Alternative use of cross-linked polyallylamine (known as Sevelamer pharmaceutical compound) as biosorbent

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ABSTRACT

In this study, an alternative use of Sevelamer carbonate (SEV, a cross-linked polyallylamine which is a widely known pharmaceutical compound) was suggested. The existence of primary and secondary amino groups (with different ratios) in its molecule increases its adsorption potential and use as biosorbent material. SEV was tested as biosorbent material aiming the removal of heavy metals and dyes from simulated effluents. As heavy metals and dyes, hexavalent chromium (Cr(VI)) and Remazol Brilliant Blue RN (RB) were used, respectively. A full adsorption study was done confirming the strong adsorption capability of SEV. The maximum theoretical adsorption capacity ($Q_m$) was 772 and 485 mg/g for single-component solutions of RB and Cr(VI), respectively; the respective values for binary mixtures of the same concentration (200 mg/L) were 445 and 309 mg/g respectively (calculated after fitting to Langmuir-Freundlich isotherm model at 25 °C). The same experiments were also done at increasing temperatures (45 and 65 °C) concluding thermodynamic remarks ($\Delta H^0 > 0$; $\Delta G^0 < 0$; $\Delta S^0 > 0$). The effect of contact time was analyzed running kinetic adsorption experiments and fitting them to pseudo-second order kinetic equation. The reusability was evaluated completing successfully 20 cycles of reuse (adsorption/desorption). The adsorption mechanism among SEV molecules and Cr(VI) or/and RB was clarified using FTIR spectroscopy before and after adsorption in line with a detailed theoretical modeling which provided important calculations. SEV was also characterized using swelling experiments, BET, SEM, XRD, TGA techniques.

Keywords: Sevelamer; Hexavalent chromium; Azo dye; Adsorption; Modeling
1. Introduction

The use of various pharmaceutical compounds is not only very common nowadays but necessary for the human health. Sevelamer carbonate (denoted as SEV) is a phosphate-binding drug and usually used to prevent patients with chronic kidney disease from hyperphosphatemia [1]. It is a copolymer of polyallylamine cross-linked with epichlorohydrin [2]. Its properties make it an environmental-friendly material, but its numerous amino groups give it the potential to be a super-biosorbent. The most promising is that none work has been published until now aiming the alternative use of pharmaceutical compounds as sorbents. The latter was another motive to study SEV as biosorbent.

Dyes and heavy metals were selected as under-investigation pollutants, due to their toxic, hazardous and carcinogenic impact on human health, when they exist in environmental effluents (commonly in aqueous media) [3]. More than 700,000 tons of dyeing effluents are generated each year [4], and nearly 40% of them corresponds to azo reactive dyes [5]. Based on the above, the effluents of heavy metals and dyes are very dangerous for the human health and need treatment. Among the numerous applied techniques (electrochemical, biological treatments etc) for decontamination of this type of effluents, adsorption shows impressive applicability due to its cost-effectiveness and simplicity of the experimental design [6-11]. This is the reason for which many researchers nowadays turn their interest to synthesis of various adsorbent materials for decontamination treatments. Many literature examples exist, having as topic the removal of dyes or metals from wastewaters [12-17].

The selection of the heavy metal and dye for the adsorption tests was very careful. Model pollutants with real existence and applicability were selected. In particular, some metal complex dyes (Cr(VI)-based) are used for fixation [18,19]. So, especially the concentration of Cr(VI) was bibliographically found to be up to 13 mg/L for azo reactive dyes during the dyeing of wool textiles [20]. Similarly, the concentration of azo dyes in the aqueous effluents
were found to be from 5 to 800 mg/L [21]. Based on the above, the alternative use of SEV seems to be a challenge for the removal of Cr(VI) (negative ion) and/or an azo dye (with negatively charged groups). In this purpose, the whole study obtains a practical concept.

This work contains the detailed characterization of SEV biosorbent used for Cr(VI) and Remazol Brilliant Blue RN removal with techniques as Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-Ray diffraction (XRD), Thermogravimetric analysis, and swelling experiments. In order to adsorptively evaluate SEV, some crucial adsorption parameters were studied as the influence of the solution pH (estimating some limitations because of precipitation etc), contact time, and initial concentration of metal or/and dye (in single-component solutions and in binary aqueous mixtures). The adsorption interactions were also calculated using 20 cycles of reuse (adsorption/desorption) were also carried out.

2. Materials and Methods

2.1. Materials

Sevelamer carbonate was used in powder-form and these solid particles were in the range of 10-50 μm. It was purchased by Formosa Laboratories (Louchu County, Taoyuan, Taiwan). The water used for the adsorption experiments was purified using a Barnstead water purification system (Dubuque, IA, USA). K₂Cr₂O₇ (puriss. p.a. ≥99.0%) was purchased from Fluka and used for the preparation of aqueous stock solutions of hexavalent chromium. Remazol Brilliant Blue RN (denoted as RB) was the azo reactive dye which supplied by DyStar and used as dye model pollutant. Fig. 1 presents the chemical structures of SEV (Fig. 1a) and RB (Fig. 1b). For the preparation of binary mixtures for selectivity tests (denoted as Mix), the concentrations of RB and Cr(VI) used were equal for being directly comparative the results.
2.2. Characterization techniques

XRD patterns were recorded on a XRD-diffractometer (model Miniflex II, Rikagu, Japan) at 40 kV, 40 mA over the range of 5-45° 2θ using a CuKα radiation wavelength of 0.15405 nm for crystalline phase identification. SEM images were performed with electron microscope (model Zeiss Supra 55 VP, Jena, Germany). The accelerating voltage was 15.00 kV and the scanning was performed in situ on a sample powder. FTIR spectra of the samples were taken with a FTIR-spectrometer (model FTIR-2000, Perkin Elmer, Dresden, Germany) using potassium bromide disks (thickness ~500 μm). The spectra were recorded from 4000 to 400 cm\(^{-1}\) at 2 cm\(^{-1}\) as resolution (32 co-added scans), presented with baseline correction and converted to the absorbance mode. A particle size microanalyzer (model Malvern MasterSizer 2000, Malvern Instruments Ltd, Worcestershire, UK) was used to determine the particle size distribution of a suspension of SEV in sunflower oil by laser light scattering. D\(_{0.9}\), D\(_{0.5}\) and D\(_{0.1}\) are the particle diameters determined respectively at the 90\(^{th}\), 50\(^{th}\) and 10\(^{th}\) percentile of undersized particles. The thermal stability of samples was measured (6 mg of sample was used for each measurement) by thermogravimetric analysis using TGA thermal analyzer (model Pyris 1 TGA, Perkin-Elmer, Dresden, Germany) with 10 K/min as heating rate and 100 mL/min as flow rate of nitrogen atmosphere. The swelling experiments were performed at the optimum pH value found/selected after adsorption experiments (pH 4). 3 g of SEV were allowed to swell in deionized water for 24 h. The pH was fixed with with micro-additions of acid or alkali (0.01 M HCl or 0.01 M NaOH). After 24 h, the solid swollen particles were collected and weighed. The swelling degree (SD, %) was calculated (Eq. (1)), where \(m_{sw}\) (g) is the mass of the swollen SEV particles after 24 h, and \(m_0\) (g) is the initial mass of the SEV particles before swelling.
All SEV particles were used after pre-swelling for 24 h in aqueous media. That was done, because the target was to simulate the conditions of adsorption columns, where the swelling of solid particles is one of the most crucial parameters regarding the effectiveness and feasibility of the adsorbent used. It is fact that if any adsorbent material presents high SD (%), it is very difficult to be used in columns due to the inevitable scenario of fouling.

2.3. Adsorption experimental procedure

The experimental design was done in batch mode and all experiments were carried out 3 times. The first parameter tested was the effect of solution pH. Conical flasks were placed in temperature-controlled shaking water bath (model Julabo SW-21C, Seelbach, Germany), having 50 mL of aqueous solutions of RB or Cr(VI) \((C_0 = 200 \text{ mg/L})\). Then, 0.05 g of SEV were added and the pH was initially adjusted using aqueous solutions of acid or base \((0.01 \text{ M HCl and/or 0.01 M NaOH})\) to reach fixed pH values of 2-12. The flasks were stoppered, the agitation speed \((N)\) of shaking bath was adjusted at 150 rpm and its temperature at 25 °C. For all experiments, the temperature accuracy was ±1 °C. The flasks were left shaking for 24 h and then the residual Cr(VI) or RB concentration was estimated after analysis. The analysis of Cr(VI) was done using UV-Vis Spectrophotometer (model U-2000, Hitachi) at \(\lambda = 540 \text{ nm}\) (according to the 1,5-diphenyl-carbazide method [22]), while the residual RB concentration was done at \(\lambda = 588 \text{ nm}\).

Having determined the optimum pH value from the aforementioned procedure, the effect of contact time on adsorption was then investigated. Keeping all parameters same \((m = 0.05 \text{ g}, V = 50 \text{ mL}, N = 150 \text{ rpm}, T = 25 \text{ °C})\) and adjusting the pH value at the optimum found above \((\text{pH} = 4)\), the content of the flasks was similarly prepared \((C_0 = 200 \text{ mg/L})\) and placed
to the bath. In order to observe the adsorption kinetic behavior, the first flask was removed from the bath after 5 min and immediately analyzed. In the same manner, after fixed time intervals (5 min - 24 h), the Cr(VI) or RB residual content of each flask was measured.

For the isotherm experiments, the procedure was the same again keeping all factors constant (m = 0.05 g, V = 50 mL, N = 150 rpm), using the optimum pH value found above (pH = 4) and allowing the shaking of flasks until equilibrium (120 min for SEV-Cr(VI) and 360 min for SEV-RB, as it is found after kinetic experiments). The only changing parameter was the initial concentration of Cr(VI) and RB (C₀ = 20 - 1000 mg/L). The isotherms were run at three different temperatures (T = 25, 45, 65 °C). The equilibrium amount in the solid phase (Qₑ, mg/g) was calculated according to the following equation (where C₀ and Cₑ (mg/L) are the initial and equilibrium concentrations of Cr(VI) and RB, respectively; V (L) is the volume of aqueous solution; m (g) is the SEV mass used):

\[
Q_e = \frac{(C_0 - C_e)V}{m}
\]  

(2)

2.4. Reuse (desorption) experimental procedure

Before running the desorption experiments, the respective adsorption experiments were carried out with the following conditions: pH = 4; C₀ = 200 mg/L; T = 25 °C; t = 24 h) After the end of adsorption experiment, the SEV particles were removed from the supernatant (with filtration). Then, these samples were placed in flasks using deionized water as eluant with pH-adjusted values (2-12). In this way, the optimum desorption pH value was found (pH =10). The reuse potential of SEV was tested after repeating the above procedures (firstly adsorption and then desorption) for 20 times.

2.5. Selectivity tests (binary mixtures)
Selectivity tests were also performed in order to find (i) the influence on adsorption of each pollutant in the co-existence of other and (ii) if it is possible to use SEV as multi-biosorbent for simultaneous removal of different types of pollutants. The experiments done were just the same as those of isotherms at only 25 °C, but using both $C_{0,\text{Cr(VI)}} = 200 \text{ mg/L}$ and $C_{0,\text{RB}} = 200 \text{ mg/L}$.

2.6. Theoretical calculations

In order to determine the adsorption behavior especially of RB molecules onto SEV, it has additionally theoretically examined the interaction of the azo reactive dye (RB) with sevelamer (SEV) within the framework of density functional theory (DFT). This was not done for the other case of interactions between SEV and Cr(VI), because ions have not many and different functional groups as RB has.

All-electron density functional theory calculations were performed including dispersion corrections (DFT-D2) within the framework of the generalized gradient approximation. The maximum interaction energy configurations of RB with SEV were identified through potential energy surface (PES) scans taking into account various distances and orientation. All of the calculations, i.e. geometry optimizations, PES scans and interaction energy computations, were performed using the B97-D functional of Grimme [23]. The B97-D functional performance is exceptionally good for non-covalently bound systems and pure van der Waals complexes [23]. The initial geometry optimizations as well as the relative conformational search was performed using the SVP basis set [24]. The larger basis set of triple-zeta quality def-TZVP [25] was used for the final round of calculations which includes the calculation of the interaction energy curves. The empirical parameterization of DFT–D methods partially accounts for basis set superposition errors (BSSE) and counterpoise (CP) corrections [26] are not needed as long as properly polarized triple zeta basis sets are used, such as the ones used here at the final round [23,27,28].
Tight convergence criteria were placed for the SCF energy (up to $10^{-7}$ Eh) and the one-electron density (rms of the density matrix up to $10^{-8}$) as well as, in regard to the geometry optimizations, for the norm of the Cartesian gradient (residual forces both average and maximum smaller than $1.5 \times 10^{-5}$ a.u.) and residual displacements (both average and maximum smaller than $6 \times 10^{-5}$ a.u.). Solvent effects were included for water using the integral equation formalism variant of the polarizable continuum model (IEFPCM), as implemented in the Gaussian package [29]. All of the calculations were performed using the Gaussian package [29].

3. Results and Discussion

3.1. Characterization of SEV biosorbent (BET, SEM, XRD, TGA, Swelling)

At first based on the particle size analysis, the particle diameters determined of SEV were $D_{0.9} = 60 \, \mu m$, $D_{0.5} = 40 \, \mu m$ and $D_{0.1} = 20 \, \mu m$. Furthermore, a first approach for investigating the surface morphology of SEV was realized taking SEM images. As it can be seen from Fig. 2a, SEV particles have not uniform shape which is accordance to the particle size analysis. It is obvious that no porosity seems to exist. The latter was also confirmed with BET measurements, according to which the total pore volume was $1.381 \times 10^{-2}$ cc/g for pores smaller than $8206.6 \, \AA$ (diameter) at $P/P_0 = 0.99767$. The surface area was calculated equal to $2.273 \, m^2/g$. After RB adsorption onto SEV particles (SEV-RB), the surface morphology of them seems to be similar (image not shown). The same was also illustrated after Cr(VI) (Fig. 2b) and Mix adsorption (Cr(VI)+RB) (Fig. 2c). To examine the distribution of Cr(VI) on SEV surface, chromium distribution maps were taken both for SEV-Cr(VI) and SEV-Mix. When the heavy metal is adsorbed in single-component mode, more in number Cr(VI) ions are adsorbed onto SEV surface. This is clear from (Fig. 2d), where the number of dots (traces) corresponded to chromium are more in number. On the contrary, in the presence of RB molecules, the adsorption phenomenon becomes antagonistic and some adsorptive sites are
covered by RB molecules and therefore the existence/distribution of Cr(VI) on SEV surface becomes limited (Fig. 2e). The latter was also confirmed observing the energy dispersive X-Ray analysis (EDAX) for SEV-Cr(VI) and SEV-Mix (Fig. 2f).

XRD patterns of the material before and after adsorption are illustrated in Fig. SI1 (Supporting information section). As it can be seen, neat SEV seems to be amorphous. The same observation was also reported in literature [30]. The same amorphous structure was observed for all loaded materials indicating that adsorption interactions did not influence the morphological structure of materials. In literature there is slight reference to the morphological structure of pure SEV.

TGA and DTA curves of neat SEV and those after adsorption (RB, Cr(VI) and Mix) are displayed in Fig. 3. The thermal degradation of SEV presents 4 main weight-loss steps. The first step of weight loss (9-10%) up to 133 °C corresponds to the weight loss of the absorbed water molecules. The second degradation step was in the range of 140-200 °C and presented a weight loss of 10 %wt due to the degradation of amino groups [31]. A weight loss of 50-55% wt (main decomposition step) was mainly taken place at the temperature range of 480-600 °C and associated with the decomposition of methylene groups (CH₂) [31]. The total weight loss of the sample was 100% at about 600 °C.

In the case of loaded materials, it is clear that all of these materials demonstrate similar decomposition mechanism, with slight differences. SEV-Cr(VI) and SEV-Mix illustrate similar mechanism of degradation, differing in the lower degradation rate for SEV-Mix. SEV-RB presents 100% degradation rate, which can be attributed to the fact that RB is an organic compound (Fig. 1b). There is a high residue for SEV-Cr(VI) and SEV-Mix (35.86 and 24.85%, respectively), due to the Cr(VI) adsorption in both cases. This is an indication that SEV is an effective biosorbent since it can adsorb large amounts of toxic Cr(VI).
Fig. 4 presents the swelling ability of SEV to adsorb/bind water molecules after its immersion on it. These experiments have been carried out studying simultaneously the kinetic swelling behavior, which can indicate how SEV can act in real conditions of adsorption-column systems. Based on the experimental swelling results, the maximum swelling degree (SD, %) was 52%. This number is in accordance to another work, which reported a complete study about swelling of sevelamer but in its hydrochloride-derivative [32]. Observing the swelling kinetics of this material, 3 stages are clear. A sharp increase of the adsorption of water molecules by SEV in the first 60 min of immersion, which then followed by a milder increase (60-280 min). After this time, SEV seemed to be saturated from water molecules and did not increase its mass, corresponding to a swelling equilibrium (280 min - 24 h). It is fact that this swelling behavior of SEV has been influence by many factors; but surely the most important is the chemical structure of the materials. SEV has complex polymeric structure and therefore, presents medium swelling ability. This is good in the case of its use as biosorbent, because higher SD (%) can prevent it from its use in columns.

3.2. Effect of pH

As it was described in the experimental procedure (section 2.2), there was a strategy to investigate and explain step-by-step the most important parameters regarding the adsorption process. Therefore, the first parameter studied was the influence of the solution pH on adsorption; Fig. 5 illustrates the aforementioned effect. A serious drawback of this work (but this strengthens its novelty) is the complete absence (until now) of comparative literature for the use of SEV as biosorbent. Therefore, it is necessary to face this material as classic/simple compound but making particular hypotheses. The parameters (a, b, c, m) of the chemical structure of SEV (Fig. 1a) will be ignored and the first hypothesis will be that SEV is a bisorbent having in its structure multiple amino groups (either primary or secondary).
Although Cr(VI) is a heavy metal ion with clear structure and particular transformations over the whole pH range, the other pollutant used (RB) has many functional groups (sulfonic, sulfuric, azo) (Fig. 1b) which is a hindrance making clear observations. In the case of Cr(VI) adsorption onto SEV, at acidic pH values, chromium occurs in higher percentages as HCrO$_4^-$, leading to the strongest electrostatic attraction between SEV and metal. The difference in adsorption capacities percentages between pH 2 and 4 (72% and 85%, respectively) may be presumably attributed to the protonation degree of amino groups of SEV at these acidic conditions. Cr(VI) presented its maximum removal at pH 6 (174 mg/g; 87%) and then at higher pH values an intense decrease was observed (126, 64, 38 mg/g at pH 8, 10, 12, respectively). This may be due to the fast transformations of protonated and deprotonated forms of SEV amino groups [33]. Explaining the above, it is known that amino groups are protonated at strong acidic pH values and deprotonated at alkaline ones. However, the charge of the whole SEV molecule is not clear at near neutral pH conditions (pH = 6-7), and the situation is complex because amino groups are in the border of protonation and deprotonation.

In the case of RB adsorption onto SEV, the explanation of the pH-behavior is more difficult because of the existence of different functional groups. Based on the chemical structure of RB molecule (Fig. 1b), the dye molecule is negatively charged in the whole pH range. As a result, the higher adsorption capacities were observed at acidic conditions (194, 196 mg/g at pH 2, 4, respectively). So, higher percentage of protonated amino groups of SEV can interact with negatively charged groups of RB at these acidic pH conditions. However, as the pH increases (pH>6), the adsorption capacity for RB decreases (150, 122, 108, 50 mg/g at pH 6, 8, 10, 12, respectively). Based on that, the optimum pH value selected for performing the next experiments (kinetics, isotherms) was 4, because at this pH value the removal of RB was the highest and the Cr(VI) was nearly the same as that at pH 6 (85% (170 mg/g), 87% (174 mg/g) at pH 4, 6, respectively).
3.3. Kinetic experiments

The determination of time period in which the adsorbent-adsorbate system reaches in equilibrium is very important. The industrial adsorbers work until this time and therefore operation time can be saved (saving energy etc). The above can be found running adsorption kinetic experiments. The experimental results in the present study were fitted to the pseudo-second order kinetic equation, as it is considered to be widely known kinetic model of adsorption literature [34]. This model can be transformed in linear form and expressed by Eq. (3) [35], where \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the rate constant:

\[
\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \left(\frac{1}{Q_e}\right)t
\]

In order to solve the above equation, the slope \((1/Q_e)\) and intercept \((1/k_2Q_e^2)\) of the plot \((t/Q_t)\) versus \(t\) can give the parameters of \(k_2\) and \(Q_{e,\text{theor}}\). The straight lines in plots of Fig. 6 show an excellent agreement of experimental data with this model.

As it is presented in Fig. 6, the kinetics of SEV-RB and SEV-Cr(VI) were not similar. In the case of metal adsorption, the phenomenon is very fast. Observing the kinetic data, in the first 5 min after the adsorption beginning, SEV adsorbed 29 mg/L from Cr(VI) (from 200 to 171 mg/L), while the residual Cr(VI) concentration after the first hour of adsorption was 51 mg/L which corresponds to 88% of its final removal. The adsorption reached in equilibrium after 2 h (120 mins). On the contrary, in the case of RB adsorption onto SEV (RB molecules are large and not such agile as Cr(VI) ions), in the first 5 min after the adsorption beginning, SEV adsorbed 15 mg/L from RB molecules (from 200 to 185 mg/L), while the residual RB concentration after the first hour of adsorption was 44 mg/L which corresponds to 70% of its final removal. The adsorption reached in equilibrium after 6 h (360 min). The rapid adsorption of Cr(VI) versus RB molecules can be explained taking into account the fast
diffusion of ions (small size of Cr(VI)) comparing to those of RB molecules). Ions can move more easily in the SEV network and cover rapidly the empty adsorptive sites.

The kinetic parameters after fitting are presented in Table SI1 (Supporting information section) and the successful fitting of this pseudo-second order equation can be confirmed calculating the absolute value of the difference between the experimental adsorption capacity ($Q_{e,\text{exp}}$) and theoretical one $Q_{e,\text{theor}}$. The theoretical values slightly differed from the experimental ones, which gave approximately 2% deviation.

3.4. Isotherms

After the determination of the optimum pH value and contact time, the next target is to find the maximum theoretical adsorption capacity of SEV and the temperature effect on equilibrium. The adsorption equilibrium results were fitted to the combinational Langmuir-Freundlich (L-F) isotherm equation [36]:

$$Q_e = \frac{Q_m K_{LF} (C_e)^b}{1 + K_{LF} (C_e)^b}$$

where $Q_m$ (mg/g) is the maximum amount of adsorption; $K_{LF}$ (L/mg)$^{1/b}$ is the L-F constant; b (dimensionless) is the L-F heterogeneity constant.

Fig. 7 illustrates the isotherms at 25, 45, and 65 °C for the adsorption of Cr(VI) and RB onto SEV. An increase of the initial concentration of either RB or Cr(VI) caused an increase in the adsorbed amount ($Q_e$) on SEV. Observing the data exported after fitting in Table 1, the maximum adsorption capacity for RB was 1.6 times larger (772 and 485 mg/g for RB and Cr(VI), respectively). This calculation is not true, because if $Q_m$ is transformed to mmol/g (instead of mg/L), the results will be 1.23 and 7.82 mmol/g for RB and Cr(VI), respectively; which corresponds to 6.4 times larger adsorption for Cr(VI). Therefore, it is not correct to directly compare dye and ion adsorption capacities.
All isotherm factors exported after L-F fitting are given in Table 1. With increasing the adsorption temperature from 25 to 65 °C, a slight increase of the adsorption capacity was observed for RB uptake, while the respective of Cr(VI) was more significant. For RB removal, SEV enhanced its Qm from 772 mg/g at 25 °C to 804 mg/g at 45 °C, and finally 811 mg/g at 65 °C. More intense increase was observed for Cr(VI) adsorption; from 485 mg/g at 25 °C to 622 mg/g at 45 °C, and finally 686 mg/g at 65 °C. A possible explanation about this differentiation is that the increase of temperature helps the mobility and diffusion of the Cr(VI) ions into the SEV network. Instead, RB molecules are larger, have smaller diffusion coefficient and therefore cannot be drastically influenced.

In order to explain the above, the diffusion coefficient of Cr(VI) and RB in water (abbreviated as \( D_{p,\text{wat}} \)) was calculated at three temperatures (25, 45, and 65 °C) according to the Wilke-Chang correlation [37,38]:

\[
D_{p,\text{wat}} = \left( \frac{T}{\eta} \right) \left( 7.4 \times 10^{-12} \right) \left( \frac{2.6M^{0.5}}{V^{0.6}} \right)
\]

(5)

where \( V \) (cm³/mol) is the molar volume of molecule or ion (calculated by BioMedCAChe 6.1 [39]); \( M \) (g/mol) is the molecular weight of the solvent (water); \( T \) (K) is temperature; \( \eta \) (cP) is the dynamic viscosity of the solvent (for water was found at three temperatures (25, 45, 65 °C) as follows (where \( A = 2.414 \times 10^{-2} \) cP; \( B = 247.8 \) K; \( L = 140 \) K) [38]:

\[
\eta = 10^{\frac{B}{T-L}} A
\]

(6)

Taking into account the different diameters of Cr(VI) ions (0.104 nm [40]) and RB molecules (1.7 nm) along with the different diffusion coefficients of them in water (at 25 °C) (Cr(VI): \( 11.32 \times 10^{-10} \) m²/s [41]; RB: \( 3.54 \times 10^{-10} \) m²/s), it can be concluded the above consideration.

3.5. Thermodynamics
The thermodynamic evaluation of the equilibrium results can give useful conclusions about the biosorbent. Three main parameters have been calculated (the change of Gibbs free energy (ΔG⁰, kJ/mol), enthalpy (ΔH⁰, kJ/mol) and entropy (ΔS⁰, kJ/mol K)) based on the isotherms at 25, 45, and 65 °C. The system of equations below can be used for the calculation of the aforementioned thermodynamic parameters (where Cₘ (mg/L) is the amount adsorbed on a solid at equilibrium and R (8.314 J/mol K) is the universal gas constant) [42]:

\[
K_c = \frac{C_s}{C_e} \quad (7)
\]

\[
\Delta G^0 = -R T \ln(K_c) \quad (8)
\]

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (9)
\]

\[
\ln(K_c) = \left(- \frac{\Delta H^0}{R} \right) \frac{1}{T} + \frac{\Delta S^0}{R} \quad (10)
\]

ΔG⁰ was given from Eq. (8), while ΔH⁰ and ΔS⁰ were given from the slop and intercept of the chart between ln(Kc) versus 1/T (Eq. (10)). These thermodynamic parameters are presented in Table SI2 (Supporting information section). As it is confirmed, SEV presented negative values of ΔG⁰ showing the spontaneous adsorption of RB and Cr(VI). The positive values of ΔH⁰ showed the endothermicity of the process [43], while the values of entropy (ΔS⁰) were positive. The latter reflected the affinity of the adsorbent towards the adsorbate species and shows the increased randomness at the solid/solution interface with increasing degree of freedom of the adsorbed species [43,44].

3.6. Desorption – Reuse

Before the reuse experiments, the first target was to investigate the optimum desorption pH. For both loaded materials (SEV-Cr(VI) and SEV-RB), the concluding remark was the same; the optimum pH desorption values was at alkaline conditions (pH = 10). At his
value, the desorption of Cr(VI) from SEV was 87% and the respective of RB was 94%. This finding seems to be correct, because in general desorption is favored in reverse conditions of adsorption. Many papers give higher desorption percentages for Cr(VI) at acidic conditions. But the appropriate desorption conditions are not constant for a pollutant (i.e. Cr(VI) in this work), but dependent on the adsorbent’s nature and consequently on the adsorbent-adsorbate system. In general, there are published works showing better desorption at alkaline conditions instead of acidic [45,46]. The existence of many functional groups in its molecule (OH, NH, NH₂, NH₂⁺, HCO₃⁻) (Fig. 1a) makes more complex the explanation for desorption interactions. The optimum adsorption pH values were acidic (pH 4), so in reverse conditions the bonds between SEV and pollutants are weakened and finally broken. However, adsorption is not considered to be fully reversible; so incomplete desorption can be suspected for all pH values.

Fig. 8 illustrates the reuse potential of SEV. SEV-Cr(VI) presented better reuse behavior during cycles, because it lost only 7% in 20 cycles (85% in 1st cycle; 82% in 5th cycle; 80% in 10th cycle; 78% in 15th cycle, and 78% in 20th cycle). On the contrary, SEV-RB presented slightly lower reuse percentages and lost 18% totally (96% in 1st cycle; 92% in 5th cycle; 86% in 10th cycle; 82% in 15th cycle, and 78% in 20th cycle). Based on the above, it can be concluded that SEV can be easily reused especially in the case of metal but also for the dye.

3.7. Selectivity tests (dye versus heavy metal)

Selectivity experiments were carried out in order to determine the antagonistic (?) phenomenon of adsorption of RB and Cr(VI) onto SEV. This was done preparing binary mixtures and testing the adsorption equilibrium. Fig. 9 displays the isotherms for binary
mixtures (equal concentrations of Cr(VI) and RB) and those for single-component solutions (for comparison).

It was observed that the isotherm of SEV-RB reduced drastically. According to Table SI3 (Supporting information section), in the presence of Cr(VI) the maximum adsorption capacity ($Q_m$) of SEV-RB from 772 reduced to 445 mg/g, corresponding to reduction of 58%. On the contrary, in the presence of RB the maximum adsorption capacity ($Q_m$) of SEV-Cr(VI) from 485 reduced to 309 mg/g, corresponding to reduction of 37%. This can be attributed to the faster diffusion of Cr(VI) ions which cover the majority of adsorptive sites on SEV surface. The RB molecules can be then adsorbed on the empty sites remaining on SEV.

3.8. Theoretical calculations

In order to identify maximum interaction sites and quantify the magnitude of the interactions between RB and SEV we performed geometry optimization calculations starting from various relative orientations. As a model system of SEV we used an oligomer of two monomers. The structure of the SEV monomer is partially defined by the a and b parameters which are fixed at $a + b = 9$. From the possible values we have chosen $(a,b) = (3,6)$. As we shall discuss the parameter values affect the availability and/or accessibility of the maximum interaction configurations, which also has an impact on the density of the active interaction sites. For the value of pH = 4 that was used for the real system the amine groups (pKa ≈ 6) of SEV are protonated. The protonation of the SEV amine groups has an impact on the structure itself as it slightly expands (swells). To examine this effect we performed geometry optimizations on SEV with and without protonated amine groups. Upon sampling the distances of backbone atoms we found an increase of the distances in the range of 15-19% relative to the unprotonated structures. The pH value was also taken into account for the RB structure. The aromatic sulfonic and aliphatic sulfuric moieties have approximate acidity...
values of pKa = -2.8 and pKa = 1.5-1.6, respectively. Using the Henderson-Hasselbalch equation it is straightforward to deduce that both moieties will remain unprotonated (more so for sulfonic group) in an environment with pH = 4. Thus, we have modeled the RB to include two sodium atoms, one for each of the aforementioned groups.

From the geometry optimizations at various relative orientation we have identified two relative configurations for the amine groups of SEV that lead to maximum interaction magnitudes with RB. The interaction energy of each RB-SEV configuration was calculated using the equation:

\[ E_{\text{int}} = E_{\text{SEV-RB}} - (E_{\text{RB}} + E_{\text{SEV}}) \]  

where \( E_{\text{SEV-RB}} \), \( E_{\text{RB}} \), and \( E_{\text{SEV}} \) are the energies of the combined (interacting) system, the RB molecule and the SEV oligomer, respectively.

In each case (configuration) the main interaction is between the sulfuric or sulfonic group of RB with two amine groups of SEV. The two configurations differ in regard to the neighboring order of (and as a result, the distance that separates) the two amine groups. In Fig. 10 we show the maximum interaction configurations. On the left side (of both the ball and stick and diagrammatic representations) is RB and we show either the active (interacting) sulfonic or sulfuric groups. On the right side is SEV and we show that the preferred (strongest interaction) configurations are with two amine groups that are either neighbors or next nearest neighbors of the SEV monomer structure. As we hinted earlier, the increase of distance associated with the protonation of the amine groups facilitates the approach to the interaction site. However, especially for the sulfonic moiety, the structural details may lead to steric effects that inhibit, or reduce the probability, of the formation of the specific interaction configuration. In Fig. 11, we show the interaction energy curves for each of these configurations.
The energy curves were produced by rigid PES scans starting from the corresponding maximum interaction configuration and subsequently sampling at various distances. The distance $R_{O-N}$ corresponds to that between one oxygen atom of the RB sulfo group with the nearest (i.e. interacting) nitrogen atom of SEV. The interaction energy has a similar form for each configuration with a maximum difference between them of about 15%. The strongest interaction noted is for the case of a sulfuric group interacting with two next nearest neighboring amine groups (site1-config1 of Fig. 11).

With these results at hand it becomes apparent that the structural details of the SEV monomer are of increased importance. Although the parameters $a$, $b$ follow $a + b = 9$, the specific values can further increase or decrease the performance of SEV with respect to its interactions with RB. This has to do with the rigidity of the structure and the availability of active interaction sites. To examine this one must account for long and short amine group chains. If either parameter takes a value of 1 or 2, then the corresponding portion of the SEV structures cannot form the described (maximum) interaction sites (either due to lack of availability or rigidity). In those cases the complementary portion of each SEV monomer will of course be a long chain and thus will have an increased amount amine groups. When these amine groups form slightly unfolded long chains, which is probable since they are protonated, then one RB can interact with amine groups of either edge of the long chain; one RB sulfo group with each edge. We note that an average distance between the sulfuric and the sulfonic groups is 14.2 Å, which is similar in range with the end-to-end distance of five unfolded amine groups. This configuration strongly inhibits a second RB on approaching and interacting with the given SEV amine group long chain. For the long chains the alternative configuration would be interaction with up to three different RB molecules (via their sulfo groups). For the short chains, i.e. those with parameter values of 3 or 4 (and complementary values of 6 or 5, respectively), the situation is much simpler; in each case the SEV monomer
can retain up to four different RB molecules. This can be either in a 1 + 3 or 2 + 2 manner, with respect to the complementary amine group chains.

Overall, the efficiency of SEV with respect to the amount of RB molecules it can retain has a dependence on the a, b parameters, which, at least in theory, can reach up to four times more. However, if secondary interaction sites, and steric effects are taken into account this estimate will be reduced.

3.9. Experimental versus theoretical FTIR spectra

In order to confirm adsorption mechanisms, a comparison of FTIR spectra of neat SEV and loaded materials was done (Fig. 12a). The main bands observed in the infrared spectrum of sevelamer were: (i) a broad band at 3325 cm\(^{-1}\) due to the stretching of \(-\text{NH}\) group, (ii) two bands centered at 2911 and 2845 cm\(^{-1}\) corresponding to the stretching of C–H bonds; (iii) a band centered at 1575 cm\(^{-1}\) which is attributed to the symmetric of N-H bond ; (iv) at 1313 cm\(^{-1}\) is corresponded at C–N bond. In the case of SEV-Cr(VI), SEV-RB, SEV-Mix, it can be found that the main band ascribed on the stretching of –NH group was shifted in lower wavenumbers because of the adsorption mechanism.

The FTIR spectrum can be invaluable on identifying changes in vibrational modes induced by the presence of (or interaction with) nearby species. We have theoretically calculated the IR spectrum of SEV, RB as well as the combined system SEV-RB, which we present in Fig. 12b. At the large wavelength region SEV displays three distinct bands each associated with very specific vibrations. The non-narrow form of these bands is a direct result of the dissimilarities in the molecular environment of the vibrational modes. The band around 3600-3650 cm\(^{-1}\) corresponds to O–H bond stretching modes. Although they are clearly visible in the theoretical spectra, these modes are combined with the second band in the experimental spectra. The second band of the high wavelength region is located around 3430-3270 cm\(^{-1}\).
There are two slightly different sub bands. The first sub band, around 3430-3330 cm\(^{-1}\), is associated with antisymmetric N–H bond stretching of the amino groups, and the second sub band which is around 3310-3270 cm\(^{-1}\) is associated with symmetric N–H bond stretching of the amino groups. The third high wavelength band is in the range of 3120-2920 cm\(^{-1}\). This band is a result of C–H bond stretching modes, and as in the previous case, there are sub bands. The antisymmetric modes, and symmetric modes mainly contribute in the regions 3210-3070 cm\(^{-1}\), and 3044-920 cm\(^{-1}\), respectively (single C–H stretching modes appear in the lower range). In the mid wavelength range the three most important peaks are found in the ranges 1700-1600 cm\(^{-1}\), 1520-1490 cm\(^{-1}\), and 1485-1435 cm\(^{-1}\), which have main contributions from antisymmetric (which exist as a result of amino group protonation) H–N–H bond bending modes, symmetric H–N–H bond bending modes, and H–C–H bond bending modes, respectively.

For the combined system of SEV-RB, a difference that stands out compared to the SEV spectrum are the peaks which we find at 2902 cm\(^{-1}\) and 2856 cm\(^{-1}\). These correspond to the N–H bond stretching modes of the hydrogen atoms that are under the “influence” of the sulfo group of RB. In the real system the peaks would correspond to a range of similar wavenumbers or a band. This is an imprint of the SEV-RB interaction. The result is that modes originally located in the SEV second high wavelength band are now (interacting system) found in this form at the SEV third high wavelength band. The difference in the relative area under these two bands, between the pure SEV and SEV-RB interacting system, can be loosely regarded as a measure of (or at least proportional to) the amount of interacting sites. When we apply this line of thought to our experimental spectra for the SEV and SEV-RB interacting system we indeed find that, for SEV the area under band two is larger than the area of band three, whereas for SEV-RB the reverse is true. Another mode of some significance for SEV-RB is that found at 1079 cm\(^{-1}\), that corresponds to an antisymmetric S–
O bond stretching mode of the sulfo group of RB and specifically for the oxygen atoms interacting with SEV. This peak is also found in the corresponding experimental spectrum, around 1000 cm\(^{-1}\).

4. Conclusions

This study investigates the use of an existed pharmaceutical compound (sevelamer), which is a cross-linked polymer (polyallylamine) as biosorbent. The under-removal model pollutants were the hexavalent chromium and a reactive dye (Remazol Brilliant Blue RN). Based on SEM images, SEV particles have not uniform shape presenting no porosity. After RB, Cr(VI) or Mix adsorption the surface morphology was not changed. XRD patterns revealed the amorphous structure of SEV. The maximum swelling of SEV was 52%, which makes it usable as material in column. The optimum pH value found to be 4 (both for Cr(VI) and RB). In the case of Cr(VI) removal, the adsorption was very fast (equilibrium after 2 h), while for RB removal slower (equilibrium after 6 h). The adsorption capacity calculated after L-F fitting showed the increased of capacity with the increase of temperature. For the loaded materials, the optimum pH desorption value was the same (pH = 10) and the reuse potential was confirmed losing only the SEV-Cr(VI) 7% in 20 cycles and 18% the SEV-RB. The adsorption mechanism of the tested pollutants on SEV was examined both using FTIR spectra (experimental), but also theoretical calculations which gave a similar results.
References

Fig. 1. Chemical structures of: (a) sevelamer carbonate (a, b are the number of primary amino groups (a+b = 9); c is the number of cross-linking groups (c = 1)); m is the large number indicating the extended polymer network groups); (b) Remazol Brilliant Blue RN ((C.I. 19), C_{22}H_{16}N_{2}O_{11}S_{3}, MW = 626.54 g/mol).
Fig. 2. SEM images of: (a) SEV; (b) SEV-Cr(VI); (c) SEV-Mix; (d) Chromium distribution map of SEV-Cr(VI); (e) Chromium distribution map of SEV-Mix; (f) EDAX of SEV- Cr(VI) and Mix.
Fig. 3. Thermogravimetric analysis (TGA) in nitrogen. (Inset: Weight loss derivative versus temperature).
Fig. 4. Effect of immersion time on swelling behaviour of SEV.
Fig. 5. Effect of pH on adsorption of Cr(VI) or RB onto SEV.
Fig. 6. Kinetic curves (fitting to pseudo-second order equation) for the adsorption of Cr(VI) and RB onto SEV at 25 °C.
Fig. 7. Isotherms (fitting to L-F equation) RB and Cr(VI) adsorption onto SEV at 25, 45, 65 °C.
Fig. 8. Cycles of reuse for SEV adsorption/desorption (Adsorption conditions: pH = 4, C₀ = 200 mg/L, m = 1 g/L, V = 50 mL, N = 150 rpm, T = 25 °C, t = 24 h; Desorption conditions: pH = 10, m = 0.05 g, V = 50 mL, N = 150 rpm, T = 25 °C, t = 24 h).
Fig. 9. Isotherms (fitting to L-F equation) RB and Cr(VI) adsorption onto SEV for mixtures.
Fig. 10. Maximum interaction configurations of RB with SEV. The configurations correspond to (a) site1-config1 (b) site1-config2 (c) site2-config1 (d) site2-config2. Sodium atoms have been omitted for clarity.
Fig. 11. Interaction energy curves between RB and SEV for specific configurations and interaction sites (see text).
Fig. 12. FTIR spectra of SEV and SEV-loaded materials: (a) Experimental; (b) after theoretical calculations.
Fig. SI1. X-ray diffraction (XRD) patterns of SEV, SEV-Cr(VI), SEV-RB, SEV-Mix.
Table S11. Kinetic constants for the adsorption of RB and Cr(VI) (C₀ = 200 mg/L) onto SEV (fitting to pseudo-second order equation).

| Pollutant | Qₑ,exp (mg/g) | Qₑ,thor (mg/g) | |Qₑ,exp – Qₑ,thor| |k₂ (g mg⁻¹ min⁻¹) | R² |
|-----------|----------------|----------------|------------------|-----------------|-------------------|-----------------|
| RB        | 195.8          | 199.6          | 3.8              | 5.01×10⁻³        | 0.998             |
| Cr(VI)    | 169.0          | 170.9          | 1.9              | 5.85×10⁻³        | 0.999             |
**Table S12.** Thermodynamic parameters for the adsorption of RB and Cr(VI) onto SEV.

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Table SI3. Equilibrium parameters for RB and Cr(VI) adsorption in mixtures onto SEV (fitting to L-F equation).

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Table 1. Equilibrium parameters for RB and Cr(VI) adsorption onto SEV at 25, 45, 65 °C (fitting to L-F equation).

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