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Cooperative adsorption of critical metal ions using archaeal poly-γ-glutamate

Yuichi Hakumai · Shota Oike ·
Yuka Shibata · Makoto Ashiuchi

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Abstract Antimony, beryllium, chromium, cobalt (Co), gallium (Ga), germanium, indium (In), lithium, niobium, tantalum, the platinoids, the rare-earth elements (including dysprosium, Dy), and tungsten are generally regarded to be critical (rare) metals, and the ions of some of these metals are stabilized in acidic solutions. We examined the adsorption capacities of three water-soluble functional polymers, namely archaeal poly-γ-glutamate (L-PGA), polyacrylate (PAC), and polyvinyl alcohol (PVA), for six valuable metal ions (Co^{2+}, Ni^{2+}, Mn^{2+}, Ga^{3+}, In^{3+}, and Dy^{3+}). All three polymers showed apparently little or no capacity for divalent cations, whereas L-PGA and PAC showed the potential to adsorb trivalent cations, implying the beneficial valence-dependent selectivity of anionic polyelectrolytes with multiple carboxylates for metal ions. PVA did not adsorb metal ions, indicating that the crucial role played by carboxyl groups in the adsorption of crucial metal ions cannot be replaced by hydroxyl groups under the conditions. In addition, equilibrium studies using the non-ideal competitive adsorption model indicated that the potential for L-PGA to be used for the removal (or collection) of water-soluble critical metal ions (e.g., Ga^{3+}, In^{3+}, and Dy^{3+}) was far superior to that of any other industrially-versatile PAC materials.

Keywords Critical metals · Archaeal *exo*polymer · Poly-γ-glutamate · Cooperative adsorption

Introduction

Critical (rare) metals (Chakhmouradian et al. 2015), including antimony (Sb), beryllium (Be), chromium (Cr), cobalt (Co), gallium (Ga), germanium (Ge), indium (In), lithium (Li), niobium (Nb), tantalum (Ta), the platinoids (such as Ru, Pd, and Pt), the rare-earth elements (REEs), and tungsten (W), are becoming increasingly expensive. The increasing cost of these materials has been attributed to their growing use in many modern industrial technologies, such as the production of catalytic filter neutralizers for exhaust gases, fiber optics, lasers, oxygen sensors, phosphors, and superconductors. Moreover, numerous biological (trace) metals are essential or beneficial for life (i.e., microorganisms, plants, and animals), including arsenic (As), boron (B), calcium (Ca), Cr, Co, copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn),

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Y. Hakumai · S. Oike · M. Ashiuchi (✉)
Graduate School of Integrated Arts and Sciences, Kochi University, Kochi 783-8502, Japan
e-mail: ashiuchi@kochi-u.ac.jp

Y. Shibata · M. Ashiuchi
Faculty of Agriculture, Kochi University, Nankoku, Kochi 783-8502, Japan

molybdenum (Mo), nickel (Ni), potassium (K), selenium (Se), silicon (Si), sodium (Na), tin (Sn), vanadium (V) and zinc (Zn). Critical metals are generally regarded as being unconnected to biological processes in living systems. However, in extreme environments, such as the deep-sea sediments from the critical metal-rich crust/nodule deposit regions of the Pacific ocean (Huo et al. 2015; Liao et al. 2011), several interesting interactions have been observed between critical metals and microorganisms. The microbial communities found in these environments are well adapted to the extreme conditions and contain many specific microorganisms (bacteria, archaea) bearing uncommon structural surface polymers and cell metabolism processes.

Some naturally occurring polymers bearing negatively charged residues can function as ion-exchange (chelating) resins in a similar manner to synthetic polymers (e.g., polyacrylate) (Beauvais and Alexandratos 1998). These naturally occurring systems could therefore be used in environmentally friendly biochemical processes and applications. *Natrialba aegyptiaca*, which is an extremely halophilic archaeon, produces extracellular poly-γ-glutamate (PGA) (Hezayen et al. 2001). PGA (Fig. 1a) possesses a nylon-like backbone bearing numerous polyacrylate-like carboxylate groups, making it highly soluble in water. PGA can form multiple (e.g., non-covalent crosslinking) interactions with certain cationic compounds, thereby suppressing its extreme hydrophilicity (Ashiuchi et al. 2013). This archaeal polymer is composed entirely of L-glutamate residues and is also called stereoregular L-PGA, making it different in stereochemistry to the DL-PGA of *Bacillus subtilis* (Ashiuchi et al. 2015). Yamasaki et al. (2010) revealed the extremolyte-like (versatile) function of archaeal L-PGA. However, it remains unclear whether water-soluble PGA could be used to adsorb heavy metals, including the critical elements. Adsorption is generally defined as the transfer of a solute (e.g., metal ion) from a liquid phase to a solid phase via the formation of specific interactions with an absorbent (e.g., functional polymer) (Sampranpiboon et al. 2014). However, there is very little information available pertaining to the mode of adsorption of different metal ions by free (water-soluble) polymers (Fig. 2), compared with immobilized (water-insoluble) polymers derived from biomasses and cell debris (Das et al. 2008; Ogi et al. 2012; Vijayaraghavan and Yun 2008).

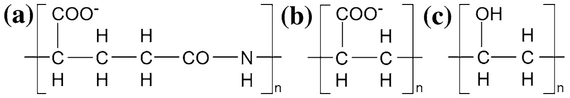


Fig. 1 Chemical structures of **a** poly-γ-glutamate (PGA), **b** polyacrylate (PAC), and **c** polyvinyl alcohol (PVA). Given that the molecular weight of archaeal L-PGA is on average over 800,000, its number-average degree of polymerization of (**a**), i.e. its n value, was estimated to be >6200

Herein, we present the adsorption capacities of L-PGA and two water-soluble synthetic polymers, i.e. polyacrylate (PAC) and polyvinyl alcohol (PVA) (Fig. 1b and c), towards six industrially valuable metal ions (Co^{2+}, Ni^{2+}, Mn^{2+}, Ga^{3+}, In^{3+}, and Dy^{3+}). The adsorption profiles of these polymers were also analyzed using the non-ideal competitive adsorption (NICA) model (Foo and Hameed 2010; Ringot et al. 2007).

Materials and methods

Materials

Sodium polyacrylate (PAC; polymerization degree (M_n), 2700–7500), polyvinyl alcohol (PVA; M_n, 3100–3900), $CoCl_2·6H_2O$, $NiCl_2·6H_2O$, and $MnCl_{2\text{-}}4H_2O$ were obtained from Wako (Osaka, Japan). $GaCl_3$ and $InCl_3$ were purchased from Tokyo Chemical Industry (Tokyo, Japan). Safranin O and $DyCl_{3\text{-}}6H_2O$ were purchased from Sigma (St. Louis, MO, USA). A QMA anion-exchange cartridge and 4-(2-pyridylazo) resorcinol (PAR) were purchased from Millipore (Bedford, MA, USA) and Dojindo (Kumamoto, Japan), respectively. All of the other chemicals used in this study were purchased as the analytical grade.

Preparation of archaeal L-PGA

N. aegyptiaca was inoculated into 200 ml of S medium (pH 7.2) comprising 25 % NaCl, 0.2 % KCl, 1 % trisodium citrate, 1 % yeast extract, and 0.75 % casamino acids, cultured at 37 °C for 4 days, before being harvested by centrifugation ($8000\times g$, 30 min) at room temperature (∼25 °C). The harvested cells (0.4 g) were cultured on a 2 % agar plate

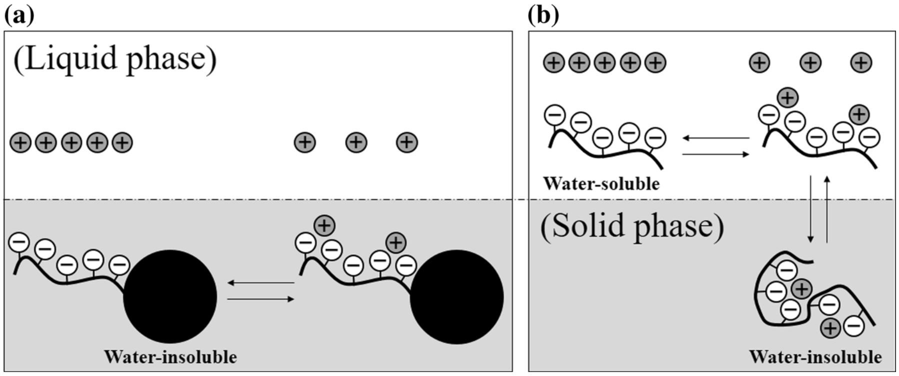


Fig. 2 Schematic diagrams of chemical adsorption using water-insoluble (**a**) and water-soluble (**b**) polymer materials for metal ions. In this case, the polymer moieties of **a** and **b** are negatively charged; metal ions are expressed by positive particles

(145 mm diameter) of S medium (50 ml) at 37 °C for 2 weeks. Extracellular PGAs were collected along with growing cells from the solid-culture system using 10 ml of 25 % NaCl solution, and centrifuged at 8000×*g* for 30 min. The resulting supernatant was injected onto QMA anion-exchange cartridge (Park et al. 2005), which was washed with 10 ml of distilled water, followed by 5 ml of 0.5 M NaCl solution. L-PGA (Mw, ~800,000; Fig. 1a) was subsequently eluted with 5 ml of 0.7 M NaCl solution.

Examination of PGA

PGA was examined as follows. A small samples of the polymer (100 µl) was diluted with 200 µl of 60 mM citrate buffer (pH 6.0), and the resulting mixtures was treated with 200 µl of 0.1 % safranin O solution, followed by 500 µl of saline and incubated for 10 min at room temperature. The mixture was then centrifuged at 12,000×*g* for 10 min to remove the water-insoluble safranin-PGA complex and the supernatant was collected and diluted 50-fold with saline. The residual concentration of safranin was determined using a Shimadzu UV-1600 spectrophotometer (Kyoto, Japan). For data standardization, the reagent blanks (lacking only safranin, normally zero) and the reactant blanks (lacking only PGA) were also analyzed. The calibration curve used to determine the PGA concentration was as follows: $y = 0.348x$, where y represents a decrease in absorbance at 520 nm relative to the reactant blank and x corresponds to the polymer concentration (mg ml^{-1}). Notably, the “x” value was linear in the range of 0.07–0.7 mg ml^{-1} ($R^2 = 0.9946$).

Examination of metal ions

Sample solutions of the different metal ions (100 µl) were mixed with 200 µl of 0.5 M citrate buffer (pH 6.8) and diluted with 500 µl of distilled water. The diluted solutions were added to 0.1 % solution of PAR in 1 M aqueous NaOH, which can form a colored chelating complex with various metal ions (Ghasemi et al. 2007), including Co^{2+}, Ni^{2+}, Mn^{2+}, Ga^{3+}, In^{3+}, and Dy^{3+}. The solutions were then incubated for 10 min at room temperature, and centrifuged at 12,000×*g* for 10 min. The concentrations of the different metal ions in the resulting supernatants were estimated spectrophotometrically. The calibration curves for the different metal ions were tested as follows:

Co^{2+} $y = 0.589x$ ($0.13 \le y \le 1.2$; $R^2 = 0.9989$);
Ni^{2+} $y = 0.589x$ ($0.13 \le y \le 1.2$; $R^2 = 0.9985$);
Mn^{2+} $y = 0.122x$ ($0.024 \le y \le 0.25$; $R^2 = 0.9952$);
Ga^{3+} $y = 1.04x$ ($0.021 \le y \le 0.22$; $R^2 = 0.9989$);
In^{3+} $y = 2.91x$ ($0.060 \le y \le 0.64$; $R^2 = 0.9932$);
Dy^{3+} $y = 0.340x$ ($0.089 \le y \le 0.69$; $R^2 = 0.9925$),

where y represents an increase in absorbance at 510 nm relative to the reactant blank (lacking only the indicated metal ions) and x corresponds to the metal concentration (mM).

Metal adsorption tests

The reaction mixture used for the metal adsorption test consisted of a metal ion (as a target) and an adsorbent polymer. The final pH values of the different mixtures are shown in Supplementary Fig. S1. Based on the detectability of the PAR assay (see above), the highly sensitive metal ions (Co^{2+}, Ni^{2+}, and In^{3+}) and several other metal ions (Mn^{2+} and Dy^{3+}) were examined at concentrations of 0.035–1.8 and 0.14–2.1 mM, respectively. For gallium, it is noteworthy that a high concentration of Ga^{3+} (>1 mM) can lead to the spontaneous formation of undesirable aggregates in the solution, making it impossible to examine the adsorption capacities of L-PGA, PAC, and PVA at Ga^{3+} concentrations >1 mM. During these examinations, L-PGA, PAC, and PVA were tested as metal adsorbent candidates, and 0.05 % solutions of these polymers (pH ~7) were added to solutions of the different metals. The final concentration of L-PGA, PAC, and PVA were maintained at final concentrations of 0.09, 0.05, and 0.03 mg ml^{-1} (for Co^{2+}, Ni^{2+}, Ga^{3+}, and In^{3+}) and 0.34, 0.19, and 0.11 mg ml^{-1} (for Mn^{2+} and Dy^{3+}), respectively, so that the concentrations of the carboxyl groups from L-PGA and PAC, and the hydroxyl groups from PVA were the same (i.e., 0.7 mM for Co^{2+}, Ni^{2+}, Ga^{3+}, and In^{3+}; 2.8 mM for Mn^{2+} and Dy^{3+}). After being incubated for 10 min at room temperature, the mixtures were filtrated using a 0.2-µm membrane filter, and subjected to the PAR assay. The critical (rare) metal adsorption capacities of the polymers were determined according to the following equation: $q_e = (m_i - m_r)/p$, where q_e is the adsorption capacity (mmol g^{-1}), m_i and m_r correspond to the initial and the residual amounts of metal in the reaction mixture being tested (V = volume of the mixture), and p represents the initial loading polymers. Alternatively, the q_e value can be determined using the initial and equilibrium metal concentrations (µM), which are also known as C_i ($=m_i/V$) and C_e ($=m_r/V$) (Sampranpiboon et al. 2014).

Equilibrium studies

Adsorption equilibrium is established when the amount of solute being adsorbed (q_e) is equal to the amount being desorbed; where the equilibrium concentration (C_e) of the solute is becomes constant. In this study, we used the NICA model (Koopal et al. 1994; 2001) to evaluate the adsorption equilibria of the different polymers. This model uses Eq. (1), which is similar to the Hill equation (Hill 1910). Notably, this equation assumes that adsorption is a cooperative phenomenon, which is dependent on the ability of solute binding at one site on a polymer to influence solute binding at a different site on the same polymer.

$$q_e = \frac{Q_0 C_e^n}{K_D + C_e^n} \tag{1}$$

This equation can be linearized using logarithmic terms (Eq. 2):

$$\log\left(\frac{q_e}{Q_0 - q_e}\right) = n \log C_e - \log K_D \tag{2}$$

The K_D corresponds to the Hill constant, which can be related to the affinity of adsorption sites: $K_D = K_d^n$, where K_d is the dissociation constant per site (or residual solute concentration at half saturation). The term "n" represents the Hill coefficient of the cooperative interaction between the polymer molecules during the adsorption. Theoretically,

$n > 1$, positive cooperativity;
$n = 1$, non-cooperativity (or hyperbolic adsorption);
$n < 1$, negative cooperativity.

Specifically, during hyperbolic adsorption ($n = 1$), this expression becomes almost identical to that of Langmuir model (Langmuir 1916) (Eq. 3):

$$q_e = \frac{Q_0 C_e}{K_d + C_e} \tag{3}$$

The linearized form of the Langmuir equation is shown below (Eq. 4).

$$\frac{1}{q_e} = \frac{K_d}{Q_0}\frac{1}{C_e} + \frac{1}{Q_0} \tag{4}$$

The K_d value is also the reciprocal of the association constant K_a. Under the analytic conditions, the K_a value was generally referred to as Langmuir constant. Furthermore, the Q_0 value indicates that maximum specific uptake corresponds to the saturation of the adsorption sites. Recent studies pertaining to the interactions formed between metal ions and anionic polyelectrolytes (e.g., PAC) have indicated the presence of different carboxylate–metal cation stoichiometries, including 2:1 and 3:1 for divalent and trivalent ions, respectively (Kogej et al. 2013). Accordingly, the theoretical Q_0 values (mmol g^{-1}) of L-PGA, PAC, and PVA were calculated to be 3.88, 6.98, and 0 (for divalent ions); 2.58, 4.65, and 0 (for trivalent ions), respectively.

Results and discussion

Several studies have been published pertaining to the chemical adsorption of divalent cations by water-insoluble (solid) materials bearing carboxylate moieties (Ewecharoena et al. 2009; Kwiatkowska-Marksa and Wójcika 2014; Wu and Li 2013). However, the water-soluble polymers tested in the current study showed apparently little or no adsorption of Co^{2+}, Ni^{2+} and Mn^{2+} (Fig. 3), indicating difficulty in the spontaneous transfer of the divalent metal ion-carboxylate polymer complexes into the solid phase. This difficulty could be attributed to negligible conformational changes to their separable (water-insoluble) complexes (Fig. 2b). In contrast, L-PGA and PAC showed good potential for the adsorption of Ga^{3+}, In^{3+} and Dy^{3+} (Fig. 3), suggesting that their complexes to trivalent cations could be readily separated from aqueous solutions without using ultra- and nanofiltration procedures (Rivas et al. 2009). These results therefore imply that anionic polyelectrolytes exhibit beneficial valence-dependent selectivity (viz., water-soluble polymers bearing multiple carboxylates) for metal ions. We have also confirmed that PVA does not adsorb metal ions under the conditions tested in the current study (see Fig. S1), because its hydroxyl groups are weakly acidic and would be deprotonated only at pH values much higher than 7 (Yokoi et al. 1986). It is well known that some critical metal ions are solubilized and stabilized in acidic solutions. For example, leached In^{3+} is converted to undesirable hydroxide precipitates at pH ~5 (Sawai et al. 2015). The crucial role of carboxyl groups in the adsorption of crucial (rare) metal ions therefore cannot be replaced by hydroxyl groups (Fig. 1). Although PVA is essentially a non-ionic polymer, it was used as a negative control in this study.

Breakthrough has been required to date for developing high-performance adsorbent polymers that can maintain their functionality even under acidic conditions. Although PAC is generally considered to be a good chelating polymer, the pK_a value of its carboxyl groups was calculated to be ~ 4.8 (Rivas et al. 2009), implying incomplete functionalization during the adsorption of some critical metal ions, such as In^{3+}. The potential of L-PGA as an adsorbent for trivalent metal ions (Fig. 3) therefore appears to be far superior to that of PAC, which has been studied extensively and used in a wide range of applications (Beauvais and Alexandratos 1998; Kogej et al. 2013). Interestingly, several recent studies (Moriyama et al. 2015; Parka et al. 2014) have reported that the pK_a of *B. subtilis*

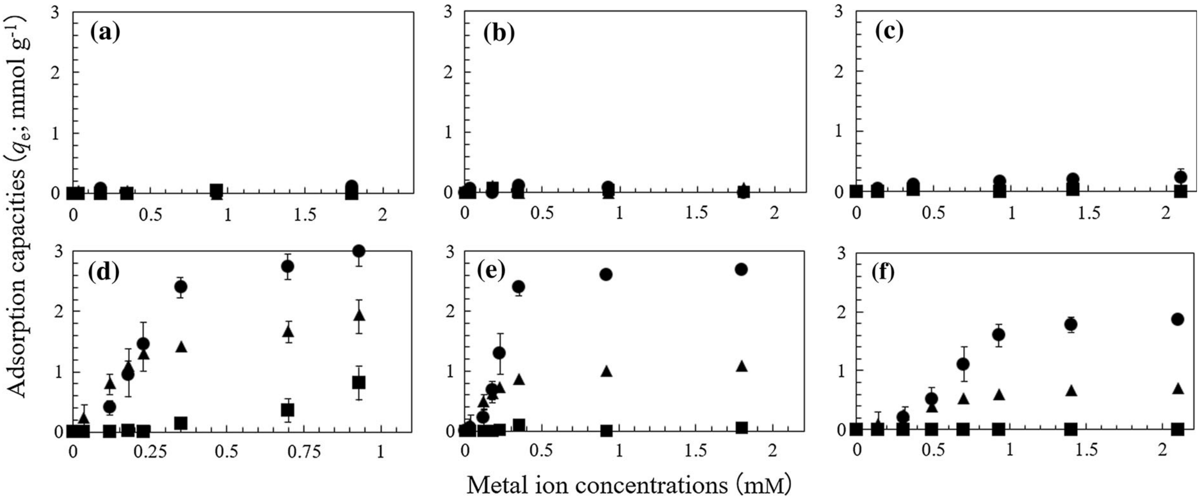
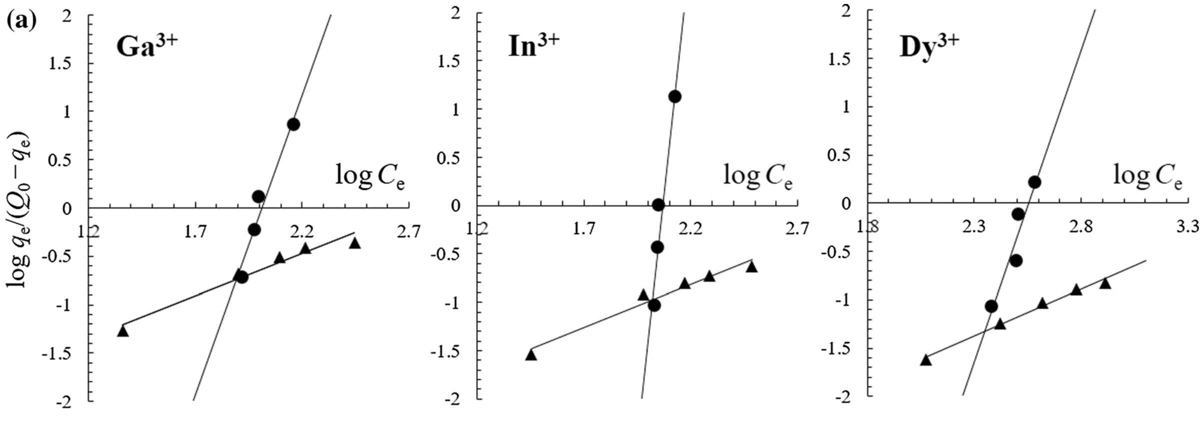


Fig. 3 Adsorption plots of **a** Co^{2+}, **b** Ni^{2+}, **c** Mn^{2+}, **d** Ga^{3+}, **e** In^{3+}, and **f** Dy^{3+} for PGA (*circles*), PAC (*triangles*), and PVA (*squares*). Data have been given as the mean values (*symbols*) ± the standard deviations (*bars*) of 12 independent tests

PGA is 4.8, which is virtually identical to that of PAC. In contrast to chemically synthesized polymers, the naturally occurring polymer PGA possesses an unusual molecular mechanism that enables it to overcome the pH problems associated with the chemical adsorption of critical metal ions. Then, the adsorption profiles of Ga^{3+}, In^{3+}, and Dy^{3+} for L-PGA and PCA (Fig. 3, panels d, e, and f) was analyzed using the NICA isotherm model. As shown in Fig. 4, PAC exhibited non- or somewhat negative cooperative adsorption towards these metal ions, whereas L-PGA showed considerable positive cooperative adsorption against all of the metal ions. We also determined the K_d values (μM) of L-PGA and PAC which were 103 and 541 (for Ga^{3+}); 117 and 1290 (for In^{3+}); and 352 and 5140 (for Dy^{3+}), respectively. The binding sites in L-PGA therefore exhibited apparently much higher affinities for trivalent cations than those in PAC (*see* also Fig. S2). Based on these results, we concluded that the success of high-performance metal adsorption using L-PGA is heavily dependent on the ability of this polymer to adopt cooperative polymer architecture. As shown in Fig. 1, PGA can be considered as a PAC analogue, with a backbone structure consisting of multiple amide linkages. The development of a deeper understanding of the features of the amide linkages in PGA could therefore provide further insights into it use as an environmentally friendly bio-sorption material for the recovery of various metal ions. This would be especially useful for the recovery of metal ion that are in great demand, including those associated with specific industrial and analytical applications.

Critical metals are being used in an increasing number of applications in medical (e.g., anti-infectious, anti-diabetic and anti-tumor agents) (Chan et al. 2014; Kelson et al. 2013; Levina and Lay 2011; Ma et al. 2013) and environmental research, as well as several other metal-dependent industries. This increase in the use of these materials therefore highlights the dramatic rise in the level of interest in the use of critical (or rare) metals for biology and biotechnology. However, our observation (Figs. 3 and 4) that L-PGA strongly adsorbs trivalent metal ions according to a sigmoidal curve (as does hemoglobin), while PAC describes a hyperbolic curve (as does myoglobin), still requires a physiological explanation. We recently discovered that a PGA-producing microorganism exhibits increased PGA productivity and growth rate in the presence of Ga^{3+} or Dy^{3+} (unpublished results). It is envisaged that these results will prompt considerable interest within the field of extremophiles to elucidate the physiological role of water-soluble PGA as a potent bio-adsorbent of multivalent metal ions.



(b)

	PGA	PAC
n	6.21	0.878
$\log K_D$	12.5	2.4

	PGA	PAC
n	20.3	0.9
$\log K_D$	42.0	2.79

	PGA	PAC
n	6.44	0.97
$\log K_D$	16.4	3.6

Fig. 4 **a** NICA isotherm plots of Ga^{3+}, In^{3+}, and Dy^{3+} for PGA (*circles*) and PAC (*triangles*) and **b** calculations of Hill parameters

Conclusion

Although the extremolyte-like (versatile) function of archaeal L-PGA has been revealed, it remains unclear whether this archaeal polymer can bind to critical (rare) metals. In the study, L-PGA was found to prefer trivalent metal ions (Ga^{3+}, In^{3+}, Dy^{3+}) and to discriminate against divalent metal ions (Co^{2+}, Ni^{2+}, Mn^{2+}), and these properties could be used to develop a selective polymer for the collection of valuable (multivalent) metal ions. In this sense, the fact that L-PGA afforded a sigmoidal curve for its metal adsorption represents a considerable advantage, because a process for metal desorption could also be established using facile manipulation steps, which would have very little impact on the adsorption capability of the polymer. In contrast, PAC exhibited hyperbolic behavior, which would be more suitable for the removal of metal ions rather than their collection. However, further work is required to improve the metal ion-binding performances of these materials. Overall, our report highlights the potential of L-PGA as a useful metal adsorbent.

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