e-Polymers **2007**, no. 141

http://www.e-polymers.org

ISSN 1618-7229

Synthesis and bharacterization of poly(vinyl alcohol)-boric acid beads from PVA with several hydrolysis degrees

Adriana de Melo, *Daniel L. G. Borges, Nito A.Debacher,** Adilson J. Curtius

Departamento de Química, Universidade Federal de Santa Catarina, 88040-900, Florianópolis, SC, Brazil; Fax: +55 48 3721 6850; * debacher@qmc.ufsc.br

(Received: 17 August, 2007; published: 27 November, 2007)

Abstract: This work describes the synthesis and characterization of poly(vinyl alcohol)-boric acid (PVA-BA) sphere-like beads. The PVA-BA beads were prepared by the dropwise addition of PVA aqueous solutions to a boric acid solution under constant stirring and controlled temperature. Different temperatures for bead formation as well as PVA with several hydrolysis degrees were used and tested. PVA with several hydrolysis degrees were characterized regarding molecular mass and intrinsic viscosity, while characterization of PVA-BA beads was carried out using thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The results obtained with TGA have shown that structural changes occurs in PVA following the reaction with boric acid and that the spheres formed are thermally stable, whereas SEM analysis demonstrated that symmetric sphere-like beads were formed, with considerable porosity, which are requisite for solid supports when applied to effluent treatment. Trace element extraction tests were carried out using inductively coupled plasma mass spectrometry (ICP-MS). Without the addition of a chelating agent, no significant extraction occurred from acidic solutions, while after the addition of ethylenediaminetetracetate, less than 10% of the trace element content was extracted from the aqueous phase by the PVA-BA beads. However, after the addition of ammonium O,O-diethyldithiophosphate (DDTP), over 10% of As, Co, Cr, Fe, Sr and Zn, 40% of Cd and 70% of Pb were extracted from acidic solutions, even without any further optimization. The results have shown that the synthesized PVA-BA beads are potential alternatives for trace element extraction in effluent treatment.

Keywords: Poly(vinyl alcohol), Boric acid, Beads, Trace element extraction, Effluent treatment

Introduction

Effuent treatment has become important because of its possible environmental impact as well as its possible adverse effects on human health. Additionally, upgradation in environmental laws is another element of pressure for paradigm changes. Due to these factors, investigations concerning efficient effluent treatments have greatly increased [1].

Effluent treatment process through organic matter biodegradation by the presence of bacteria fixed onto solid supports is largely favored. This procedure not only accelerates the biodegradation process, but also allows the recovery and reuse of the bacteria at the end of the process [2]. This method for the immobilization of activated sludge was used for wastewater treatment and for immobilization of cells for ferrous sulphate oxidation [3].On the other hand, water contamination by toxic elements is one of the forms of pollution of the environment that has been more thoroughly discussed lately. The effects derived from the presence of toxic elements

in natural systems arise from their non-biodegradability, and many of the elements can be toxic even at very low concentrations [4]. The purification in this case can be very complex, and some attempts have already been described using chelating agents, such ethylenediaminetetraacetate (EDTA) [5, 6].

Up to now, several methods of immobilization using PVA have been reported [7-9]. Poly(vinyl alcohol) (PVA) is obtained from the polymerization reaction of vinyl acetate, with subsequent partial hydrolysis of poly(vinyl acetate) [10]. Following the polymerization reaction, poly(vinyl acetate) is submitted to a hydrolysis reaction, where the acetate groups are replaced by hydroxyl groups, generating PVA. By carefully controlling this reaction, PVA can be produced with hydrolysis degrees that may vary from 70% to 100%, which represents the extent to which acetate groups have been converted to hydroxyl groups in the polymeric chain. PVA is usually classified as partially hydrolyzed or completely hydrolyzed, and their properties are based on the molecular weight and on the hydrolysis degree [11].

In this work, the synthesis of PVA-boric acid (PVA-BA) sphere-like beads using PVA with several hydrolysis degrees will be described and investigated, and the spheres formed will be characterized and their ability to extract trace elements from aqueous solutions will be evaluated.

Results and Discussion

Determination of viscosity and molar mass of PVA with several hydrolysis degrees

The several types of PVA used in this work have been characterized regarding their viscosity and molar mass, intending to establish a relationship among the physical-chemical characteristics of the pure PVA and the characteristics of the PVA-BA beads. The intrinsic viscosity was derived from the relative, specific and reduced viscosity, determined experimentally. Table 1 contains data on the intrinsic viscosity of five types of PVA with different hydrolysis degrees, which have been chosen due to their ability to form PVA-BA beads under the experimental conditions adopted. As the intrinsic viscosity (η) is a measure of the hydrodynamic volume of the macromolecules in solution, the value of η provides information on the average size of the macromolecules and their solubility in pure water. A high intrinsic viscosity represents a more favorable interaction between polymer and solvent, meaning that the polymeric aggregate is more expanded in solution. This characteristic may induce a higher interaction of the hydroxyl groups in the polymeric chain with boric acid molecules in solution, which would result in an efficient formation of the PVA-BA beads. The practical aspects deriving from this characteristic have been noticed, as the PVA 14OH, which has the highest intrinsic viscosity among the PVA studied, was one of the PVA that formed PVA-BA beads more efficiently, as will be shown and discussed later.

The molar mass of the same group of PVA with different hydrolysis degrees was also determined, using the Mark-Kuhn-Houwink-Sakurada equation and viscosity measurements. The results can be seen in Table 1. PVA 14OH is the polymer with the highest mean molar mass, which means that the polymeric chain for this polymer is longer. It can be assumed that a high hydrolysis degree combined with the length of the polymeric chain implies that a larger number of hydroxyl groups may act as reaction sites after addition of boric acid. This would be partly responsible for the successful formation of PVA-BA beads with this specific group of PVA, although

other factors, such as conformational changes, which have a direct effect on the availability of hydroxyl groups, also play an important role.

Tab. 1. Intrinsic viscosity and mean molar mass determined for PVA with several hydrolysis degrees.

PVA	Intrinsic viscosity (mL g^{-1})	Molar mass (kDa)	Hydrolysis degree (%)
M 10.98	57.45	35.5	98.4 ± 0.4
M 26.88	84.25	58.8	87.7 ± 1.0
C 325	84.11	58.6	98.0
C HA70	83.46	58.0	99.9
14OH	131.19	105.2	99.7

Formation of PVA-BA beads

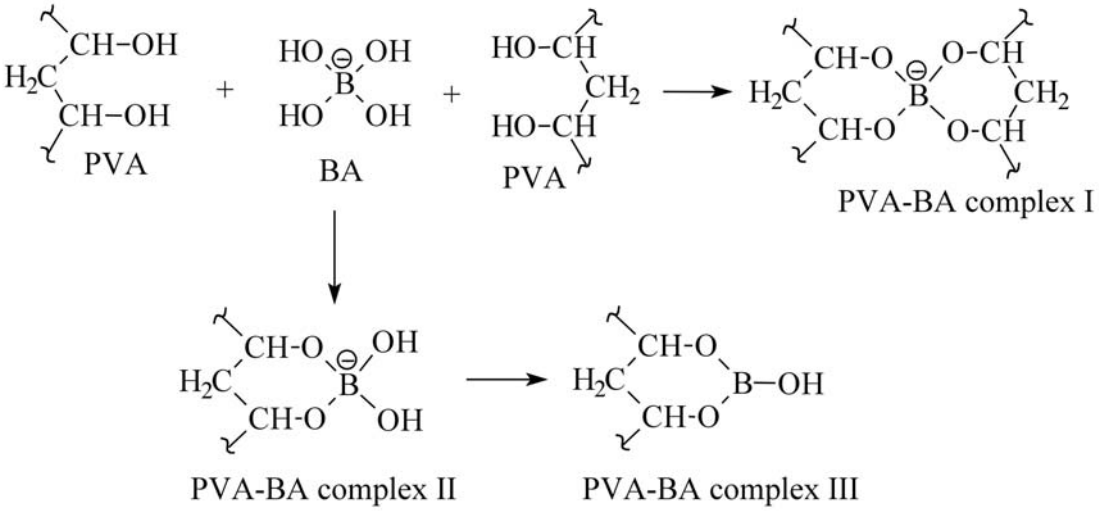
Table 2 presents the hydrolysis degree, concentration, density and temperature of solubilization of several PVA and relationship with the temperature of formation of beads following reaction with boric acid. From the data presented in Table 2, it is possible to assume that the hydrolysis degree of PVA is strongly related to the temperature of solubilization and to the formation PVA-BA beads. The PVAs C HA-70, 14OH and C 325 required 80 ºC for solubilization, whereas for the PVAs M 10.98, M 26.88, C 203 and C 203S complete solubilization was achieved already at 60 ºC. This may be related to the considerably higher number of OH groups on the highly hydrolyzed PVA (98 to 99.9%), as in this case the OH groups promote strong intra and intermolecular interaction by means of hydrogen bonding, therefore requiring more energetic conditions to promote interaction with water. On the other hand, the residual acetate groups present in the chain of partially hydrolyzed (87 to 89%) PVA are responsible for weaker inter and intramolecular interactions, facilitating the interaction of the polymeric chain with water mostly via hydrogen bonding with OH groups. The solubilization of PVA with high hydrolysis degree requires, therefore, higher temperatures due to the high energy associated to the dissolution of the crystalline phase [12]. After solubilization, PVA is stable in solution even at room temperature, most likely due to interaction with surrounding water molecules instead of inter and intramolecular interactions, which justifies the ability to form beads after reaction of PVA C HA-70, 14OH, C 325 and M 10.98 with boric acid without the need for temperature control to induce bead formation. However, beads were more easily formed with HA-70 and 14OH, not needing temperature control and requiring a lower concentration of PVA. Despite the fact that the hydrolysis degree of PVA M 4.88 is the same as PVA M 26.88, PVA-BA beads could not be obtained using the former, which may be at least in part explained by conformational changes in the polymeric chain that induce strong intramolecular interaction involving the remaining hydroxyl groups. This is evidence for the formation of beads following reaction with boric acid does not depend solely on the hydrolysis degree, as discussed previously.

Tab. 2. Hydrolysis degree, concentration and temperature of solubilization of several PVA and the relationship with the temperature of formation of beads following reaction with boric acid.

PVA	Hydrolysis degree (%)[a]	Concentration (% m/v)	Density (g cm^{-3})	T_1 (ºC)[b]	T_2 (ºC)[c]	PVA-BA bead formation
C HA70	99.9	6	0.44	80	25	Yes
14OH	99.7	6	0.42	80	25	Yes
M 10.98	98.4 ± 0.4	10	0.44	60	25	Yes
C 325	98.0	10	1.16	80	25	Yes
M 26.88	87.7 ± 1.0	10	0.85	60	60	Yes
M 4.88	87.7 ± 1.0	5-20	-	60	-	No
C 203	87.0-89.0	5-20	-	60	-	No
C 203S	88.0	5-20	-	60	-	No

[a] Data provided by the supplier, determined with a 4% m/v solution at 20 ºC.
[b] Solubilization temperature.
[c] PVA-BA bead-formation temperature.

Another important factor to be taken into account in order to produce water-insoluble homogeneous beads is the rate of the PVA-BA reaction. By adding dropwise the PVA solution to the boric acid solution, the reaction should occur instantaneously in order to form the insoluble PVA-BA complex and generate beads with spherical shape. If the reaction is not instantaneous, the PVA disperses on the boric acid solution and the bead becomes deformed. In order to promote the surface reaction of formation of the PVA-BA complex, it is necessary to have the OH groups of the polymeric chain lying closely and arranged in a way to allow the formation of the oxygen-boron complex, as shown in the Scheme I below. It can be seen that there are several possibilities of formation of PVA-BA complex.



Scheme 1. Different mechanisms involved in the formation of PVA-BA complex.

In general, the study of reactions between boric acid and diols suggests that the most favorable mechanism involves the complex-formation reaction with the borate anion,

instead of the reaction with non-dissociated boric acid. In the specific case of addition of PVA to an aqueous solution of boric acid, the reaction initially takes place on the PVA drop surface and, therefore, the most favorable equilibrium leads to the formation of the type III complex. Pizer *et al* [13] have shown that the formation of type III complex for reactions with lactic acid, measured using the stopped-flow kinetic method, is three times higher than the formation of type II complex. In the case of PVA-BA complex formation as described here, there is a higher possibility to form type II complex, since PVA is not added in excess to the boric acid solution (i.e., no PVA exists in the boric acid solution prior to addition, using a Pasteur pipette).

Thermogravimetric analysis

Tab. 3. Thermogravimetric parameters determined for pure PVA, PVA-BA beads and for boric acid (T = temperature, in ºC, of maximum degradation in the stage; P = mass loss percent in the stage).

PVA	Stage 1		Stage 2		Stage 3		Residual mass at 900 ºC (%)
	T	P	T	P	T	P	
C HA70	147	7	308	72	455	13	10
14OH	171	4	305	72	451	15	9
M 10.98	236	48	324	43	-	-	9
C 325	175	6	317	71	469	16	7
M 26.88	158	5	372	62	474	28	5
PVA-BA beads							
C HA70	83	59	444	23	-		18
14OH	81	62	432	25	-		13
M 10.98	90	70	418	10	-		20
C 325	69	58	412	13	-		29
M 26.88	61	46	383	17	-		37
Boric acid	154	29	190	16	-		55

Thermogravimetric analysis was carried out in an inert atmosphere. Parameters obtained from TGA for pure PVA, boric acid and for PVA-BA beads can be seen in Table 3.

As a general property, all pure PVA have shown three main mass loss stages, except for PVA M 10.98, for which only two mass loss steps were detected, and the PVA-BA beads have shown two mass loss stages. The residual mass obtained at 900 ºC for all pure PVA oscillated between 5 and 10%, while for PVA-BA beads this parameter oscillated between 13 and 37%. The residual mass for boric acid was determined as 55%. This significant change in the residual mass obtained after a 900 ºC step for pure PVA and PVA-BA beads is, therefore, associated to the presence of boric acid.

It is known that the thermal decomposition of PVA generates complex products, mostly from intramolecular, cyclization and elimination reactions Gilman *et al*. [14] assumed that the first mass-loss stage (147 – 236 ºC) is due to the pyrolysis of PVA, with fast elimination of water until the temperature approaches the beginning of the decomposition stage. This process, along with melting, induces the formation of foam in the remaining material or intumescence as it decomposes. This and other decomposition reactions result in color changes and promote the occurrence of cross-bonding, producing foam-like insoluble residues. In PVA, the second degradation step, with maximum degradation temperatures above 305 ºC, corresponds to the dehydration of the polymeric chain through a series of elimination reactions, resulting in a polyene chain. On this second stage, a significant mass loss is detected, with losses ranging from 43 to 72%. It is important to emphasize that PVA with higher hydrolysis degrees (C HA70 and 14OH) presented the higher mass loss on this stage. This is according to expectations, as dehydration occurs to a larger extent with higher hydrolysis degree. The third degradation step occurs above 450 ºC, with mass losses ranging from 13 to 28%. This step comprises intramolecular cyclization, radical and Diels-Alder reactions, which generate unsaturated cyclic compounds and aromatic hydrocarbons [14].

The PVA with higher thermal stability is M 26.88, which also has the lower hydrolysis degree. This additional stability may be related to the presence of residual acetate groups, which represents an additional steric barrier to the occurrence of intramolecular reactions that take place at elevated temperatures.

The profile of the thermogram obtained for the PVA-BA beads differs significantly from those obtained for pure PVA. This confirms that structural changes in the PVA polymeric chain occurred following the reaction with boric acid. The first mass-loss stage corresponds to the dehydration of the beads (mostly from adsorbed water), with water mass losses from 46 to 70%. The second degradation stage occurs above 380 ºC, and it is most likely due to degradation of the main polymeric chain, similarly to what is proposed for pure PVA.

The thermogravimetric curves obtained for pure PVA and PVA-BA beads confirm the differences between the thermograms and, therefore, structural changes of the reagents that lead to the formation of PVA-BA beads. The thermogram obtained for pure boric acid showed only two degradation steps: the first between 100 and 160 ºC, with 30% mass loss, and the second between 160 and 200 ºC, with a mass loss of 16%. The first degradation stage corresponds to dehydration of boric acid, generating metaboric acid, while the second stage corresponds to dehydration of HBO_2 to form B_2O_3, as proposed by Jimenez *et al* [15].

Morphological analysis

The morphological aspects of the PVA-BA beads were verified using SEM, as shown in Fig 1.

Fig. 1A shows the micrograph obtained for the external surface of a single PVA-BA bead, formed from PVA M 10.98. As can be seen, the bead assumed a spherical shape with a uniform surface, and an average diameter of approximately 2 mm was measured for the beads. These same characteristics, although not shown here, were observed for the PVA-BA beads formed from the other PVA used in this work.

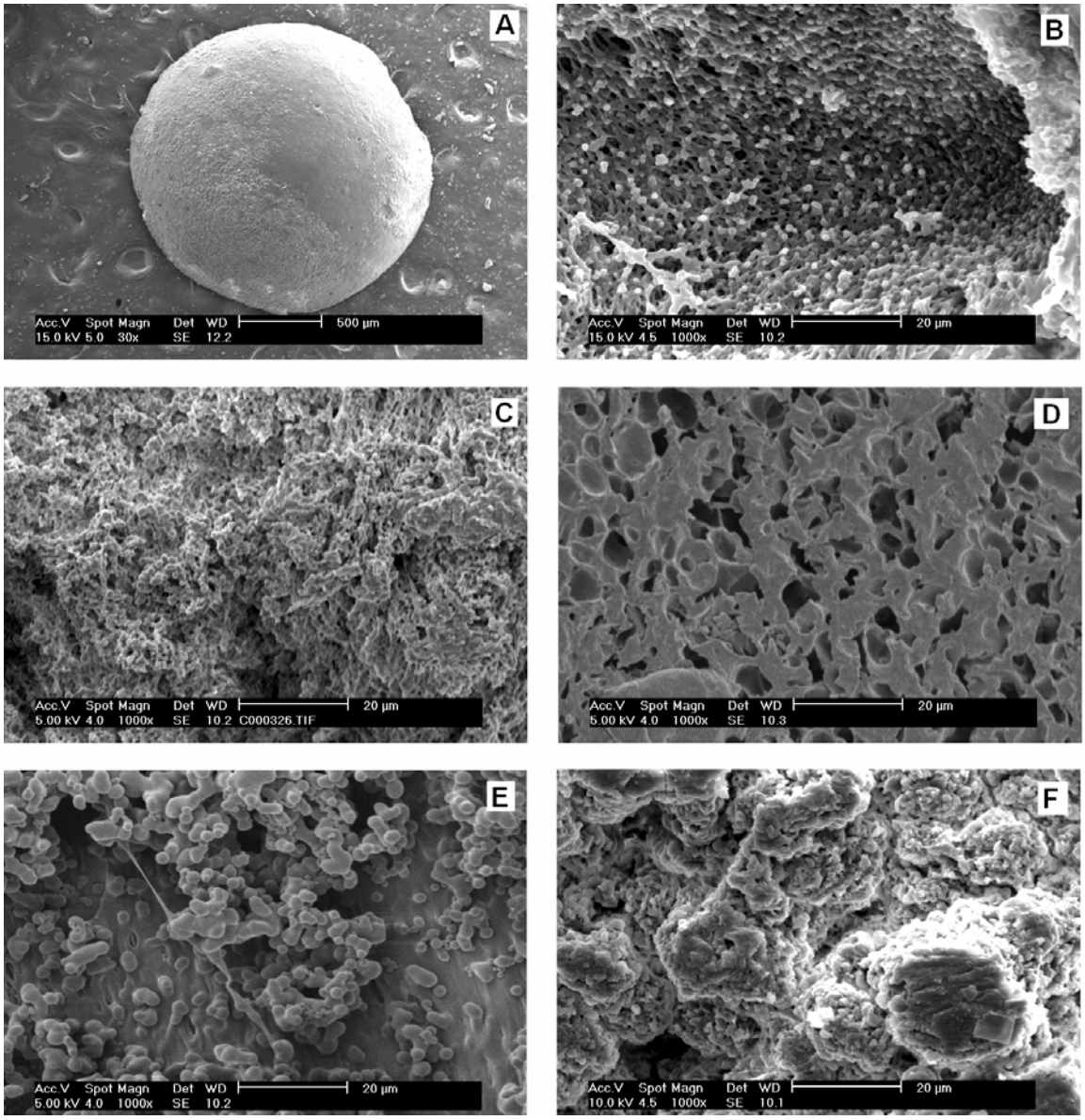


Fig. 1. Micrographs obtained with SEM for PVA-BA beads synthesized from different PVA: (A) surface micrograph for PVA-BA from M 10.98, 30x magnification; and fracture micrographs for PVA-BA beads synthesized from (B) C HA-70, (C) 14OH, (D) M 10.98, (E) C 325, and (F) M 26.88, 1000x magnification.

Figs. 1 B-F show the micrographs obtained for the inner surface of PVA-BA spheres obtained from reaction of the several PVA used with boric acid. One relevant

characteristic can be visualized, which is the high porosity inherent to all the different PVA-BA beads synthesized. The micrographs obtained show that the pore volumes appear to be slightly smaller for the PVA-BA beads produced from the PVA with higher hydrolysis degrees (Fig. 1B and 1C), which may be due to the closeness of the OH groups, generating a more compact material. A high porosity is considered an important characteristic of the material synthesized, allowing its application in effluent treatment, which would allow, for instance, bacteria fixation to occur, as well as metal extraction by sorption processes. The density of the PVA-BA beads has also been determined, as shown in Table 2. All beads, except those formed from PVA C 325, had lower density than water at 25 ºC. However, once in contact with water, all beads readily submerse, which is yet another evidence of the high porosity of the synthesized beads (in contact with water, the inner pores are fully filled and the beads sink).

Trace element extraction tests

In order to evaluate the possibility to extract trace elements from aqueous solutions by the PVA-BA beads, extraction tests were performed with nine elements in a 0.1 mol L^{-1} HNO_3 solution using the beads formed from PVA C HA70. The extraction tests were performed using PVA-BA beads synthesized from the PVA prepared at two different temperatures (room temperature and at 60 ºC), in order to verify possible effects on the extraction efficiency, which would be an indication of changes on the morphology of the polymeric material. The acidic medium has proved to be necessary to promote the stability of trace elements in the liquid phase, avoiding losses by volatilization or precipitation/adsorption on the recipient walls.

The first tests were carried out using only an acidified aqueous solution containing As, Cd, Co, Cr, Cu, Fe, Pb, Sr and Zn at a concentration of 10 mg L^{-1}. The PVA-BA beads were added to the solutions containing the trace elements and the mixture was left to stand at room temperature for 12 h under constant stirring using a magnetic bar. The remaining concentrations of the trace elements in solution after the extraction were determined by ICP-MS using ^{103}Rh as an internal standard to correct for non-spectral interference, using external calibration against aqueous standards in 0.5% v/v HNO_3. No attempt was made to elute the adsorbed species. The concentrations obtained after the extraction were compared to those initially added, which were taken as 100%. The first results have shown that the extraction from an acidic solution was not effective, as over 95% of the original concentration of all trace elements could be recovered after the extraction period. This means that the PVA-BA beads were unable to extract the elements in their ionic forms, which is believed to be due to the low density of free OH groups in the PVA polymeric chain after reaction with PVA. Although some OH groups remain from the reaction, mostly originating from the boric acid itself, these groups may be highly hydrated, which results in lower ability to interact with ions in solution by physical sorption processes. Nevertheless, the OH groups in the aliphatic chain are probably not dissociated under the conditions adopted in this work, and extraction through chemical processes, such as exchange reactions, is unlikely to occur.

The next attempt was to consider the evaluation of the ability to adsorb trace elements as neutral complexes, by the addition of EDTA or DDTP to the acidic solution containing the trace elements at 10 mg L^{-1}. The results obtained are shown in Table 4. It can be seen that with the addition of EDTA, about 10% of the trace element content of the aqueous solution could be extracted by the PVA-BA beads

prepared from C HA-70 at room-temperature, while slightly higher amounts could be extracted using PVA-BA beads synthesized from PVA dissolved at 60 ºC. This difference may be attributed to conformational changes in the polymeric chain that occur by heating the PVA solution, resulting in a higher number of active sorption sites of the synthesized PVA-BA bead. The extraction efficiency can still be considered relatively low, which is most likely due to the fact that complex formation of most elements with EDTA occurs preferentially at higher pH. Nevertheless, a significant improvement was obtained when compared to the extraction in the absence of a chelating agent, which leads to the conclusion that sorption of complexed ions occurs preferentially, as occurred with other commonly used sorbents, such as C_{18} immobilized on silica or activated carbon [16,17].

Tab. 4. Trace element extraction with different chelating agents, in %, obtained using PVA-BA beads synthesized from PVA HA70 and determined by ICP-MS using ^{103}Rh as internal standard (n.e. = not extracted).

Element	EDTA[a]	EDTA[b]	DDTP[a]	DDTP[b]
Cu	9	13	n.e.	n.e.
Cr	8	11	8	16
As	9	9	9	12
Pb	8	8	41	35
Sr	10	12	9	14
Co	10	13	9	15
Cd	10	n.e.	72	73
Zn	11	13	11	15
Fe	7	6	8	14

[a] PVA-BA beads synthesized from PVA solubilized at room temperature
[b] PVA-BA beads synthesized from PVA solubilized at 60 ºC

These results were considerably improved by the addition of DDTP to the aqueous solution, which also results in the formation of complexes in solution. Extraction efficiencies around 8-9% for PVA-BA beads synthesized from PVA dissolved at room temperature were obtained, while the extraction was considerably higher (14-15%) for PVA-BA beads synthesized from PVA dissolved at 60 ºC, similarly to the results obtained for the extraction with EDTA. This improved extraction efficiency may be at least in part attributed to the efficiency of complex formation with DDTP in acidic medium, unlike what should be expected with EDTA. The most significant results were obtained for the extraction of Cd and Pb, two elements well-known for their high toxicity, for which over 40 and 72% of the initially added amount, respectively, could be extracted by the PVA-BA beads from an acidified solution containing DDTP. The formation constants for these two elements with DDTP are recognizably high, particularly at pH < 1, which justifies at least in part this somewhat successful extraction. The interesting results obtained particularly for these two elements instigate future investigations, in order to determine the sorption mechanism and optimize the extraction conditions. It is important, however, to emphasize that the

concentrations of DDTP and EDTA used on this study, as well as the concentration of HNO_3 added to the solution have not been optimized and were chosen simply to assure a large excess over the analytes. Therefore, a significant improvement should be expected under optimum conditions, which will certainly be the subject of future investigations.

Conclusions

The synthesis of beads from the reaction of PVA with boric acid resulted in a stable PVA-BA material, with properties that would allow its use in effluent treatment processes, such as trace element extraction. The increase in PVA hydrolysis reduces the solubility of PVA in water, although the best results were obtained with totally hydrolyzed PVA, as the reaction with boric acid occurred without need for temperature control. Parameters such as the length of the polymeric chain and the degree of interaction with solvents, which may be indirectly deduced from data related to the original PVA such as molar mass and viscosity, are also important factors to explain the formation of beads following reaction with PVA. Thermogravimetric analysis has demonstrated that structural changes on the PVA chain occurred following the reaction with boric acid, and SEM has showed that the synthesized material has a high porosity and spherical morphology. Trace element extraction tests have shown that the synthesized beads can be used as a sorbent material for hydrophobic species.

Experimental

Materials

The following PVA with differing hydrolysis degrees were used without further purification: Mowiol (M) 4.88, M 10.98 and M 26.88 (Clariant, Alemanha); Celvol (C) 203, C 203S, C 325 and HA-70 (Celanese, USA); and 14OH (Kuraray, USA). Boric acid (Nuclear, São Paulo, Brazil) was used as supplied.

All reagents used for trace element extraction tests were at least of analytical grade. Water was deionized to a resistivity of 18 MΩ cm in a Milli-Q system (Millipore, Bedford, MA, USA). Nitric acid (Merck, Darmstadt, Germany) was doubly sub-boiling distilled in a quartz still (Kürner Analysentechnik, Rosenheim, Germany). Stock standard solutions of As, Cd, Co, Cr, Cu, Fe, Pb, Sr and Zn were prepared by dissolution, in acidified de-ionized water, their respective high-purity salts (SPEX, Eddison, NJ, USA). Calibration solutions were prepared just before use in 0.5% v/v HNO_3. The sodium salt of ethylenediaminetetraacetic acid (EDTA Titriplex, Merck) as well as ammonium O,O-diethyldithiophosphate (DDTP, Sigma, Milwaukee, USA) were used without previous purification.

Solution preparation

Several PVA solutions with concentrations ranging from 5% m/v to 20% m/v were prepared. Each PVA was dissolved in deionized water under constant stirring and heating, from room temperature to 80 ºC, until complete solubilization was achieved. A 20% m/v boric acid solution in water was prepared under constant stirring and heating at 40 ºC.

PVA viscosity and molar mass determination

The viscosity of PVA solution was determined by preparing 1% m/v solutions of several PVA under constant stirring for 24 h. The stock solutions were then diluted and the flow off time was measured using a Cannon – Frenske viscosimeter, coupled to an optical reading device AVS 350 (Schott). All experiments were carried out at 25 ºC. From the flow off time of solution and solvent, the relative, specific and reduced viscosity have been determined mathematically. A plot of reduced viscosity *versus* concentration was established, and linear regression was applied. The intrinsic viscosity was determined by extrapolation of the line plots to zero concentration. The molar mass was calculated using Mark-Kuhn-Howwink-Sakurada equation, i.e., $[\eta] = K M^a$, where "η" is the intrinsic viscosity, "M" is the molar mass and "K" and "a" are constants that depend on the polymer, temperature and solvent used. The values for "K" and "a" were adopted as 2.0×10^{-2} mL mol g^{-2} and 0.76, respectively [18].

Synthesis of PAV-BA beads

PVA-BA beads were synthesized from dropwise addition of each PVA solution using a Pasteur pipette to the 20% m/v boric acid solution maintained at 40 ºC, under constant stirring using a magnetic bar. The temperature of the PVA solution varied from 25 to 60 ºC. The synthesized beads were stored in a 5.5% m/v boric acid solution until use.

Determination of density of PVA-BA beads

In order to determine the density of PVA-BA beads, several individual beads were weighed and their diameter was measured using a pachymeter. In each bead, four diameter measurements were performed, and an average diameter was used to calculate the volume of the individual bead.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out in a TGA 50 instrument (Shimadzu, Kyoto, Japan). Measurements were performed from 25 ºC to 900 ºC in an inert nitrogen atmosphere at a flow rate of 50 mL min^{-1}, with a heating rate of 10 ºC min^{-1}.

Scanning Electron microscopy (SEM) analysis

Prior to the analysis, the synthesized beads were fractured using liquid nitrogen to observe the morphology of the fracture region. The micrographs were obtained using a XL 50 microscope (Phillips, The Netherlands), equipped with a tungsten filament as the electron source. Samples were coated with a thin layer of gold using a D2 diode sputtering system.

Trace element extraction tests

To determine the removal efficiency of trace elements from aqueous solutions by the PVA-BA beads, approximately 20 mL of a solution containing 10 mg L^{-1} of each metal in 0.1 mol L^{-1} HNO_3 were added to a glass flask with a screw cap. Approximately 300 mg (dry mass) of PVA-BA beads synthesized with PVA HA-70 were added to each flask containing the trace elements solution at room temperature. The solution was maintained under magnetic stirring for 12 hours. After this period, the remaining concentration of trace elements in solution was determined using an Elan 6000 inductively coupled plasma mass spectrometer (Perkin Elmer-Sciex, Norwalk, CT,

USA), with a cross-flow nebulizer. Rhodium was added as an internal standard, and the isotopes ^{75}As, ^{111}Cd, ^{59}Co, ^{52}Cr, ^{63}Cu, ^{57}Fe, ^{208}Pb, ^{88}Sr and ^{66}Zn were monitored, based on the lower possibility of spectral interference. External calibration was carried out for the determination. Blank solutions were measured parallel to each sample.

Acknowledgements

The authors are thankful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for financial support. A.M. and D.L.G.B. have scholarships from CAPES and CNPq, respectively, and A.J.C. has a research scholarship from CNPq.

References

[1] Farinella, N. V.; Matos, G. D.; Arruda, M. A. Z. *Bioresource Technology*. **2007**, *98*, 1940.
[2] Hashimoto, S.; Furukawa, K. *Biotechnol Bioeng*. **1987**, *30*, 52.
[3] Long, Z. E.; Huangb, Y.; Caia, W. C.; Ouyanga, F. *Process Biochem*. **2004**, *39*, 2129.
[4] Kelter, P. B.; Grundman, J.; Hage, D. S.; Carr, J. D.; Castro-Acuña, C. M. *J. Chem. Educ*. **1997**, *74*, 1413.
[5] Valentini, A.; Laranjeira, M. C. M.; Fiori, S.; Fávere, V. T. *Quim. Nova*. **2000**, *23*, 12.
[6] Dung, P. I.; Milas, M.; Rinaudo, M.; Desbrières, J. *Carbohydr. Polym*. **1994**, *24*, 209.
[7] Imai, K.; Shiomi, T.; Uchida, K.; Miya, M. *Biotechnol. Bioeng*. **1985**, *28*, 1721.
[8] Ariga, O.; Itoh, K.; Sano, Y.; Nagura, M. *J. Ferment. Bioeng*. **1994**, *78*, 74.
[9] Ariga, O.; Takagi, H.; Nishizawa, H.; Sano, Y. *J. Ferment. Technol.* **1987**, *65*, 651.
[10] Rodwell, D. E.; . Kelly, C.M.; Demerlis, C. C.; Shoneker, D. R.; Borzelleca, J. F. *Food and Chemical Toxicology*. **2003**, *41*, 729.
[11] DeMerlis, C. C.; Schoneke, D. R. *Food and Chemical Toxicology*. **2003**, *41*, 319.
[12] Aranha, I. B.; Lucas, E. F. *Polímeros: Ciência e Tecnologia.* **2001**, *11*, 174.
[13] Pizer, R.; Selzer, R. *Inorg. Chem.* **1984**, *23*, 3023.
[14] Gilman, J. W.; Vanderhart, D. L.; Kashiwagi, T. *Thermal decomposition chemistry of poly(vinyl alcohol);* ACS Symposium Series 599; American Chemical Society, **1995**.
[15] Jimenez, M.; Duquesne, S.; Bourbigot, S. *Thermochim. Acta*. **2006**, *449*, 16.
[16] Dressler V.L, Pozebon, D., Curtius, A. J. *Spectrochim. Acta Part B* **1998**, *53*, 1527.
[17] Piperaki, E., Berndt, H., Jackwerth, E. Anal. Chim. Acta **1978**, 100, 589.
[18] Brandrup, J; Immergut, E.H; Grulke*. Polymer handbook*. 4th. ed. New York: J. Wiley, **1999**.