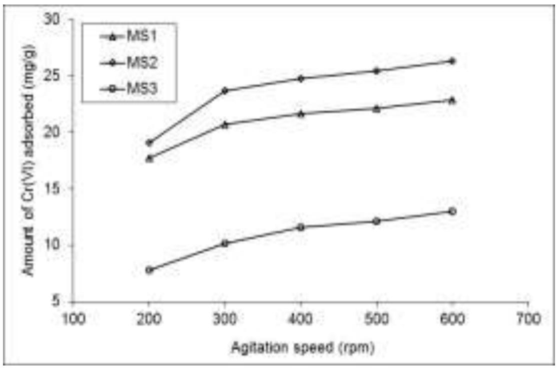

Figure 6. *Effect of agitation speed on the adsorption capacity of Cr(VI) by the different microspheres (C_0 : 60 mg/l, pH: 7.4, microspheres dose: 0.5 g/l and contact time: 48h).*

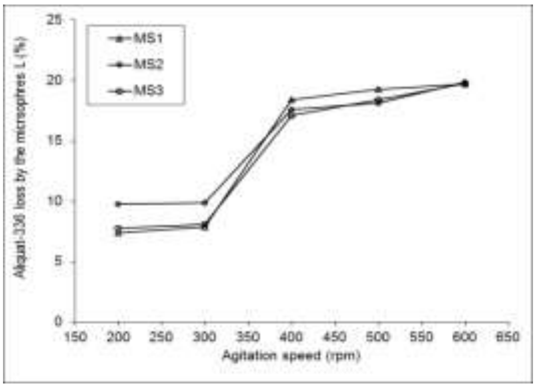

Figure 7. *Effect of agitation speed on Aliquat-336 loss by the microspheres (C_0: 60 mg/l, pH: 7.4, microspheres dose: 0.5 g/l and contact time: 48h).*

III.4.4. Effect of pH

Chromium(VI) may exist in the aqueous phase in different forms; the total amount of chromium and the pH are the main variables which govern the chromium species in an aqueous phase [6,52]. The following are the important Cr(VI) equilibrium reactions [35,36,42]:

$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^-$ $K_1 = 1,21$ (3)

$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$ $K_2 = 3,0 \times 10^{-7}$ (4)

$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$ $K_3 = 35,5$ (5)

$HCr_2O_7^- \rightleftharpoons H^+ + Cr_2O_7^{2-}$ $K_4 = 0.85$ (6)

For the low concentrations, $HCrO_4^-$ is by far the most predominant species for pH between 2 and 5, below pH 2 the amount of $HCrO_4^-$ decrease and H_2CrO_4 rise and above pH 5 the amount of $HCrO_4^-$ decrease and CrO_4^{2-} rise. In case of Aliquat-336 ($R_3(CH_3)N^+Cl^-$), the extractant reacts as an anion-exchanger forming an ion-pair with the metal species from the aqueous solution, depending on the chromate speciation in solution according to the reactions (1) and (2).

Hence, for a Cr(VI) concentration of 60 mg/l the extraction must reach a maximum at pH between 2 and 5. In our case this not observed; the adsorption capacity of Cr(VI) increases with decreasing the pH (Figure 8). It may be attributed to the microsphere loss of Aliquat-336 as shown in figure 9, were the decrease of pH decreases the amount of Aliquat-336 loss by the microspheres and approach zero value at pH 1. Hence, pH 1 was chosen for the farther studies.

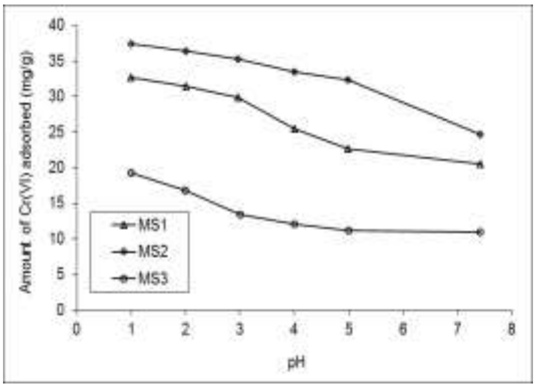

Figure 8. *Effect of pH on the adsorption capacity of Cr(VI) by the different microspheres (C_0 : 60 mg/l, agitation speed: 300 rpm, microspheres dose: 0.5 g/l and contact time: 48h).*

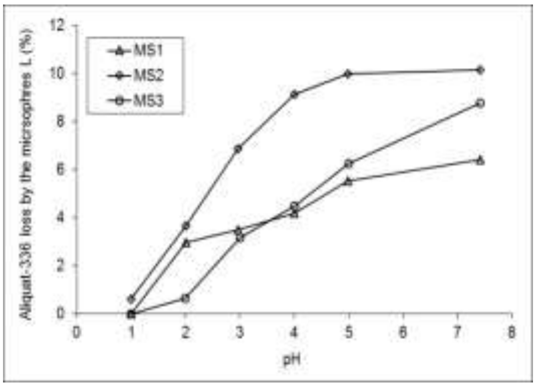

Figure 9. *Effect of pH on Aliquat-336 loss by the microspheres (C_0: 60 mg/l, agitation speed: 300 rpm, microspheres dose: 0.5 g/l and contact time: 48h).*

III.4.5. Effect of chromium initial concentration

The initial concentration of Cr(VI) was varied from 5 to 100 mg/L. The uptake of Cr(VI) increased with increase in initial metal concentration (figure 10). At low concentrations, below 40 mg/L, the amount of Cr(VI) adsorbed increase with increasing the chromium initial concentration due to availability of adsorption sites. However, at higher concentration, above 40 mg/L, the amount of Cr(VI) adsorbed reach a plateau due to the saturation of adsorption sites and microspheres reach maximum adsorption capacities.

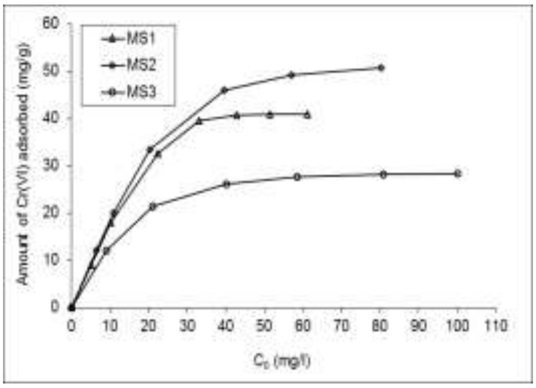

Figure 10. *Effect of initial concentration on the adsorption capacity of Cr(VI) by the different microspheres (agitation speed: 300 rpm, microspheres dose: 0.5 g/l, pH =1, contact time: 48h).*

III.4.6. Adsorption kinetics

Adsorption processes dependent and controlled by different kinds of mechanisms such as diffusion control, mass transfer, chemical reactions and particle diffusion. The pseudo-first-order kinetic model, the pseudo-second-order kinetic model, the inter-particle diffusion model and the intra-particle diffusion model were used for testing dynamic experimental data at the initial concentrations 10 and 20 mg/l, of Cr(VI) ions. The experimental data was fitted with the theoretical data for each model by minimizing the error Δq (equation (7)) using the solver function in Microsoft Excel. Table (4) summarizes the different kinetics model used to fit the experimental data. The average normalized standard deviation Δq [53-55]:

$$\Delta q(\%) = 100\sqrt{\frac{\sum\left[\left(q_{t,exp} - q_{t,the}\right)/q_{t,exp}\right]^2}{(n-1)}} \quad (7)$$

Where:

$q_{t,exp}$: experimental data of Cr(VI) amount adsorbed at time t;

$q_{t,the}$: theoretical data of Cr(VI) amount adsorbed obtained by the kinetics model at time t.

n: the number of the experimental data.

The model was validated if its average standard deviation $\Delta q(\%)$ is inferior to 5%, the theoretical adsorption capacity at equilibrium $q_{e\text{-}the}$ is near to the experimental adsorption capacity at equilibrium $q_{e\text{-}exp}$ and in case of diffusion models the constant C must tend to zero. The obtained results were shown in table (5). From the results, the Dumwald-Wagner model seems to be the only model describing the kinetics of adsorption of hexavalent chromium ions by the microspheres. This model has an average normalized standard deviation $\Delta q(\%)$ inferior to 1, the absolute value of the constant C inferior to 10^{-3} and an adsorption capacity at equilibrium near to those of experimental data for all microspheres and for the tow initial concentration of 10 and 20mg/L.

The kinetics adsorption of Cr(VI) by the different microspheres is controlled by intra-particle diffusion through the pores of microspheres and the channels of organic matter (Aliquat-336) inside the polymer matrix. The latter, is occurred by two different mechanisms; the mobile carrier-diffusion mechanism (diffusion of the complex formed (Aliquat-336_Chromate)) or the fixed-site jumping mechanism (complexation reaction between the Aliquat-336-chromate and the adjacent Aliquat-336) [56]. The different constant of the Domwald-Wagner model are shown in table (6) and the different amounts of Cr(VI) adsorbed q_t was depicted in figure 11.

Table 4. *The kinetics model equations used to fit the experimental kinetics data.*

Model	Kinetic equation	Adsorption capacity $q_{t,the}$
Pseudo-first-order model	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$q_t = q_e(1 - e^{-k_1 t})$
Pseudo-second-order model	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$
Elovich model	$\frac{dq_t}{dt} = a\, e^{-bq_t}$	$q_t = \frac{1}{b}\left(ln(t) + ln(ab)\right)$
Intra-particle diffusion : Weber and Morris model	$q_t = k_{id}t^{1/2} + C$	$q_t = k_{id}t^{1/2} + C$
Intra-particle diffusion : Dumwald-Wagner model	$ln\left[1 - \left(\frac{q_t}{q_e}\right)^2\right] = -k_{DW}t + c$	$q_t = q_e(1 - e^{-k_1 t + C})^{0.5}$

Inter-particle diffusion model	$ln\left(1-\frac{q_t}{q_e}\right)=-k_{if}t+c$	$q_t=q_e(1-e^{-k_1t+C})$

Table 5. The constants obtained by the fitting of different kinetics models with experimental data for the different microspheres.

C_0 (mg/L)	Microsphere	Experimental q_e (mg/g)	Kinetics Model						
			Calculated constants	Pseudo-first order	Pseudo-second order	Elovich	Wiber & Moris	Domwal-Wagner	Film diffusion
10	MS1	20.33	q_e (mg/g)	16.54	19.06	/	/	20.12	18.99
			Δq (%)	**18.4377**	**11.3590**	**8.1741**	**21.7571**	**0.6278**	**4.1720**
			C	/	/	/	3.8235	0.0002	-0.1572
	MS2	22.23	q_e (mg/g)	17.27	19.93	/	/	21.84	20.05
			Δq (%)	**19.6725**	**12.7311**	**10.2008**	**11.4696**	**0.7389**	**4.6116**
			C	/	/	/	1.6127	-0.0001	-0.1465
	MS3	15.49	q_e (mg/g)	12.36	14.26	/	/	14.76	14.15
			Δq (%)	**17.4233**	**10.0705**	**6.0438**	**22.9410**	**0.8727**	**4.6397**
			C	/	/	/	0.8229	0.0005	-0.1678
20	MS1	32.65	q_e (mg/g)	27.14	30.90	/	/	31.79	30.28
			Δq (%)	**17.3427**	**10.6330**	**7.8923**	**14.5000**	**0.7318**	**4.0261**
			C	/	/	/	3.6016	-0.0005	-0.1635
	MS2	34.73	q_e (mg/g)	28.30	32.54	/	/	34.62	32.16
			Δq (%)	**18.7251**	**12.0055**	**9.6443**	**12.5460**	**0.5906**	**4.9781**
			C	/	/	/	2.9075	-0.0001	-0.1500
	MS3	23.08	q_e (mg/g)	17.94	20.38	/	/	23.49	19.91
			Δq (%)	**16.9064**	**10.1536**	**7.1955**	**14.8696**	**0.4161**	**4.1461**
			C	/	/	/	2.4616	0.0002	-0.1640

Table 6. The different constants obtained by Dumwald-Wagner models

$[Cr(VI)]_0$	Model Constants	Microspheres		
		MS1	MS2	MS3
10 mg/L	k_i (h^{-1})	0.0637	0.0507	0.0764
	q_e (mg/g)	20.12	21.84	14.76
	C	0.0002	-0.0001	0.0005
20 mg/L	k_i (h^{-1})	0.0699	0.0549	0.0740
	q_e (mg/g)	31.79	34.62	23.49
	C	-0.0005	-0.0001	0.0002

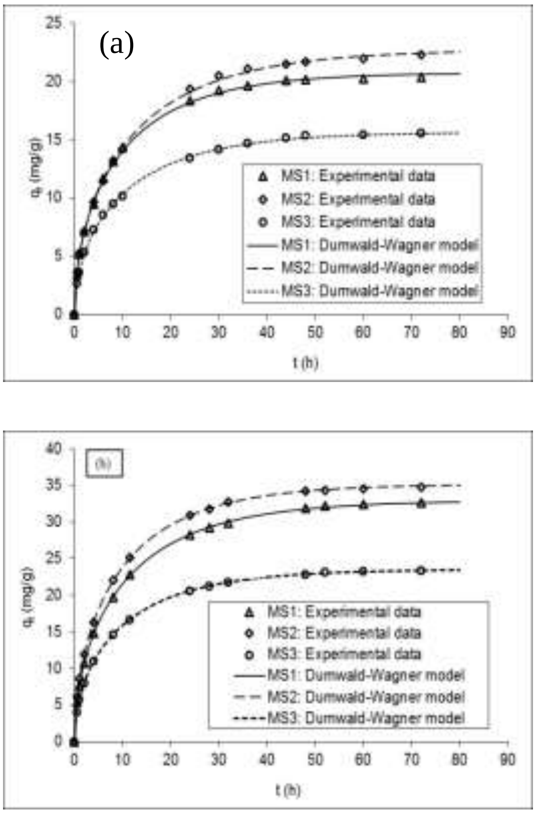

Figure 11. *Kinetics of chromium(VI) adsorption by the different microspheres: Symbols are experimental data and lines are the intra-particle diffusion data fitted with Dumwal-Wagner model. Agitation speed: 300 rpm, microspheres dose: 0.5 g/l, pH: 1 and Initial concentration: (a) 10 mg/L and (b) 20mg/L.*

In this study, the adsorption of Chromium(VI) on PVC microspheres included with Aliquat-336 is evaluated and compared with popular two and three parameter single solute isotherm models given in table 7. The experimental data was fitted with the theoretical data for each model by minimizing the error □q (Equation (8)) using the solver function in Microsoft Excel. The average normalized standard deviation □q [58]:

$$\Delta q(\%) = 100\sqrt{\frac{\Sigma[(q_{e-exp}-q_{e-the})/q_{e-exp}]^2}{(n-1)}} \qquad \textbf{(}1)$$

Where:

$q_{e\text{-}exp}$: experimental data of adsorption capacity; $q_{e\text{-}the}$: theoretical data obtained from the adsorption isotherm model used; n: the number of the experimental data.3.4.7. Adsorption isotherm

An adsorption isotherm describes the relationship between the amount of adsorbate that is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Several studies with two or three parameter models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently used models. The Langmuir model is obtained under the ideal assumption of a totally homogenous adsorption surface, whereas the Freundlich isotherm is suitable for a highly heterogeneous surface. The Redlich–Peterson equation is a combination of Langmuir and Freundlich models [57].

Table 7. *The adsorption model equations used to fit the experimental equilibrium data.*

Adsorption isotherm Model	Kinetic isotherm equation
Langmuir model	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$
Freundlich mode	$q_e = K_F C_e^{1/n}$
Tamkin model	$q_e = \frac{RT}{b_T}\ln(a_T) + \frac{RT}{b_T} ln(C_e)$
Dubinin–Radushkevich model	$q_e = q_m \exp(-k\varepsilon^2); \quad \varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right)$
Redlich–Peterson model	$q_e = \frac{K_R C_e}{1 + \propto_L C_e^{\beta}}$

The model was validated if its average standard deviation Δq(%) is inferior to 5%, the theoretical maximum amount adsorbed at equilibrium $q_{m\text{-}the}$ is near to the experimental maximum amount adsorbed $q_{m\text{-}exp}$. The obtained results were shown in table (8). The different adsorption isotherms obtained experimentally and with Langmuir model are depicted in figure 12.

The adsorption isotherm of chromium (VI) onto microspheres shows a high maximum adsorption capacity more than 35 mg/g (table (8)). Adsorption isotherm models were applied and the results show that Langmuir model describes better the adsorption of chromium(VI) onto the different microspheres as shown in table (8) with an average normalized standard deviation □q(%) inferior to 1, a maximum adsorption capacity q_m near to that of experimental data and the constant □ of Redlich-Peterson isotherm close to 1 indicate that it describes Langmuir model [59,60]. This may be attributed to the chemisorption of Cr(VI) with Aliquat-336; in the way that a chromate reacts with Aliquat-336 so one monolayer adsorption can be obtained and the homogeneity of adsorption sites energy made of Aliquat-366 only witch are the assumptions of the Langmuir model [24]. The separation factor R_L, which is defined by the following equation: $1/(1+(1/k_L))$, obtained with Langmuir isotherm ranged between 0.01 to 0.9 for a concentration between 1 to 100 mg/L indicated that the adsorption is favorable [22,59]. The adsorption energy E $((-2k_{D\text{-}R})^{-0.5})$ obtained with Dubinin-Radushkevich model for the different microspheres used (between 13 and 15 kJ/mol) is great then 8 kJ/mol indicate that the adsorption is controlled with chemisorption [22,61,62].

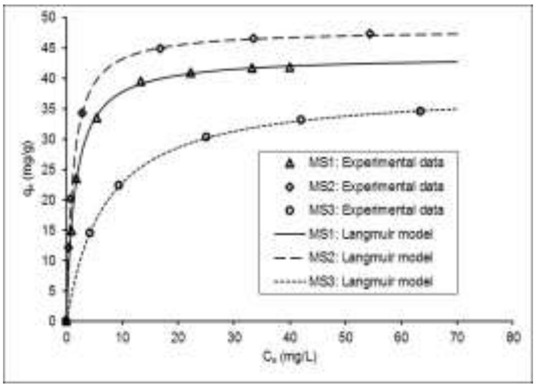

Figure 12. *Adsorption isotherm of chromium(VI) onto different microspheres. Agitation speed: 300 rpm, microspheres dose: 0.5 g/l, pH: 1, Temperature: 25°C and contact time: 72h.*

Table 8. *The constants obtained by the fitting of different isotherm models with experimental data for the different microspheres.*

Adsorption isotherm model	Model parameters	Adsorbents		
		MS1	MS2	MS3
Experimental data	$q_{m\text{-}exp}$ (mg/g)	**41.78**	**47.30**	**36.02**
Langmuir	k_L (l/mg)	0.6391	0.8933	0.1467
	q_m (mg/g)	43.66	48.03	38.36
	R_L	0.0151-0.1352	0.0111-0.1007	0.0638-0.4053
	Δq (%)	**0.6796**	**0.4956**	**0.4934**
Freundlich	k_F (mg/g (L/mg)$^{1/n}$)	18.1534	18.7097	10.8817
	n	3.9406	3.7700	3.6039
	Δq (%)	**12.2603**	**18.1597**	**9.2292**
Temkin	a_T (L/g)	10.0923	13.4708	1.9654
	b_T (kj/mol)	0.3283	0.3124	0.3433
	Δq (%)	**7.3033**	**9.6357**	**5.3509**
Dubinin-Radushkevich	E (kJ/mol)	14.7581	14.6448	13.1077
	$k_{D\text{-}R}$ (mol^2/kJ^2)	0.0023	0.0023	0.0029
	q_m (mg/g)	94.27	103.97	77.43
	Δq (%)	**10.2181**	**15.0517**	**7.4907**
Redlich-Peterson	k_R (l/g)	27.9116	43.5114	5.5018
	α_R (l/mg)$^{\beta}$	0.6395	0.9252	0.1372
	β	0.9999	0.9936	1.0102
	Δq (%)	**0.6795**	**0.2726**	**0.3839**

IV. Conclusion

Asymmetric and spherical PVC microspheres included with Aliquat-336 were successfully prepared by immersion –precipitation techniques and efficiently used for chromium (VI) removal from aqueous solution. The morphology and the structure of the prepared microspheres were affected drastically by increasing the polymer concentration from 6 to 14 % in weight.

Chromium(VI) can be effectively removed from aqueous solutions by the prepared microspheres in batch mode. Chromium (VI) uptake by the microspheres was dependent on the pH, agitation speed, microsphere dosage, the microspheres content of Aliquat-336 and polymer concentration. The adsorption capacity was increased with increasing microsphere content of Aliquat-336, agitation speed and hexavalent chromium concentration, but decreased with increasing the pH and the microspheres dosage. The adsorption capacity of Cr(VI) onto microspheres and Aliquat-336 loss also strongly dependent on the solution pH. The decrease of the pH decreases the Aliquat-336 loss by microspheres and no loss observed at pH= 1. The intra-particle model seam to describe the adsorption kinetics of Cr(VI)

adsorption by microspheres and Langmuir model describe the thermodynamic of adsorption.

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