



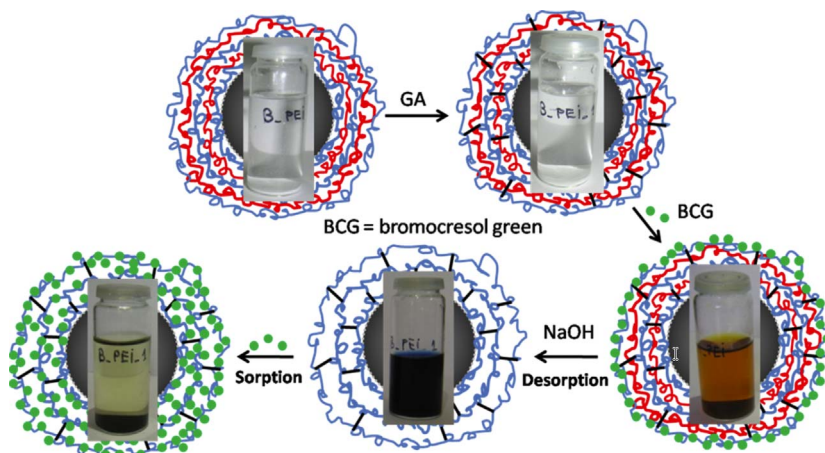
## Cross-linked multilayer films deposited onto silica microparticles with tunable selectivity for anionic dyes



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### GRAPHICAL ABSTRACT



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### ABSTRACT

Cross-linked multilayer thin films assembled using weak polyelectrolytes with specific functional groups are useful materials in solid phase extraction techniques. Herein, we report a facile strategy to modify silica microparticle surfaces for the separation of two anionic dyes [Congo red (CR) and Bromocresol green (BCG)]. Different multilayer films, consisting of poly(ethyleneimine) (PEI) and poly(vinyl amine) (PVAm), as weak polycations, and poly(acrylic acid) (PAA), as a weak polyanion, were deposited onto silica using a layer-by-layer technique. The amount of anionic dyes sorbed onto the composite surface depended on the nature of polycation, deposition conditions, number of polycation layers, cross-linker concentration and on the nature of dyes. The degree of crosslinking by glutaraldehyde (GA) of the composite microparticles strongly influenced the extraction of PAA chains from multilayer during strong basic treatment and subsequently, the sorbed amount of dye and selective desorption capacity of composite. Daisogel/(PEI/PAA)<sub>4,5</sub> cross-linked with 1.00% GA, can be used successfully as a solid support in sorption and selective desorption of two anionic dyes (BCG and CR) only by pH tuning.

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## 1. Introduction

Inorganic/organic composite surfaces have been used in water purification, controlled release of bioactive compounds, sensors design, in catalytic processes, chromatography or in solid phase extraction techniques [1–9]. To synthesize such composites with controlled properties at nanometric scale, several techniques, such as plasma polymerization [10,11], deposition of self-assembled monolayers [12,13] or the layer-by-layer (LbL) strategy [14–21], were applied successfully. LbL deposition using different building blocks (polyelectrolytes, dyes, inorganic nanoparticles, proteins etc.) is employed for surface modification of polymeric membranes to produce novel composite membranes for separation of different species (ions, mono and disaccharides, proteins, alcohols, dyes, etc.) [22–27]. Using different stabilization methods of the deposited organic part, such as thermal [28,29] or chemical cross-linking [30,31], the new synthesized composites could be used/reused in the same sorption/desorption processes [32,33]. Such inorganic/organic composite surfaces with different functional moieties, controlled porosity of the organic network and high stability of polymer chains in different media can be used in solid phase extraction techniques [34]. Using the same LbL technique, Li and coworkers [35,36] obtained innovative systems based on capsules and vesicles with very good loading properties for different chemical and biological species.

In our previous studies, we have investigated the construction and loading/release of some enzymes, drugs and proteins onto different cross-linked multilayer architectures deposited onto inorganic surfaces [37–40]. The amount of loaded species depended on the type and number of polyelectrolytes used in multilayer formation, on cross-linking degree, on the substrate electrical charge and on the isoelectric point of the studied compound.

In this study we focused less on how such composites are made, but more on how they work. Thus, we tried to find the best solution to construct a composite sample with high sorption/desorption capacity, stability in extreme media and high selectivity with potential use in solid phase extraction techniques. The main objective of this work was to investigate the sorption/desorption capacity of two anionic dyes onto/from composite silica microparticles with LbL cross-linked multilayer films on the outer surface. To fabricate the cross-linked multilayers onto Daisogel microparticles, poly(ethyleneimine) (PEI), poly(vinyl amine) (PVAm) and poly(acrylic acid) (PAA), as polyelectrolytes and a cross-linker [glutaraldehyde (GA)] have been used. After deposition of the films, the composite microparticles [Daisogel// (PVAm/PAA)<sub>n</sub> and Daisogel// (PEI/PAA)<sub>n</sub>] were tested in multiple sorption/desorption cycles of two anionic dyes with nearly the same molar mass but with different number of charged groups. To the best of our knowledge, there is no systematic investigation on selective desorption of two anionic species previously sorbed onto modified composite microparticles with cross-linked polyelectrolyte multilayers reported before.

## 2. Materials and methods

### 2.1. Materials

Silica microparticles (Daisogel type with particle diameter of 40–60 μm and 100 nm pore diameters) were purchased from Daiso co. (Japan). Poly(vinyl amine) (PVAm) with molar mass of  $M_n = 15000 \text{ g mol}^{-1}$  was provided by BASF (Ludwigshafen, Germany). Branched PEI ( $M_w = 25000 \text{ g mol}^{-1}$ ) and PAA ( $M_w = 10,000 \text{ g mol}^{-1}$ ) were purchased from Aldrich and were used as received. Congo red (CR) and Bromocresol green (BCG) were purchased from Sigma and were used without further purification. The structures of the anionic dyes are presented in Fig. 1.

### 2.2. Construction of (PVAm/PAA)<sub>n</sub> and (PEI/PAA)<sub>n</sub> cross-linked multilayers onto daisogel microparticles

LbL multilayers were assembled onto Daisogel microparticles by alternated deposition of PVAm or PEI and PAA. The silica microparticles (4 g) were dispersed first in aqueous solutions of PVAm (or PEI) ( $5 \cdot 10^{-3} \text{ mol L}^{-1}$ ). After 60 min, the Daisogel//PVAm (or Daisogel//PEI) composite microparticles were rinsed with water at pH 3.5 to remove the weak polycation excess from the composite. The assembly step of PAA onto Daisogel//PVAm (or Daisogel//PEI) composites was performed at the same polyelectrolyte concentration ( $5 \cdot 10^{-3} \text{ mol L}^{-1}$ ). Following the PAA deposition, the obtained Daisogel//PVAm/PAA (or Daisogel//PEI/PAA) microparticles were rinsed with water at pH 9.5 to remove the weak PAA excess. This protocol was repeated until multilayer architectures with certain number of polyelectrolyte layers was fabricated onto silica. All the samples obtained by this protocol, in which the rinsing steps were carried out with water at alternately pH, were noted with „A”. A similar protocol was applied to obtain the same types of Daisogel// (PVAm/PAA)<sub>n</sub> and Daisogel// (PEI/PAA)<sub>n</sub> composite microparticles, only the rinsing was performed with distilled water (pH 6.5). In this case, all samples were noted with „B”. The letter „n” represents the number of double layers deposited onto solid surface, meaning that a „2n” polyelectrolyte layers were deposited alternately onto Daisogel. If  $n = 4$  then 8 polyelectrolyte layers were deposited alternately (4 layers of PEI + 4 layers of PAA), if  $n = 4.5$  we deposited a total of 9 polyelectrolyte layers (5 layers of PEI + 4 layers of PAA). In the last case, the first and the last deposited layer has been PEI.

After the construction of the films, all the samples were thermally (120 °C) or chemically cross-linked with GA at different concentrations (such as 0.25; 0.50 and 1.00% w/w GA/composite microparticles).

### 2.3. Characterization methods

*Potentiometric titrations* were carried out from acidic to basic range of pH using solutions of HCl and NaOH. A particle charge detector device (PCD 03) (Mütek GmbH, Germany) was used to measure the potential vs. pH for the determination of the point of zero charge (*pzc*) of the Daisogel composite microparticles, *pzc* being defined as the pH where the potential is 0 mV. For each measurement, approximately 10 mg of composites were suspended in the cell in 10 mL distilled water followed by the addition of two drops of HCl 1 M. After an equilibration time of 10 min the titration was carried out by further addition, drop by drop, of 0.01 M NaOH solution. During titration the ionic strength of the suspension in the cell was generated only by the neutralization reaction, without adding any salt in the system. The terms isoelectric point and *pzc* are used interchangeably. Electrokinetic phenomena, like streaming potential, measures zeta potential and when this parameter is zero, meaning that the net charge at the shear plane is zero, we can identify the isoelectric point of the composite. The isoelectric point is expected to be different than *pzc*, but this difference is ignored in practice.

*UV-vis measurements* of BCG and CR solutions in the sorption/release experiments were performed with a SPECORD 200 Plus Analytic Jena spectrophotometer (Germany) at the characteristic wavelengths of 616 nm and 498 nm, respectively.

### 2.4. Sorption/desorption experiments of BCG and CR

The sorption of the anionic dyes BCG and CR onto Daisogel// (PVAm/PAA)<sub>n</sub> and Daisogel// (PEI/PAA)<sub>n</sub> composite microparticles was performed by a batch procedure. Stock solutions of BCG and CR with a concentration of 200 mg dye/L were prepared first, aqueous solutions of various concentrations being prepared subsequently by suitable dilution. Samples of 25 mg composite microparticles were suspended for 60 min (at room temperature) in solutions with different concentrations

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