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A linear free-energy relationship for the prediction of metal ion complexing properties in hybrid carbon-based scavengers†

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A novel and straightforward approach to accurately predict, through direct potentiometric measurements, the complexing properties and adsorption capacity of novel carbon-based hybrid scavengers toward particular metal ions is described. This innovative approach establishes a linear free-energy relationship (LFER) between the complexing properties of the free-complexing function in solution and the complexing retention capacity of the functionalized carbon-based hybrid material (complexing function supported). In particular, we report the first detailed study concerning the metal ion complexing properties, as well as the complexing mechanisms involved in covalently-bonded carbon-supported hyperbranched polyethyleneimines, towards a series of metal ions of environmental and technical interest, such as Mn^{2+}, Cd^{2+}, Hg^{2+}, Pd^{2+} and Cr^{3+}. The study based on adsorption isotherm measurements and potentiometric studies of non-bonded hyperbranched polyethyleneimines (HBPEIs) (free in solution) and carbon-supported HBPEI (hybrid material, C-PEI) revealed that bonded HBPEI molecules fully define and control the metal ion complexing abilities of C-PEI, while the carbon structure acts only as a solid support. These results corroborate the prevalence of a reliable linear free-energy relationship (LFER) between the retention capacities of the hybrid material (C-PEI) and the complexing properties of free HBPEI in solution, which supposes a novel approach to easily predict the metal ion complexing properties of carbon-based hybrid materials, through a simple potentiometric titration analysis of the free complexing ligand in solution. This approach has the potential to predict retention capacities of solid materials (actual or proposed) exhibiting surfaces functionalized with HPBEI.

Introduction

The presence of heavy metals in our environment, as a consequence of daily life activities and industrial processes, has led to the need for developing highly efficient metal ion scavengers for industrial effluent treatment and drinking water purification, mainly with two objectives, environmental preservation and recovery of metal ions of economic interest.[1–6] Consequently, many diverse procedures have been proposed to remove metal ions from water and wastewater, including the development of new cost-effective and highly selective metal ion scavengers,

although the design of innovative metal ion analysis methodologies continues to be a great challenge.[7–12]

In the last few decades, activated carbons (ACs) have been extensively used as adsorbents to remove metals from industrial and municipal wastewater, as they are cheap and accessible materials, especially suitable for large scale applications.[13–16] However, AC manufacturing by conventional methodologies has limited efficiency and selectivity toward particular metal ions because its scavenging capacity is mostly controlled by its surface area and pore size distribution, while its surface chemical functionalization is not controlled by defined complexing functional groups. For this reason, the development of novel methodologies capable of producing materials with high adsorption capacity and high selectivity through the control of their chemical functionalization is an important task for a wide range of applications.[17–21]

We recently reported the preparation of a hybrid material (C-PEI) consisting of activated carbon functionalized with HBPEI covalently bonded to its surface,[22,23] whose properties as a metal scavenger will be discussed in this paper.

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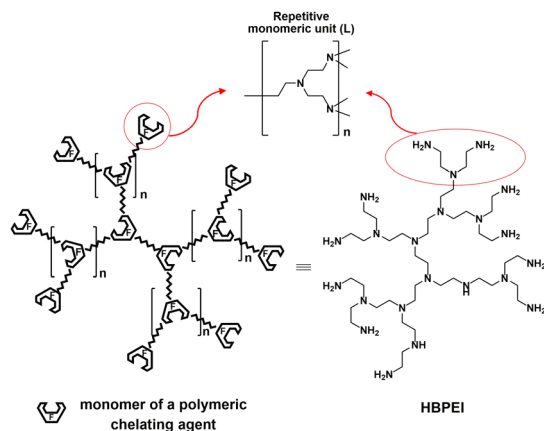
Fig. 1 Polychelatogen structure of hyperbranched polyethyleneimines based on repetitive units (functional unit = L) of triethylenetriamine [$-NH(CH_2)_2$] [$-(CH_2)_2NH_2$] N [$-(CH_2)_2-$].

HBPEIs are water soluble polymers with polyelectrolyte nature, under acidic conditions, and polychelatogen character due to the basic properties of the amine-type sp^3 nitrogen atoms (organized in repetitive and N-branched 1,2-diamine units), see Fig. 1. Generally, HBPEIs are extensively used as solid polymer electrolytes in polymer-based batteries,[24] as gene delivery polymers,[25] as coagulation agents for ultrafiltration,[26] as chelating components in the preparation of reverse osmosis membranes[27] or as scavengers to remove metal-ions from liquid phases. These applications include HBPEI supporting strategies in order to achieve higher performances or easy HBPEI recovery. In this respect, the fixation of HBPEI onto a solid support can be conducted due to its reactive primary amino groups, at terminal positions, which can be easily bound to defined electrophilic groups generated on the solid support, or by using appropriate linkers. Many different materials based on HBPEIs covalently bonded to the surface of solid supports,[28,29] specially carbon-based solids and silica gel, have been prepared and their capacities to retain diverse metal ions have been studied.[30–33]

Carbon-supported HBPEIs have received special attention due to their metal scavenging properties. Thus, it is worth mentioning the studies performed by Aroua et al. reporting the capture of metal ions from water solutions by ACs impregnated with HBPEI, where HBPEI was assumed to be supported on the carbon surface by electrostatic interactions between the negatively charged carboxylate groups of the oxidized AC and the positively protonated amines of HBPEI.[34] However, these carbon-supported HBPEI materials showed low stability in aqueous media due to the high water solubility of HBPEI, which made it impossible to perform any rigorous study regarding the metal ion complexing mechanisms.

Herein, we report the first detailed study concerning the metal ion complexing mechanism involved in covalently-bonded carbon-supported HBPEI polymers (C-PEI), towards a series of metal ions of environmental and technical interest (Mn^{2+}, Cd^{2+}, Hg^{2+}, Pd^{2+} and Cr^{3+}). The complexing mechanisms and retention capacity of C-PEI, towards each metal ion, were

defined and compared with the HBPEI reactivity in aqueous solution, according to the model proposed by Jarvis and Wagener,[35] where HBPEI polymers are defined as a composition of repetitive units (functional unit = L) of triethylenetriamine, ($-NH(CH_2)_2-N[-(CH_2)_2NH_2]-(CH_2)_2-$) (Fig. 1), which are capable of acting as independent complexing units with identical behavior. A good correlation between the HBPEI/Mn+ and C-PEI/Mn+ data sets was obtained, which provides a detailed and reliable linear free-energy relationship (LFER) between the retention capacities of the hybrid material (C-PEI) and the complexing properties of HBPEI in solution. Such results revealed that the complexing ability of HBPEI is unaltered after its grafting onto the AC surface. Therefore, the methodology here presented constitutes a novel approach to easily predict the complexing properties of AC-based hybrid materials toward particular metal ions by using potentiometric measurements.

Experimental

Materials

The hybrid activated carbon (C-PEI) was synthesized following a previously reported method.[22,23] HBPEI (Mn 600), $MnCl_2$, $CdCl_2$, $HgCl_2$, $KPdCl_4$, $Cr(NO_3)_3$, KCl, KOH and HCl were purchased from Aldrich and used without further purification.

Preparation and characterization of C-PEI

The hybrid C-PEI was prepared from HBPEI (Mn 600) and commercial activated carbon, F (Filtracarb – SKI 8 × 30 from CPL Carbon Link; elemental analysis of N (0.36%), C (90.34%), H (0.22%), O (8.83%) and pHpzc = 5.50). The procedure consisted of three-reaction steps: (i) oxidation of F with HNO_3; (ii) esterification of carboxylic groups introduced after oxidation of F to transform them into methyl esters; (iii) bonding of HBPEI (Mn 600) to the AC through amide linkages obtained by the reaction of the carboxylic esters on the carbon surface with the primary amino groups of HBPEI.[22,23] The hybrid C-PEI had a high N content according to combustion elemental analysis [N (9.22%), C (73.95%), H (3.22%), O (13.36%)], which correspond to 0.37 mmol per gram of grafted HBPEI (Mn = 600, DP = 14). The preservation of the covalent structure of polyethyleneimine in the hybrid was confirmed by ^{13}C-NMR (relevant signals at around 50 ppm due to $N-CH_2-CH_2-N$ groups) and XPS analyses (peak at 399.6 eV in the N1s region due to nitrogens of alkylamino functions). The linkage through amide bonds was confirmed by XPS analyses (shoulder at 407.1 eV in the N1s region due to amide nitrogens) compared with those of model compounds. The point of zero surface charge of the hybrid occurs at pH 9.07 in coherence with the amine functionalization at the surface. C-PEI showed a very low specific surface area (by the BET equation) of only 77 m^2 g^{-1}, which compared with that of its direct precursor (oxidized and esterified carbon) of 661 m^2 g^{-1}, indicates blockage of the porous system of the carbon support due to fixation of the polyamines at the internal surface of pores.[22,23]

Potentiometric studies

All the acid–base titrations were performed with an automatic potentiometric titrator (Methrom 765 Dosimat) endowed with a Methrom glass electrode and a Metrohm 713 pH meter for pH measurements.[36] The system was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by Gran's method,[37] which allows to determine the standard potential, Eo, and the ionic product of water ($pK_w = 13.83$, 0.10 M KCl) at 298.0 K. At least three potentiometric titrations (about 100 data points each one) were performed for all systems (see below) in the 2.5–10.5 pH range.

(a) **HBPEI/H$^+$ and HBPEI/M^{n+} systems.** Protonation equilibria of HBPEI and their corresponding constants were determined from the pH data obtained in the potentiometric titration of an HBPEI water solution with ionic strength 0.1 M KCl, at 298.0 K. Considering HBPEI molecules as constituted by the repetition of triethylenetriamine structural units (L) (see the Results and discussion section), in all titrations the concentration of HBPEI (as a concentration of L units) was 10^{-3} M.

The reactivity of the HBPEI/M^{n+} systems was studied by the analysis of the pH data obtained from potentiometric titrations of 0.1 M KCl water solutions (except 1.0 M KCl for Hg^{2+}) of HBPEI/M^{n+} mixtures, in 1/1 molar ratios, at 298.0 K by using 0.1 M KOH as the titrant. In all the experiments, the concentration of HBPEI (as a concentration of L units) was 10^{-3} M, and metal concentrations were 10^{-3} M. Then, pH of the HBPEI solution was initially adjusted to *ca.* 2.5 by adding aqueous HCl. After 30 min of equilibration time under a N$_2$ atmosphere, the metal ion was added and the solution was kept stirring for 16 hours to reach equilibrium. Subsequently, the suspension was titrated with 0.1 M NaOH up to pH 10.5. Equilibration time of 600 s elapsed between each titrant addition (0.03 mL). The Hyperquad software[38] was used to calculate the equilibrium constants from the emf data.

(b) **C-PEI/H+ and C-PEI/Mn+ systems.** Protonation equilibria of C-PEI and their corresponding constants were determined from the pH data obtained in the potentiometric titration of a C-PEI water suspension (0.1 g of C-PEI, 0.18 mmol of grafted triethylenetriamine units, L) with ionic strength 0.1 M KCl, at 298.0 K.

For the analysis of the reactivity of C-PEI/M^{n+} systems, a suspension of 0.1 g of C-PEI (0.18 mmol of grafted triethylenetriamine units, L) in 40 mL of 0.1 M aqueous KCl solution was prepared. Then pH was adjusted to *ca.* 2.5 by adding HCl aqueous solution. After 48 h of equilibration time under a N$_2$ atmosphere the metal ion was added to the solution and kept stirring for 48 hours until equilibrium was reached. Subsequently, the suspension was titrated with 0.1 M NaOH up to pH 10.5. Equilibration time of 1800 s elapsed between each titrant addition (0.03 mL). In all the experiments, an HBPEI (as L units)/metal ion molar ratio of 1/1 was used. The Hyperquad software[38] was used to calculate the equilibrium constants from the emf data.

Metal retention measurements

Water solutions of MnCl$_2$, CdCl$_2$, HgCl$_2$, K$_2$PdCl$_4$ and Cr(NO$_3$)$_3$ salts were used in the metal retention experiments of metal ions by C-PEI. The equilibration times were preliminarily determined by means of independent experiments. For this purpose, different flasks containing 25 mL of 10^{-3} M (Mn^{2+}, Cd^{2+}, Hg^{2+}, Cr^{3+}) or 3×10^{-3} M (Pd^{2+}) metal ion solution and 25 mg of C-PEI hybrid were prepared and kept under shaking. Then, the metal concentration in solution was measured at different times. Once the equilibrium times were determined, the retention isotherms of metal ions were obtained at 298.0 K. The metal ion concentration was varied between 6×10^{-5} and 1×10^{-3} M for Mn^{2+}, Cd^{2+} and Cr^{3+}, between 6×10^{-5} and 2×10^{-3} M for Hg^{2+} and between 6×10^{-5} and 3×10^{-3} M in the case of Pd^{2+}. The required initial pH values of the metal ion solutions (8.5 for Mn^{2+}, 6.5 for Cd^{2+}, 5.0 for Hg^{2+}, 5.0 for Cr^{3+} and 4.0 for Pd^{2+}) were attained by adding the required quantities of aqueous HCl or NaOH solutions. The metal concentration at equilibrium was determined by means of ICP-MS (in the case of Cr^{3+}), atomic absorption (for Mn^{2+} and Cd^{2+}) and UV spectroscopy (for Hg^{2+} and Pd^{2+}) measurements. In addition, metal retention experiments toward each particular ion on the original activated carbon, F (pristine AC), were performed in order to compare the maximum metal retention capacity (X_m) on F against the X_m values obtained on C-PEI; such experiments rendered X_m values lower than 0.01 mmol ion g^{-1} for carbon F. Blank experiments were also performed to verify that neither the ligand nor the metals were adsorbed by the plastic flasks.

Results and discussion

The development of the innovative metal ion complexing material, C-PEI, and the analysis of its complexing properties through a linear free-energy relationship (LFER) between the retention capacities of the hybrid material (C-PEI) and the complexing properties of HBPEI is described by assuming that the complexing properties of C-PEI and HBPEI are defined by triethylenetriamine complexing units (TETACU model in the following). Thus, the TETACU approach and the analysis to corroborate the model are described below.

TETACU model and acid-base behavior of HBPEI and C-PEI systems

The TETACU model is based on arguments that support the hypothesis that triethylenetriamine complexing units are the most reasonable complexing units to be considered in the interpretation of HBPEIs and C-PEI reactivity towards metal ions.[35] In order to prove this hypothesis, firstly, the assessment of the protonation equilibria and the corresponding constant values of HBPEI in aqueous solution were obtained from potentiometric data collected by acid–base titrations, which were performed as described in the Experimental section. The best fit of the experimental data ($\sigma = 0.25$) was obtained by assuming the TETACU approach, indicating that HBPEI is formed by independent repeating units of triethylenetriamine, (L = –NH(CH$_2$)$_2$–N[–(CH$_2$)$_2$NH$_2$]–(CH$_2$)$_2$–), which are capable of bearing a maximum of three protons.[35] The protonation equilibria of the monomeric unit and their stability constants are

Table 1 Protonation equilibria and stability constant values of HBPEI/H+ and C-PEI/H+ systems in aqueous systems*

		Log K_n	
Equilibrium	Constant	HBPEI[a]	C-PEI[b]
L + H⁺ ⇄ [HL]⁺	K_1	9.47 (1)	9.83 (1)
[HL]⁺ + H⁺ ⇄ [H₂L]²⁺	K_2	7.45 (1)	6.42 (2)
[H₂L]²⁺ + H⁺ ⇄ [H₃L]³⁺	K_3	2.61 (1)	—
2 L + H⁺ ⇄ [HL₂]⁺	K_4	12.29 (4)	12.10 (1)
2 LH⁺ + H⁺ ⇄ [H₃L₂]³⁺	K_5	10.98 (2)	9.81 (3)
2 LH₂²⁺ + H⁺ ⇄ [H₅L₂]⁵⁺	K_6	7.26 (3)	4.36 (5)

*Values in parentheses are standard deviations in the last significant figure. [a] Aqueous solution. [b] Suspension in water.

summarized in Table 1. This set of equilibria includes not only those corresponding to the successive protonations of the three nitrogen atoms in the functional unit, L (constants K_1, K_2 and K_3), but also other processes of "cooperative protonation" of two functional units (those involving L_2, with constants K_4, K_5 and K_6), which are necessary to get a good fitting of the experimental data because they are intermediate stages between the equilibria denoted by K_1–K_3.

The in-depth analysis of protonation equilibria and stability constants of HBPEI/H⁺ show the first protonation step of L with a large constant (log K_1 = 9.47), similar to those of terminal amino groups in linear polyamines made of ethyleneimine functional units ((–NH$_n$–[CH₂CH₂]–)$_m$, n = 1,2; m = 2–5)],[39] therefore, K_1 can be attributed to the protonation of terminal amino groups in HBPEI, considering their lower steric demand as primary amines, that enables the formation of intramolecular hydrogen bonds with nearby nitrogen atoms,[40] and their external location and higher mobility, that allow to locate each positive charge as much apart as possible from each other.[41]

Successive protonations of L and L_2 show a decrease in K_n values due to the lowering in basicity caused by the introduction of positive charges in the surroundings of the basic centers. Thus, the small equilibrium constant of the last protonation process (log K_3 = 2.61) is the logical outcome of the large and progressive charge accumulation in HBPEI molecules, as their protonation progresses close to completion. Accordingly, 85% was the maximum protonation ratio reached at the lower pH values worked in the titration experiments, pH 2 (see Fig. 2).

Once the protonation equilibria and corresponding constant values of HBPEI in aqueous solution were determined, the TETACU model was applied to C-PEI, and the protonation equilibria and corresponding constant values of C-PEI in aqueous solution were obtained from potentiometric titrations (see Fig. 3). As result, a similar Brönsted acid–base behavior of C-PEI to HBPEI was determined (see Table 1). Therefore, these data confirm that HBPEI preserves the same protonation behavior after being grafted onto the carbon surface. Interestingly, such data show lower basicities of the secondary and tertiary amino groups for the grafted-HBPEI molecules than for the non-grafted ones (HBPEI in solution). A tentative explanation for this finding can be based on the effect of an increase in cooperative protonation of close neighbouring molecules fixed onto the carbon surface that would favour the first protonation
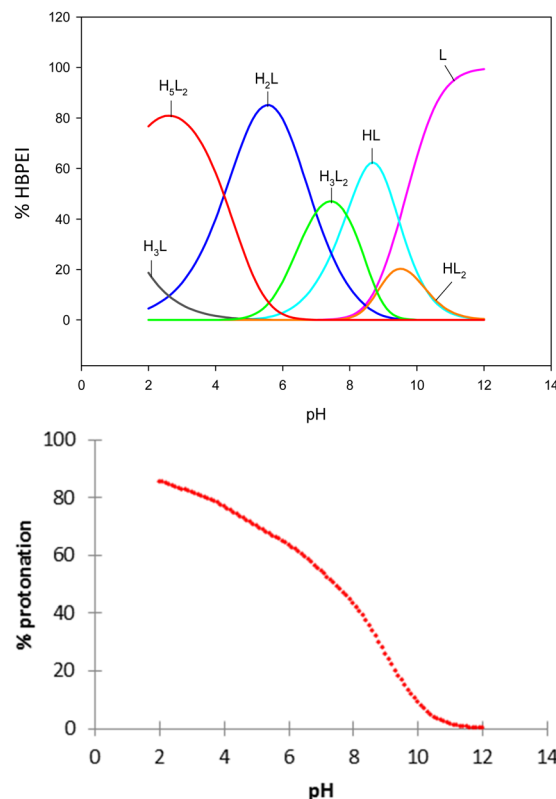

Fig. 2 Species distribution plot for the HBPEI/H⁺ system in aqueous solution as a function of pH, and evolution of the percentage of protonation (of the total of nitrogen atoms) vs. pH.

step. Later, progressive charge accumulation, however, tends to be difficult after protonation processes in such surface-fixed and conformational restricted PEI molecules of C PEI.

Complex formation in HBPEI/M^{n+} systems

The reactivity studies of HBPEI/M^{n+} mixtures ([L]/[M^{n+}] = 1/1, [L] = 10^{-3} M) were performed by analyzing the pH data obtained from acid–base titrations. The potentiometric data were interpreted assuming the TETACU model, so that each functional unit (L) of HBPEI acts as a single chelating ligand. In the cases of Hg(II) and Pd(II) systems, Cl⁻, as a competitive ligand against HBPEI was considered, and the formation constants obtained from the literature,[42–44] for the processes mCl⁻ + M^{n+} → Cl$_m$M$^{(+n-m)}$, were considered in the simulation model. Thereby, different equilibrium models were assessed by removing or adding different species for each studied system, so that, only resulting models determined using HYPERQUAD software, with a variance of the residuals $\sigma^2 < 9$ were considered acceptable. Such a condition was unambiguously met by a single model for each system, which is shown in Table 2. It is worth mentioning that the determined models showed that in a very low pH range Cl–M species are not detected (neither mixed ligands M/HBPEI/Cl nor single ligands M/Cl), except for the HgCl₄²⁻ system. The best data fit obtained for the different HBPEI/M^{n+} systems corresponds to the equilibria and stability constant values (log K) shown in Table 2. It is worth noting that
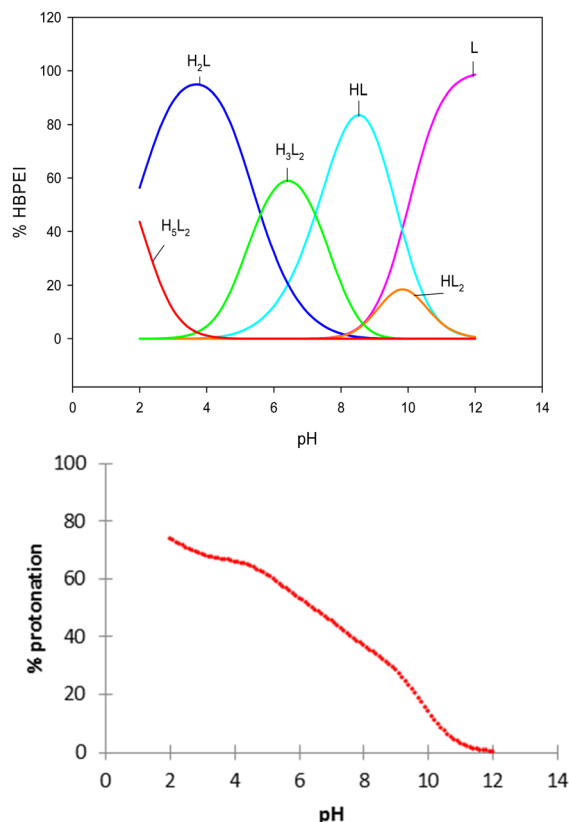
Fig. 3 Species distribution plot for the C-PEI/H$^+$ system in aqueous solution as a function of pH, and evolution of the percentage of protonation (of the total of nitrogen atoms) *vs.* pH.

this is a procedure that determines stability constants of metal/ligand complex species indirectly, through proton concentration. Then, it enables the determination of very high constants, as those found for Hg^{2+} and Pd^{2+} (Table 2), corresponding to processes that leave practically no free metal at equilibrium, which would be unreachable by direct measurement of metal concentrations.

The titration analysis shows the formation of complexes with a partially protonated triethyleneimine chelating unit (L)

only in the case of metal ions with higher nitrogen affinities (Cr^{3+}, Hg^{2+} and Pd^{2+}), which are, besides, capable of complexing with the polyamine ligand at low pH values. In addition, it is observed that the formation of complexes with L/M^{n+} = 1/1 stoichiometries is predominant in intermediate pH ranges (see Fig. 4A and 2B), as well as, metal ion complexes containing L and additional hydroxyl groups are observed in all the systems, although the formation of such species is much more relevant for Cr^{3+}, which is consistent with its higher affinity to oxygen donors. In addition, the formation of complexes with L/M^{n+} = 2/1 stoichiometries is also observed for Mn^{2+}, Cd^{2+} and Pd^{2+}, due to the formation of a double chelate by the reaction of the three nitrogen atoms of triethylenetriamine units (see Fig. 4C). It is worth mentioning that additional adjacent complexing units (four), linked to the same metal center, should result in a higher chelating effect; however, this possibility has to be discarded due to the steric hindrance emerging from folding of the HBPEI (see Fig. 4D). In the same way, a cooperative complexing behavior can be considered through non-adjacent complexing units (see Fig. 4E and 2F), however, this results in an 8-member or in higher chelate structures, which are much less stable than the 5-membered ones, due to the so called *trans*-annular strain.[45–47]

Interestingly, the log K values observed in all systems (HBPEI/M^{n+}) are slightly higher than those corresponding to the analogous metal complexes with non-polymeric triamine ligands,[48] and is attributed to a cooperative network contribution to global stability. Besides, the stability of analogous L/M^{n+} complexes is defined according to the sequence L/Mn^{2+} < L/Cd^{2+} < L/Cr^{3+} < L/Hg^{2+} < L/Pd^{2+}, which is in agreement with the affinities of each metal ion toward nitrogen donors.[49]

Complex formation in C-PEI/M^{n+} systems

Assuming the TETACU model, the metal ion complexing properties of C-PEI suspensions, toward Pd^{2+}, Hg^{2+} and Cr^{3+} in water, were accomplished and successfully interpreted in terms of complex species distribution (see Table 3). However, in the case of Mn^{2+} and Cd^{2+} no complex formation was observed in

Table 2 Stability constants of HBPEI/M^{n+} complexes in solution (0.1 M KCl, 298.0 K)*

Equilibrium	Log K				
	Mn^{2+}	Cd^{2+}	Cr^{3+}	Hg^{2+}	Pd^{2+}
$[H_3L]^{3+} + [HgCl_4]^{2-} \leftrightarrows [H_2L(HgCl_4)]^+$				11.93 (4)	
$[H_2L]^{2+} + [HgCl_4]^{2-} \leftrightarrows H_2L(HgCl_4)$				10.64 (4)	
$M^{n+} + HL^+ \leftrightarrows [MHL]^{(n+1)+}$			9.05 (2)	13.37 (4)	
$2M^{n+} + HL_2^+ \leftrightarrows [M_2HL_2]^{(2n+1)+}$					28.49 (4)
$M^{n+} + L \leftrightarrows [ML]^{n+}$	4.84 (3)	8.90 (1)	13.77 (2)	16.95 (2)	31.76 (5)
$[ML]^{n+} + L \leftrightarrows [ML_2]^{n+}$	4.05 (9)	7.35 (8)			
$M^{n+} + 2L + OH^- \leftrightarrows [ML_2(OH)]^{(n-1)+}$					13.18 (3)
$[ML]^{n+} + OH^- \leftrightarrows [ML(OH)]^{(n-1)+}$	3.84 (1)	4.66 (2)	8.60 (5)	4.67 (3)	4.58 (2)
$[ML(OH)]^{(n-1)+} + OH^- \leftrightarrows [ML(OH)_2]^{(n-2)+}$		2.84 (2)	7.10 (3)	2.42 (4)	
$[ML(OH)_2]^{(n-2)+} + OH^- \leftrightarrows [ML(OH)_3]^{(n-3)+}$			5.11 (2)		
$[ML(OH)_3]^{(n-3)+} + OH^- \leftrightarrows [ML(OH)_4]^{(n-4)+}$			3.93 (2)		

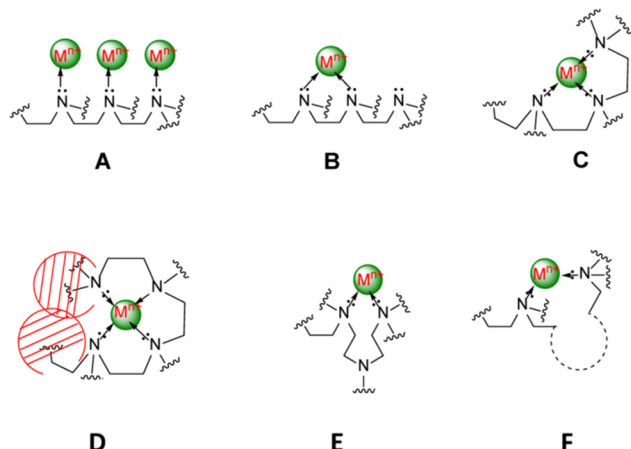*Values in parentheses are standard deviations in the last significant figure.

Fig. 4 Possible structures originating from non-cooperative and cooperative binding of non-adjacent monomeric units to a metal ion center.

the low pH range, which is in agreement with the species distribution found for the non-grafted HBPEI. Besides, the precipitation of insoluble Mn^{2+} and Cd^{2+} hydroxy species during the titration experiments avoids the complex formation of these metal ions with C-PEI at pH values higher than 6. This fact is probably due to the higher stability of HL species in grafted-HBPEI than in non-grafted HBPEI (Table 1), which shift the deprotonation pH value of grafted-HL species to higher values, and consequently, the L-metal ion complex formation is hindered.

The species distribution and the apparent stability constants of Cr^{3+}, Hg^{2+} or Pd^{2+} and C-PEI tabulated in Table 3 show that the L-complexes, formed between Cr^{3+}, Hg^{2+} or Pd^{2+} and C-PEI, are very similar to their analogues formed with the non-grafted HBPEI (Table 2). Nevertheless, the HL complexes of Cr^{3+} and Hg^{2+} have slightly lower apparent stability constants than those formed with HBPEI. This fact is consistent with two factors: (a) the decrease in the basicity of the amino groups of grafted-HBPEI, associated with the HL species (Table 1), which acts as donor atoms to Cr^{3+} and Hg^{2+}, and (b) the existence of some structural restrictions, when the functional unit has a positive charge, which are limiting conformational changes of the grafted-HBPEI. Concerning the Pd^{2+} complexes, it is worth mentioning that the high affinity of the nitrogenated ligand

toward Pd^{2+} determines the insignificant differences in the species distribution on C-PEI and HBPEI systems.

Linear free-energy relationship between HBPEI and C-PEI systems

According to the aforementioned results, a linear free-energy relationship (LFER) between the species distribution of HBPEI/M^{n+} and C-PEI/M^{n+} systems and the metal ion sorption capacity of C-PEI has been established and proven. Thus, the maximum sorption capacity, X_m, of C-PEI toward a specific metal ion has to depend on the species distribution and apparent stability constants of HBPEI molecules grafted onto the AC surface, because the C-PEI complexing mechanism is governed by the HBPEI complexing ability in solution, as it was previously described.

In order to confirm the correlation between the stability constants of HBPEI/metal complex species in solution and metal retention capacity of C-PEI, the retention tests with Mn^{2+}, Cd^{2+}, Hg^{2+}, Pd^{2+} and Cr^{3+} by C-PEI were performed. Metal ion sorption isotherms (Fig. 5) were recorded by making C-PEI come into contact with aqueous metal ion solutions at different concentrations. The selection of an appropriate pH value is critical to perform the C-PEI/metal ion retention tests, due to the strong influence on the metal–polyamine complex species formation. Then, a compromise pH value was defined for each metal ion (see the Experimental section), depending on its acid–base behavior in aqueous solution.

The retention isotherms for each C-PEI/metal ion system, as well as the maximum retention capacity values (X_m) obtained from their Langmuir equation (X_m Mn^{2+} = 0.29 mmol g^{-1}, X_m Cd^{2+} = 0.31 mmol g^{-1}, X_m Hg^{2+} = 0.87 mmol g^{-1}, X_m Pd^{2+} = 1.72 mmol g^{-1}, X_m Cr^{3+} = 0.55 mmol g^{-1}) were determined. The tests show remarkably high X_m values for the assessed C-PEI/metal ion systems, however, adsorption capacities of C-PEI toward Pd^{2+} and Hg^{2+} were extremely high. In particular, the value for Pd^{2+} (1.72 mmol g^{-1}) proves that C-PEI can be one of the most efficient reported Pd(II)-scavenger, even better than other commercial materials.[22] Furthermore, the good fitting of the retention isotherms (Fig. 5) to the Langmuir model proves the existence of a single predominant retention mechanism in all systems, which is defined by the complexing properties of grafted HBPEI molecules. As expected, a good correlation was

Table 3 Apparent stability constants of C-PEI/M^{n+} complexes in aqueous (0.1 M KCl, 298.1 K) suspension*

	Log K		
Equilibrium	Cr^{3+}	Hg^{2+}	Pd^{2+}
$M^{n+} + HL^+ \leftrightarrows [MHL]^{(n+1)+}$	8.19 (1)	11.52 (2)	
$2M^{n+} + HL_2^+ \leftrightarrows [M_2HL_2]^{(2n+1)+}$			28.99 (3)
$M^{n+} + L \leftrightarrows [ML]^{n+}$	13.30 (4)	16.84 (1)	32.23 (4)
$[ML]^{n+} + L \leftrightarrows [ML_2]^{n+}$			
$M^{n+} + 2L + OH^- \leftrightarrows [ML_2(OH)]^{(n-1)+}$			11.68 (1)
$[ML]^{n+} + OH^- \leftrightarrows [ML(OH)]^{(n-1)+}$	8.67 (4)	3.97 (4)	4.98 (5)
$[ML(OH)]^{(n-1)+} + OH^- \leftrightarrows [ML(OH)_2]^{(n-2)+}$	8.12 (3)	2.91 (2)	
$[ML(OH)_2]^{(n-2)+} + OH^- \leftrightarrows [ML(OH)_3]^{(n-3)+}$	5.34 (2)		
$[ML(OH)_3]^{(n-3)+} + OH^- \leftrightarrows [ML(OH)_4]^{(n-4)+}$	2.87 (1)		

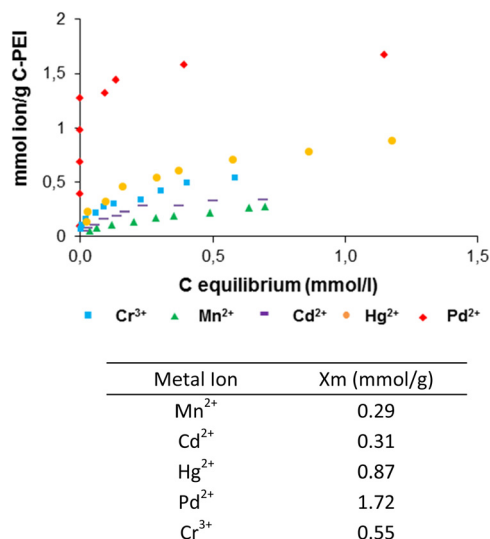*Values in parentheses are standard deviations in the last significant figure.

Fig. 5 Adsorption isotherms of C-PEI/M^{n+} systems and maximum metal ion retention capacity (X_m).

Metal Ion	Xm (mmol/g)
Mn^{2+}	0.29
Cd^{2+}	0.31
Hg^{2+}	0.87
Pd^{2+}	1.72
Cr^{3+}	0.55

observed between C-PEI/M^{n+} and HBPEI/M^{n+} stability constants for each metal ion, as well as, the measured X_m sorption values for C-PEI/M^{n+} systems and the HBPEI/M^{n+} species formation in aqueous solution.[50]

Regarding the analysis of C-PEI and HBPEI stability constants for Pd^{2+}, Hg^{2+} and Cr^{3+} an irrefutable correlation was

observed, which results in a straight line with the slope close to unity and intercept close to zero (Fig. 6). Therefore, the data obtained for Pd^{2+}, Hg^{2+} and Cr^{3+} prove that the HBPEI molecules grafted onto C-PEI keep their complexing ability, so that HBPEI molecules transfer their complexing behavior to the activated carbon (C-PEI).

In addition, HBPEI and C-PEI stability constants ($\log K$) for each assessed metal ion (at the pH value at which the sorption experiments were performed), were plotted against the maximum metal ion sorption capacity, X_m (in mmol g^{-1}) of C-PEI see Fig. 7. The good linear fit between $\log K$ and X_m for HBPEI and C-PEI systems, $R^2 = 0.97$ and $R^2 = 0.98$, respectively, not only confirms that the adsorption capacity of C-PEI is governed by the complexing ability of its HBPEI component, but also, that the TETACU model is a valid instrument to interpret the complexing behavior of HBPEI and C-PEI from potentiometric data.

This fact has relevant practical implications concerning the current strategies used to determine the metal ion complexing properties of supported complexing molecules, because the defined LFER strategy allows replacing laborious sorption experiences by easily workable potentiometric measurements. In this respect, it has to be considered that one potentiometric titration covers a wide pH range, so giving (after interpretation in terms of complex species distribution) the information required to choose the best pH value to perform adsorption experiments under optimal conditions. In contrast, by means
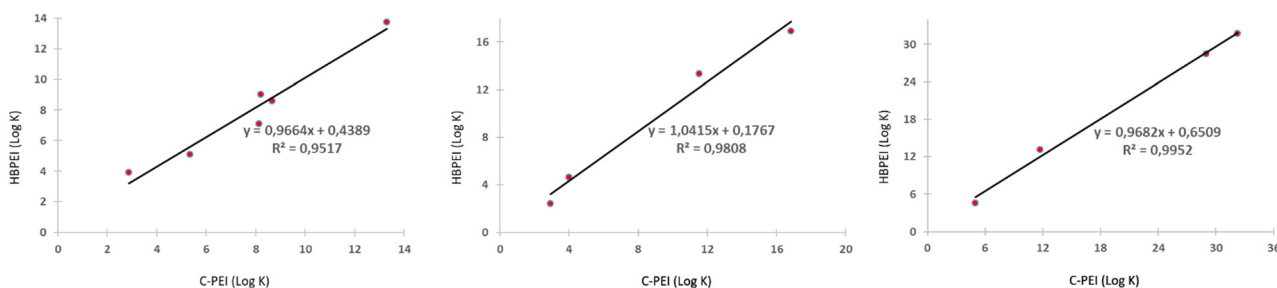

Fig. 6 Correlation between HBPEI ($\log K$) and C-PEI ($\log K$) for: (A) Cr^{3+}, (B) Hg^{2+} and (C) Pd^{2+}.
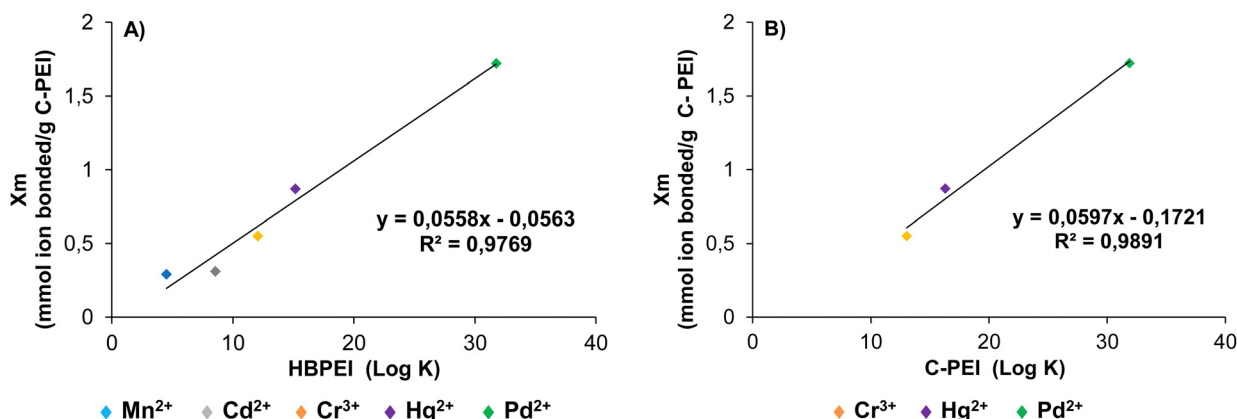

Fig. 7 Correlation between $\log K$ and X_m values of (A) HBPEI/M^{n+} and (B) C-PEI/M^{n+} systems.

of sorption experiments, such optimization requires performing multiple experiences under several pH conditions.

Consequently, the data obtained by potentiometric titrations of a given HBPEI/M^{n+} mixture will be valid for different hybrid materials based on grafted-HBPEI solid supports, as long as the complexing ability of HBPEI molecules is preserved in the hybrid material, and the capacity of the solid support to retain metal ions was negligible compared with the linked HBPEI molecules.

It is also worth noting that this approach has potential for predicting valuable information related to metal ion retention capacities of solids bearing surface-anchored HBPEI (as C-PEI) on the basis of potentiometric titrations of HBPEI solutions. Such predictable information includes the maximum retention capacities of the HBPEI-functionalized material through LFER, as demonstrated in this work, but also comprises other relevant aspects to be worked on in future research. For example, the anticipation of selectivities in competitive sorption processes involving different metal ions that can be expectedly foreseen taking the relative values of the stability constants of the complexes of each competing metal ion with HBPEI in solution; or the depiction of strategies to achieve effective loading–releasing cycles of metal retention on C-PEI, based on the complex species distribution in the pH range studied in the potentiometric titrations in solution.

Conclusions

A straightforward approach to accurately predict, through direct potentiometric measurements, the complexing properties and adsorption capacity of novel carbon-based hybrid scavengers toward particular metal ions was proven. This innovative approach was applied to determine the complexing capacity and complexing mechanisms involved in covalently-bonded carbon-supported hyperbranched polyethyleneimines (C-PEI), towards a series of metal ions of environmental and technical interest, such as Mn^{2+}, Cd^{2+}, Hg^{2+}, Pd^{2+} and Cr^{3+}. The data obtained from reactivity studies (adsorption isotherm measurements and potentiometric studies) reveal that C-PEI shows a high retention capacity with potential applications in the cleaning up of polluted waters, as well as, in industrial applications as a supported metal-scavenger. Interestingly, the collection of potentiometric studies on HBPEI/M^{n+} and C-PEI/M^{n+} systems demonstrated that simply by using potentiometric measurements of HBPEI in aqueous media, the behaviour of hybrid ACs toward particular metal ions can be predicted, which is a very useful tool in order to anticipate the efficient design of supported metal scavengers.

Author contributions

Antonio Peñas Sanjuán: conceptualization, investigation, formal analysis, and writing-original draft. Rubén Cruz Sánchez and Celeste García Gallarín: methodology, investigation and formal analysis. Manuel Pérez Mendoza: investigation and writing – original draft. Rafael López Garzón: methodology, validation and witting – review & editing. Manuel Melguizo: conceptualization, validation and witting-review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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