3D MICROSIZED PROTEIN AMYLOID PARTICULATES AS EFFECTIVE BIOADSORBERS FOR Pb^{2+} IONS

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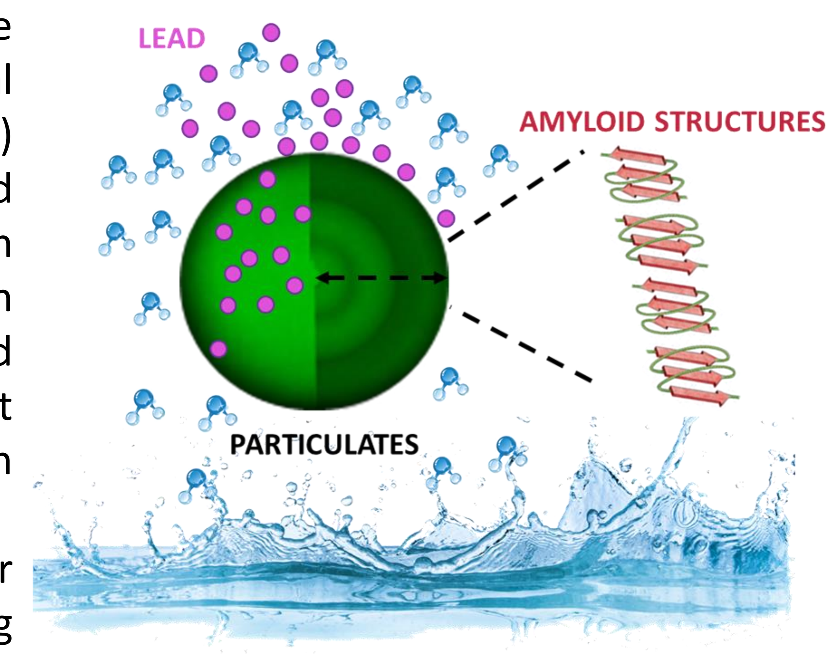
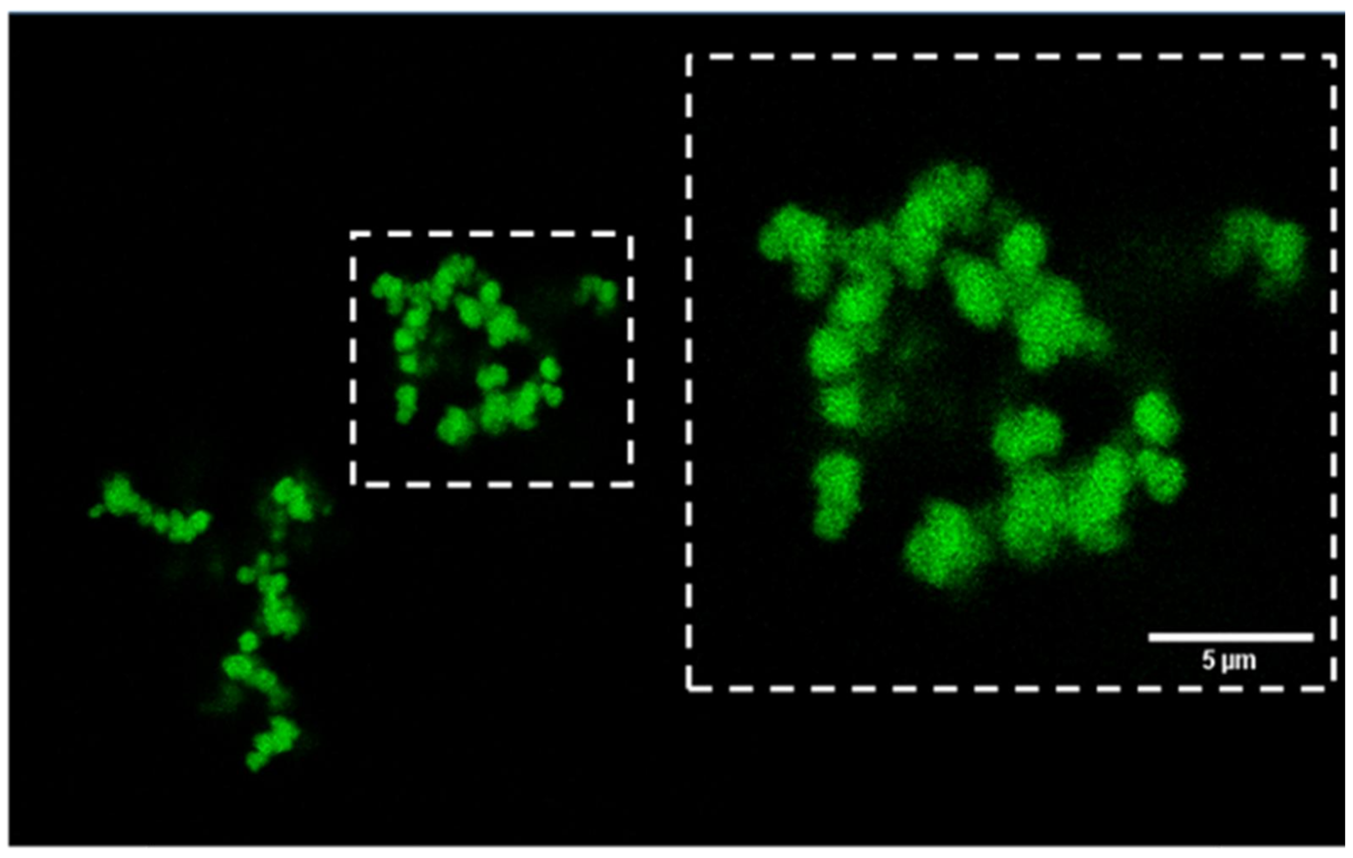
The production of new cost-effective biocompatible sorbent sustainable materials, with natural origins, able to remove heavy metals from water resources is nowadays highly desirable in order to reduce pollution and increase clean water availability. In this context, self-assembled protein materials with highly ordered amyloid structures, stabilised by H-bonds, seems to have a great potential as natural platform for a broader development of highly-tunable structures. By suitably varying solution conditions it is possible to tune aggregate size, surface area and morphologies as well as their physicochemical (hydrophobicity, hydrophilicity, swelling/deswelling properties) and mechanical properties. In this work we show how Bovine Serum Albumin (BSA) particulates, a generic form of protein aggregates, with spherical microsized shape can be used as adsorbents of Pb^{2+} ions from aqueous solution. We used spectroscopy and microscopy methods to characterize the aggregates formation, structure and morphologies. Inductively coupled plasma Optical Emission Spectroscopy (ICP – OES) and Differential Pulse Anodic Stripping Voltammetry (DP-ASV) techniques are used to evaluate uptake/release of metal ions in different conditions of pH, ionic medium, ionic strength, and temperature as a function of time and of adsorbate – adsorbent ratio in kinetic and thermodynamic experiments. The most used kinetic and isotherm equations were used to fit experimental data in order to obtain information about adsorption mechanism, which is the result of the balance of specific interactions with functional groups in protein structure and not specific ones common to all polypeptide chains, and possibly related to amyloid state and to modification of particulates hydration layer.

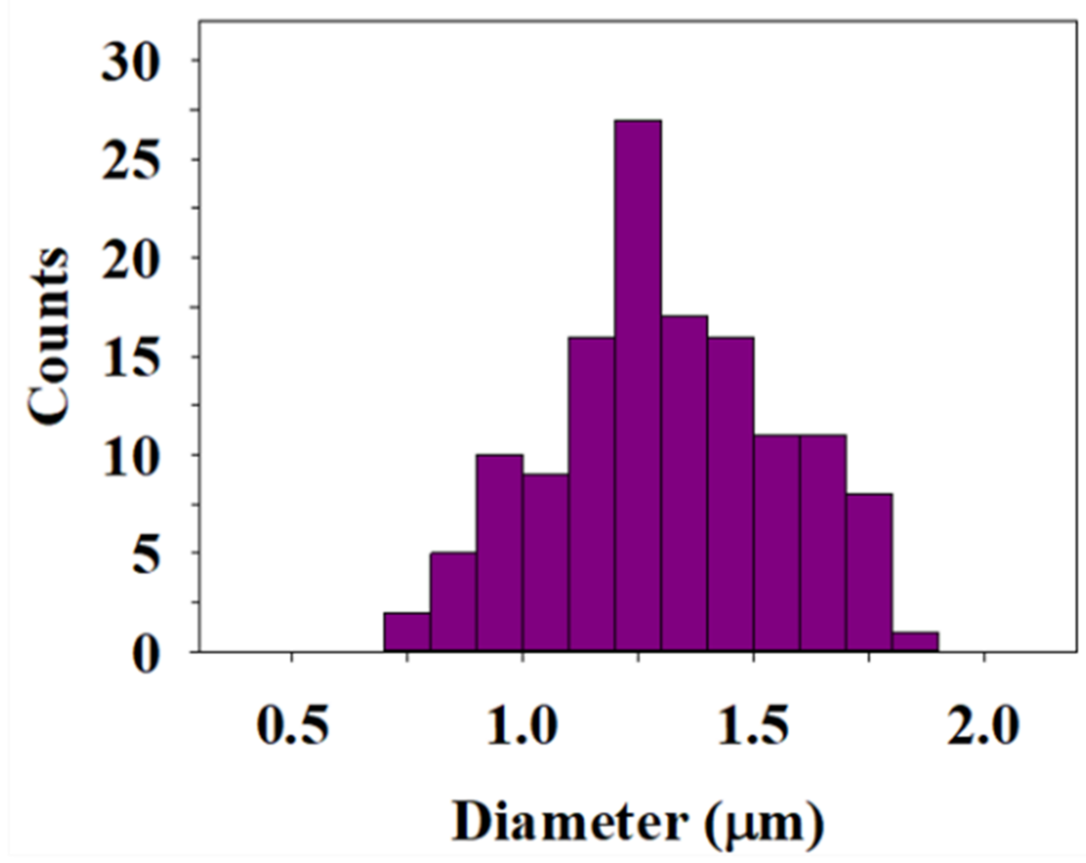
Therefore, it is possible to highlight peculiar structural features essential for metal binding changing aggregation conditions and in turn molecular properties of aggregates. This knowledge may provide extraordinary opportunities towards the design and production of new tailorable bio sorbents using natural raw materials and which can also be exploited for several cycles of purification with minimal reduction in performance.

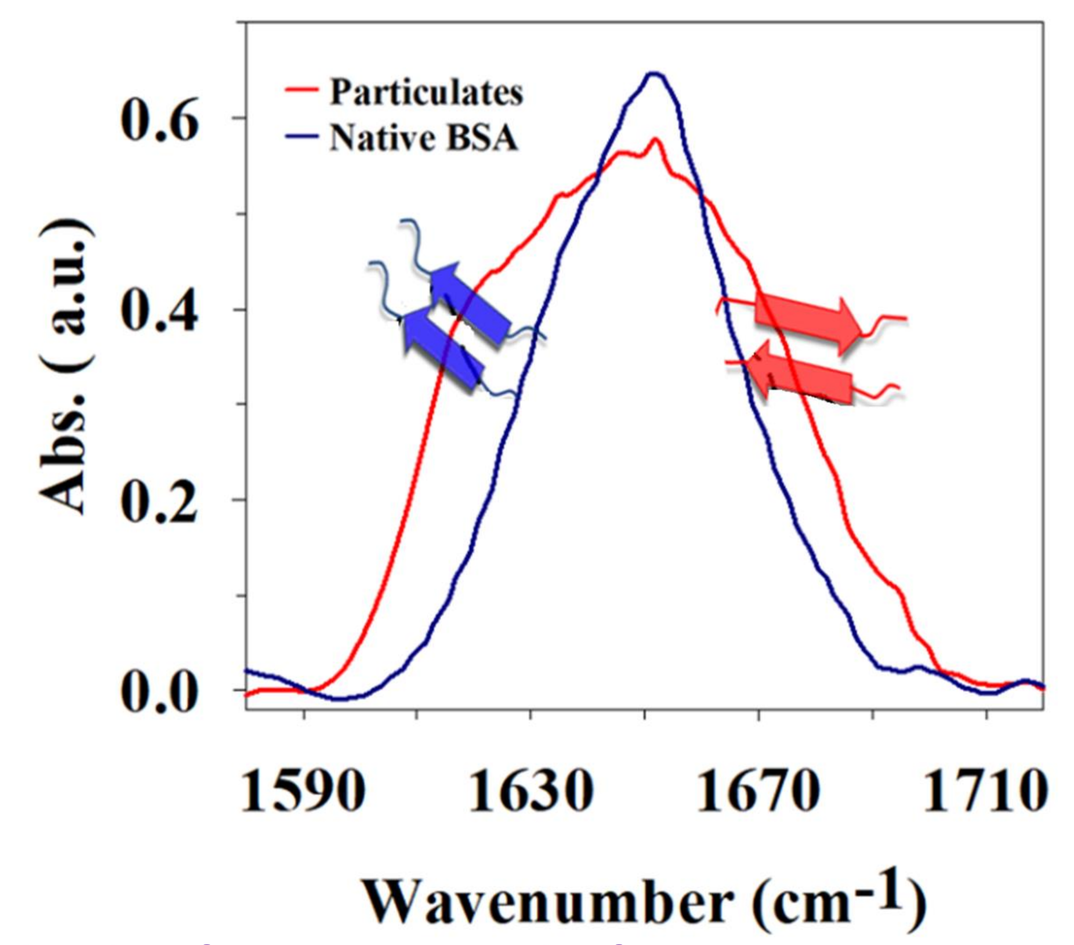


PARTICULATES CHARACTERIZATION

Conditions to form **BSA particulates**: 3 mg mL^{-1} of protein in 20 mM phosphate buffer at pH 5.4, 65 °C, 24 h



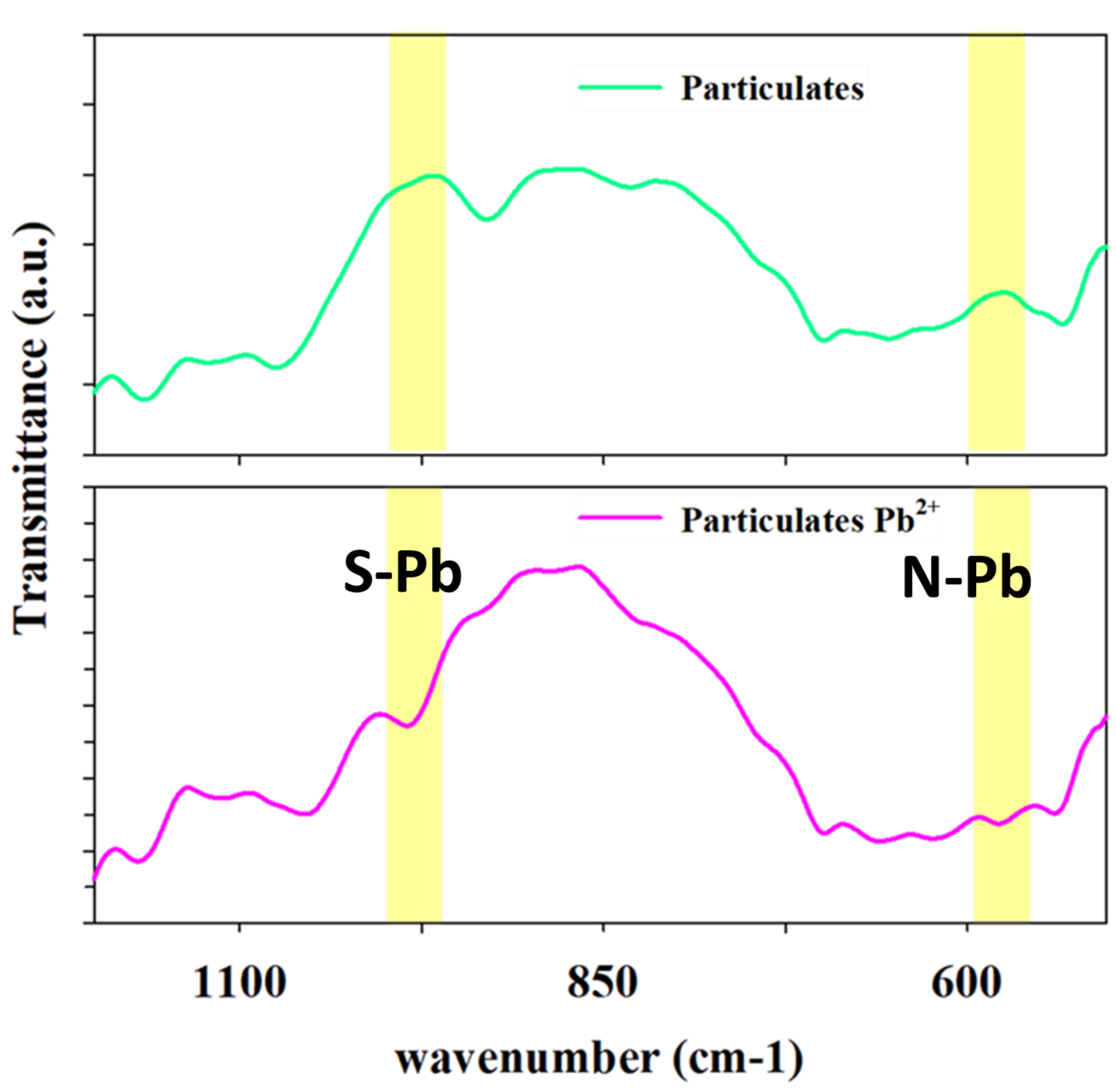




- 3D-microsized spherical aggregates
- Positive to ThT
- ThT uniformly stains the sample: unvaried structural organization between particulates
- Aggregation process induces conformational changes: from α-helix to parallel and antiparallel β-sheets

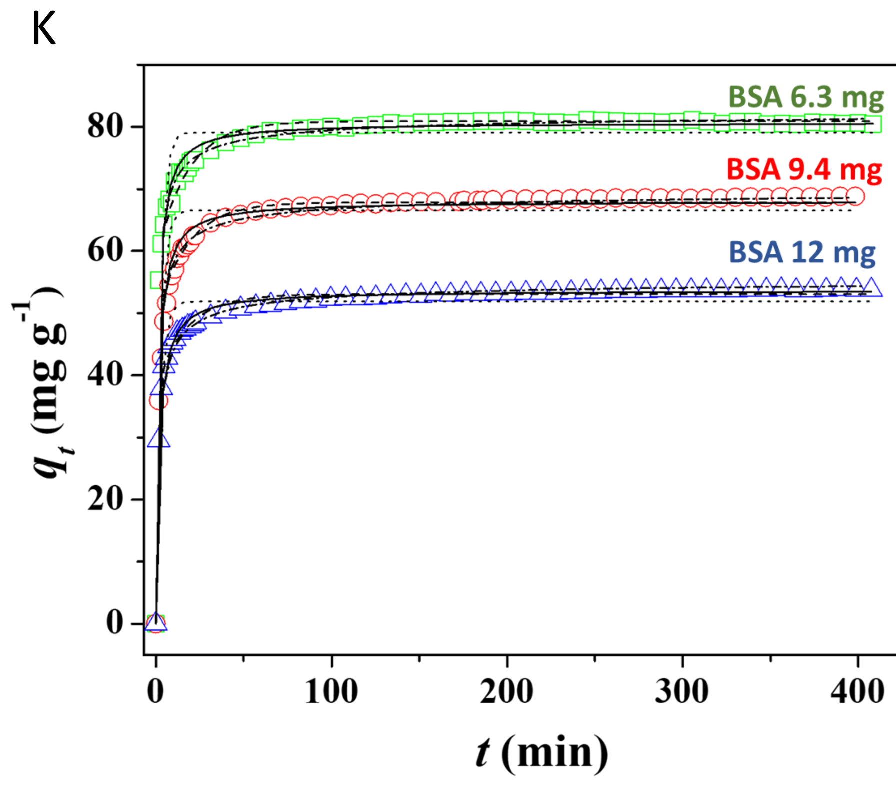
EVALUATION OF LEAD UPTAKE

Lead binding sites



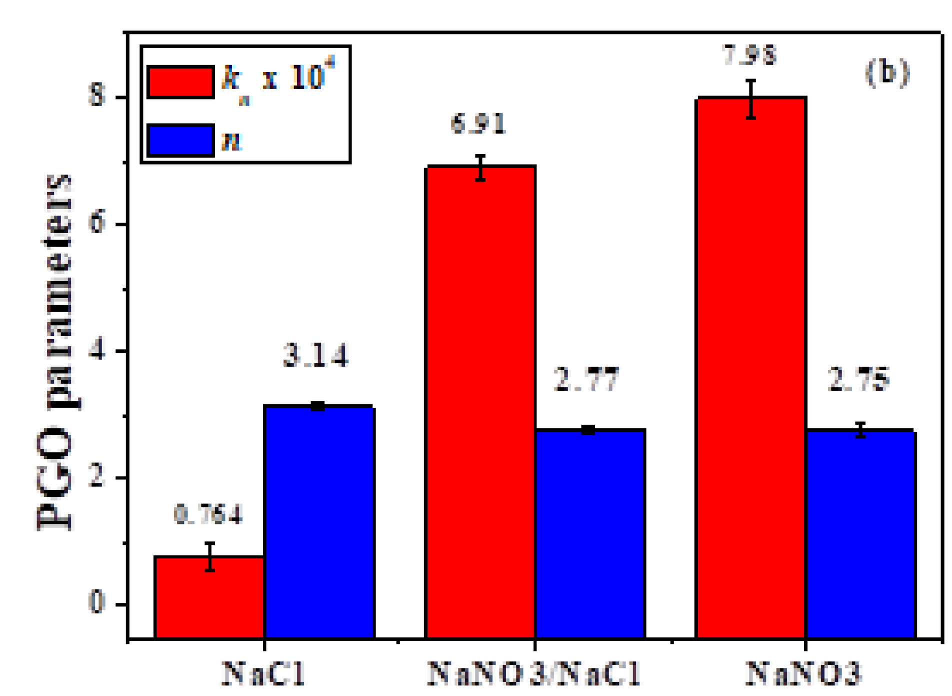
Kinetics of Pb^{2+} adsorption

Experimental conditions: NaCl and $NaNO_3$ both 0.05 mol L^{-1}; c_{Pb2+} = 30 mg L^{-1}, pH = 5, T = 298.15 K



The q_t decreases with the increasing of the amount of particulates

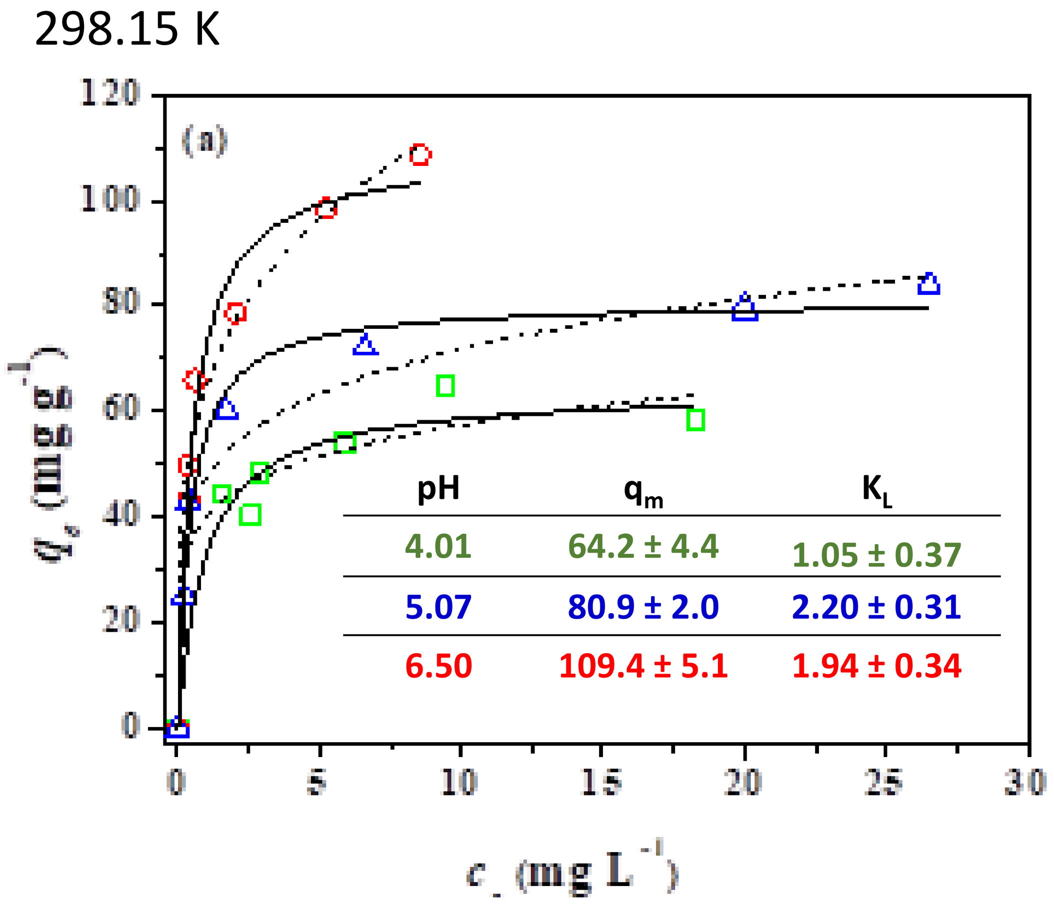
Experimental conditions: different ionic media, at I = 0.1 mol L^{-1}, at pH = 5 and at T = 298.15 K



- k_n depends on ionic medium and decreases with the increasing of chloride concentration
- Pb^{2+} forms species with chloride that hinder the Pb^{2+} adsorption onto particulates

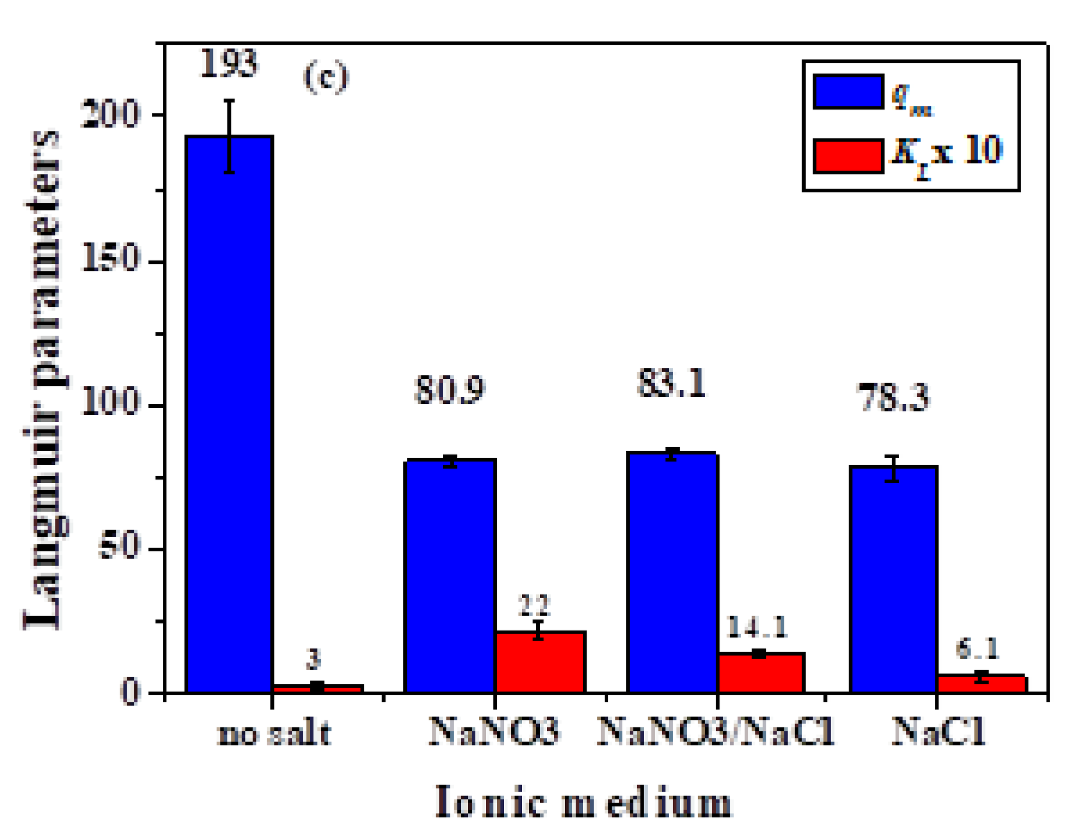
Adsorption equilibria of Pb^{2+}

Experimental conditions: $NaNO_3$ 0.1 mol L^{-1}, at pH = 4.01 (□), at pH = 5.07 (□), at pH = 6.50 (○) and *T* = 298.15 K



- Adsorption ability increases with the increasing of the pH
- At pH 6.5 more groups of BSA are deprotonated and are available for binding with Pb^{2+}

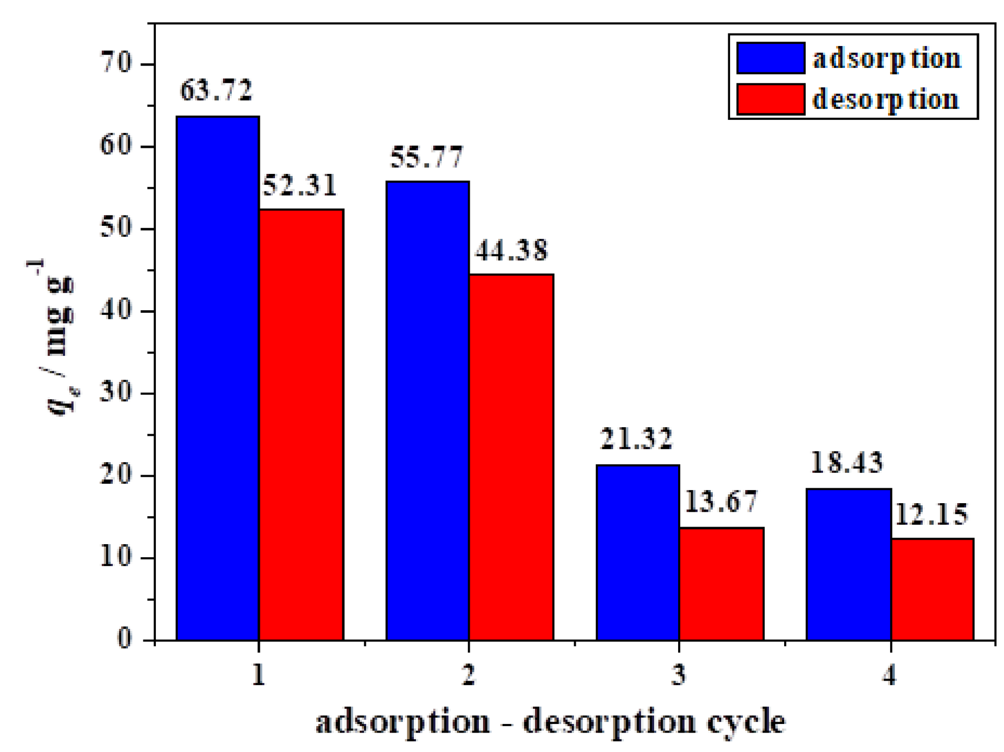
Experimental details: I → 0 or 0.1 mol L^{-1}, pH = 5, T = 298.15 K



- lowest K_L values have been obtained in absence of salt
- Salt could modify water organization favoring Pb^{2+} accessibility

Recycle and reuse of BSA particulates

Experimental details: : c_{Pb2+} = 30 mg L^{-1} , pH = 5.10, $NaNO_3$ 0.1 mol L^{-1} and T = 298.15 K; extractant solution: 20 mL of EDTA 0.1 mol L^{-1}.



Good reuse capacity in the first two cycles although the adsorption ability at the second adsorption step decreases of ~ 12 %

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