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Isothermal titration microcalorimetry to determine the thermodynamics of metal ion removal by magnetic nanoparticle sorbents†

Yuxiong Huang and Arturo A. Keller*

Isothermal titration microcalorimetry, a novel approach, was applied to determine key thermodynamic parameters directly for the adsorption of metal ions to a magnetic nanoparticle sorbent (Mag-Ligand), measuring the energy exchange during the binding process. We demonstrate that the interactions are enthalpically driven and energetically favorable, with exothermic binding reactions, giving the selectivity sequence: $\text{Cr}^{3+} < \text{Cu}^{2+} < \text{Zn}^{2+} < \text{Ga}^{3+} < \text{Ce}^{3+} < \text{Cd}^{2+} < \text{In}^{3+} < \text{Hg}^{2+} < \text{Pb}^{2+}$. The sorption kinetic and isothermal studies demonstrated effective and fast removal of nine different metal ions including three rare earths, in competitive and non-competitive conditions across a range of pH and water hardness. Sorption is dominated by the complexation reactions between metal ions and Mag-Ligand and adsorption of metal ions onto Mag-Ligand. Maximum sorption capacity can be predicted based on the thermodynamic data, although kinetics plays a role during competitive sorption. Furthermore, the magnetic behavior of Mag-Ligand results in fast and efficient solid-liquid separation after the sorbent has extracted the metal ions from the contaminated waters, and Mag-Ligand can be regenerated for reuse by a simple acid wash, providing a more sustainable, fast, convenient, and efficient approach for heavy metal remediation.

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Nano impact

The emergence of tailored nanomaterials (Mag-Ligands), with magnetic properties and high adsorption capacity for a wide range of metal ions, provides a fast and effective tool to deal with these persistent contaminants. In order to better understanding the interaction between metal ions and magnetic nanoparticles sorbents, we introduce a novel approach, isothermal titration calorimetry (ITC) to directly obtain thermodynamic information. These key thermodynamic parameters are quantified by directly measuring the energy exchange during sorption process, which provides the information needed to predict the sorption capacity of these magnetic nanoparticle sorbents.

1. Introduction

Chromium (Cr), mercury (Hg), cadmium (Cd), lead (Pb), zinc (Zn) and copper (Cu) can be hazardous metals even at low concentrations, representing a significant threat to the environment and public health due to their toxicity and accumulative characteristics.^{1–4} Rare earth elements, such as gallium (Ga), cerium (Ce) and indium (In), are also a major concern in terms of environmental contamination;^{5,6} efficient and cleaner methods of recovery from their ores are also needed.

These metals can be released into the environment through a number of activities, such as mining,⁷ metal processing and finishing, welding and alloy manufacturing,⁸ the use of vehicles and coal combustion,⁹ as well as volcanic eruptions and forest fires.¹⁰ The metals can also enter the food supply chain *via* pesticides or fertilizers where they are found as impurities, with gradual accumulation in living organisms over their life span causing progressive toxic effects.^{11–14}

The application of engineered nanomaterials in water treatment is very promising.^{15–17} In a recent study,¹⁰ we reported the synthesis and proof-of-concept of a magnetic nanoparticle sorbent, namely Mag-Ligand, which is structured as a magnetic nano-scale core coated with a silica porous layer that covalently bonds with an organic ligand, ethylenediaminetetraacetic acid (EDTA). The interactions between metal ions and Mag-Ligand are a combination of complexation reactions, adsorption onto porous structures and electrostatic interactions (Fig. 1A). The attached EDTA can bind dissolved metal ions, while the magnetic core allows for rapid

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† Electronic supplementary information (ESI) available: Chemicals, synthesis, characterization, analysis, ITC measurement and sorption kinetic data for nine different metal ions, effect of pH and water hardness on Pb^{2+} removal, and Langmuir isotherm model fitted parameters for each metal ion in group competitive sorption, equi-molar competitive adsorption for multiple metal ions and zeta potential of Mag-Ligand. See DOI: 10.1039/c6en00227g

Fig. 1 (A) Schematic representation of the interactions between Mag-Ligand nanoparticle sorbents and metal ions; (B) TEM micrographs of Mag-Ligand, scale bar = 50 nm.

separation of the Mag-Ligand from solution by applying a magnetic field. Mag-Ligands have proven to be effective sorbents for removal of individual metal ions such as Cd^{2+} and Pb^{2+} under various environmental conditions (e.g. range of pH and water hardness) as well as shown good regenerability and reusability.

Though magnetic nanoparticle sorbents have successfully been applied to remove heavy metal ions,^{10,18–22} hydrophobic compounds,^{23–25} pesticides,^{26,27} natural organic matter,^{22,28,29} oxyanions^{30,31} and emerging organic contaminants,^{25,32,33} those studies focused on the synthesis and characterization of physicochemical properties of these engineered nanomaterials, as well as their environmental application. However, the key quantitative thermodynamic data (e.g. actual heat exchange and binding constants) of interactions between ions and these magnetic nanoparticle sorbents have not been determined.

Isothermal titration microcalorimetry (ITC) can directly measure the heat absorbed or released during the interaction (e.g. bond formation), providing accurate, rapid and label free thermodynamic data to determine the changes in enthalpy ΔH , entropy ΔS , and Gibbs free energy ΔG of the adsorption process, as well as provide information on the affinity binding constant K_d and the interaction reaction stoichiometry in a single titration experiment.³⁴ This advanced technology has been widely applied in the chemical and biochemical fields to study protein interactions^{35,36} and macromolecular assembly,³⁷ protein membrane interactions,³⁸ enzyme kinetics,³⁹ molecular dynamics simulations,⁴⁰ and incremental and DNA–ligand binding.⁴¹ Karlsen *et al.* (2010) conducted a very general study to investigate the use of ITC to determine the thermodynamics of Al^{3+} , Cr^{3+} , and Pb^{2+} binding to the biopolymer chitin, and found that the binding reactions were entropically driven.⁴² Loosli *et al.* used ITC to probe the agglomeration mechanisms and thermodynamics of the interactions between TiO_2 nanoparticles and natural organic matter, in-

cluding Suwannee River humic acid⁴³ and alginate,⁴⁴ indicating the TiO_2 –natural organic matter interactions were entropically and enthalpically favorable, with exothermic binding reactions and that the mixing order is also an important factor. The study showed the potential of ITC for understanding the fate and transport of nanoparticles in the environment. Thus, ITC could be used as a novel approach to investigate the thermodynamics of water treatment using magnetic nanoparticle adsorbents.

In this present work, we apply ITC to obtain key quantitative thermodynamic binding data of the interactions between Mag-Ligand and nine metal ions as well as to better understand the sorption process. The individual isotherm sorption studies were conducted to determine the adsorption capacity and kinetics. Furthermore, three groups of competitive sorption studies were conducted to determine the selectivity sequence among multiple metal ions. Adsorption mechanisms were proposed based on the thermodynamic and kinetic data. To scale the use of Mag-Ligand for real world applications, this fundamental quantitative knowledge of the thermodynamics, kinetics and competitive equilibrium of Mag-Ligand/metal ion interactions is needed to ascertain the minimum amount of Mag-Ligand particles needed to remove metal cations to a specified level, particularly in complex matrices with multiple metals.

2. Experimental

2.1. Synthesis and characterization of Mag-Ligand

The synthesis protocol followed our previously reported method.¹⁰ Briefly, by means of cooperative assembly of silica oligomers and EDTA on the maghemite nanoparticles (30 nm in diameter), Mag-Ligand particles were prepared with a core–shell structure. The final products were characterized by transmission electron microscopy (TEM), thermogravimetric analyses (TGA), Fourier transform infrared (FTIR) spectrometer, superconducting quantum interference device (SQUID) magnetometer, nitrogen gas adsorption analyzer and zetasizer. The detail of synthesis and characterization is available in ESI.†

2.2. Isothermal titration calorimetry measurement

A TA Instruments Nano Isothermal Titration Calorimeter (ITC) instrument was used to measure the heat exchange between Mag-Ligand particles and metal ions at 298 K to determine the thermodynamic data and binding constants. Generally, a well-dispersed suspension of Mag-Ligand particles (degassed DI water) was placed in the 1 mL ITC sample cell, and a metal ion(s) solution (1000 mg L^{-1}) was loaded into the 100 μL injection syringe. Metal ions were titrated into the sample cell as a sequence of 20 injections of 4.91 μL aliquots. The rotational speed of the stirrer was 250 min^{-1} and the equilibrium time between two injections was set at 800 s for the signal to return to the baseline.

Estimated binding parameters were obtained from the ITC data using the NanoAnalyze Data Analysis software (Version

3.30). Data fits were obtained using the independent set of multiple non-interacting sites (MNIS)⁴⁵ model, for which the analytical solution for the total heat measured, Q (kJ) is determined by the formula:

$$Q = \frac{(1 + [M]nK_d + K_d[L_T]) - \left[(1 + [M]nK_d + K_d[L_T])^2 - 4[M]nK_d^2[L_T] \right]^{1/2}}{2K_d} \quad (1)$$

$$V\Delta H$$

where V is the volume of the calorimeter cell, ΔH is enthalpy (kJ mol^{-1}), and K_d (M^{-1}) is the equilibrium binding constant. Free energy, ΔG (kJ mol^{-1}), was determined from the binding constant ($\Delta G = -RT \ln K$, where R is the gas constant and T is the absolute temperature in Kelvin) and entropy, ΔS (kJ mol^{-1}), from the second law of thermodynamics ($\Delta G = \Delta H - T\Delta S$). $[L_T]$ is the total ligand concentration and $[M]$ is the macromolecules concentration. To consider the j -th injection, the molar charge ratio can be calculated as:

$$N = \frac{[L_j]}{[M]} \quad (2)$$

with

$$L_j = L_{j-1} + V_j[L]_m \quad (3)$$

$$M = [M]_m \cdot V \quad (4)$$

where V_j is the volume of each titration, while $[L]_m$ and $[M]_m$ are the molar charge concentrations of ligand and macromolecules. In the current study, since metal ions were titrated into the Mag-Ligand suspension, we considered metal ions as ligand (L), and Mag-Ligand as macromolecules (M). $[L]_m$ and $[M]_m$ are calculated using:

$$[L]_m = [\text{Metal}]_M \div \text{MW}_{\text{metal}} \cdot \zeta_{\text{metal}} \quad (5)$$

$$[M]_m = [\text{Mag-Ligand}]_M \cdot \rho_{\text{EDTA}} \div \text{MW}_{\text{EDTA}} \cdot \zeta_{\text{EDTA}} \quad (6)$$

where $[\text{Metal}]_M$ and $[\text{Mag-Ligand}]_M$ is the mass concentration of metal ions and Mag-Ligand particles; ζ_{metal} and ζ_{EDTA} is the molecule charge and binding site, respectively, for example, $\zeta_{\text{Cd}^{2+}} = 2$, $\zeta_{\text{Cr}^{3+}} = 3$ and $\zeta_{\text{EDTA}^{4-}} = 4$. ρ_{EDTA} is the mass percentage of EDTA associated with Mag-Ligand particles, and determined by thermogravimetric analyses (TGA), as 12.5% (Fig. S1B†).

2.3. Batch sorption of metal ions

For most experiments 5.0 mg of Mag-Ligand particles were mixed with 25 mL of metal ion ($\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}/\text{Hg}^{2+}/\text{Cr}^{3+}/\text{Ga}^{3+}/\text{In}^{3+}/\text{Ce}^{3+}$) solution (10 mg L^{-1}) in 50 mL conical tubes, and pH was adjusted by using 0.1 M NaOH and HCl. Then, these tubes were mixed in an end-over-end shaker on a Dayton-6Z412A Parallel Shaft (USA) roller mixer with a speed of 70 rpm at room temperature for 24 h to ensure sufficient

equilibration time. Adsorption kinetics studies were carried out at the same conditions as previously stated but for a set amount of time, varying from 1 min to 24 h, with pH = 7. After mixing the Mag-Ligand particles with dissolved contami-

nants for a specified time, the particles were separated from the mixture with the Eclipse magnet. All experiments were conducted at ambient temperature (298 K).

Competitive sorption was conducted for three groups: (1) Cd^{2+} and Pb^{2+} , for which Mag-Ligand has the highest sorption capacity; (2) rare earth elements: Ga^{3+} , In^{3+} and Ce^{3+} ; (3) six metals: Cd^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , Hg^{2+} and Cr^{3+} . In each group, 10 mg of Mag-Ligand particles were mixed with 25 mL of equal concentrations (varied from 1 to 20 mg L^{-1}) of each metal ion.

The concentration of adsorbent was varied from 0.04 to 0.28 g L^{-1} to study the adsorption isotherms of metal ions onto Mag-Ligand at pH 7. Additionally, solutions with varying initial concentrations of metal ions, which ranged from 1 mg L^{-1} to 30 mg L^{-1} were treated with the same procedure as above at pH 7 and 5.0 mg Mag-Ligand.

A Thermo iCAP 6300 inductively coupled plasma with atomic emission spectroscopy (ICP-AES) and an Agilent 7900 ICP-MS were used to analyze the concentration of metal ions.

3. Results and discussion

3.1. Characterization of Mag-Ligand

The core/shell structure of Mag-Ligand is shown in the TEM micrograph (Fig. 1B), and the surface area was determined to be $21.68 \text{ m}^2 \text{ g}^{-1}$ (Table S1†). The FTIR spectra (Fig. S1A†) confirmed that EDTA was successfully attached on the surface of Mag-Ligand, and the TGA curve (Fig. S1B†) suggests the weight percentage of EDTA is approximately 12.5%. Mag-Ligand was also demonstrated to be superparamagnetic with excellent magnetic responsivity (Fig. S2†). More details about the results and discussion of the characterization is available in the ESI†

3.2. Determination of Mag-Ligand/metal ion thermodynamic binding parameters by ITC

To quantify the strength of binding of various metal ions to Mag-Ligand, nine different metal cations were titrated into a suspension with Mag-Ligand particles in individual experiments using ITC. The thermodynamic process due to the interactions between metal ions and Mag-Ligand as the metal ions are titrated into the suspension is shown in the real-time thermogram in Fig. 2A, which presents the isothermal titration of a 0.5 g L^{-1} Mag-Ligand dispersion with 5 mM Pb^{2+} added sequentially. During the titration, heat provides the binding energy between metal ions and Mag-Ligand

Fig. 2 (A) Real-time thermogram for 0.5 g L⁻¹ Mag-Ligand titration with 5 mM Pb²⁺ at 298 K; and (B) integrated binding isotherm as a function of molar ratio of Pb²⁺ ions to Mag-Ligand particles, fitted with MNIS model; symbols represent experimental data, and red line represents model prediction.

particles,⁴⁶ which can be obtained by directly measuring the differential power between the reference cell (filled with degassed DI water) and the sample cell (filled with the Mag-Ligand dispersion). Each injection of metal ions results in the evolution of heat (exothermic) within the sample cell

causing a negative change in the heat flow, shown as negative peaks in the thermogram (Fig. 2A). In Fig. 2A, the peak amplitudes and area gradually decrease as more metal ions are added, since the number of available negatively charged ligand binding sites on Mag-Ligand particles decreases. The thermograms for 8 other metal ions are presented in the ESI† as Fig. S4.

The energy exchange as a function of the Pb²⁺ to Mag-Ligand charge ratio is presented in Fig. 2B. MNIS (eqn (1)) was applied to process the data. The heat flow data fitted with eqn (1) for the eight other metal ions are shown in Fig. S5,† and all the fitted and calculated thermodynamic parameters are listed in Table 1. All metal Mag-Ligand interactions showed negative enthalpy (ΔH) of reaction values at 298 K, implying that these interactions are all enthalpically favored for the formation of complexes. We obtained negative changes in free energy (ΔG) of reaction values ranging from -18.08 to -24.21 kJ mol⁻¹ in our experiments, indicating all of the studied interactions between metal and Mag-Ligand are energetically favored spontaneous processes at 298 K. Most of the metal Mag-Ligand interactions have positive changes in entropy, but Hg²⁺ and Pb²⁺ have a negative ΔS , indicating strong bonds between Hg²⁺ or Pb²⁺ with hydration water (metal–oxygen bonds), as the entropies of hydration are negative^{47,48} between Hg²⁺ or Pb²⁺ and Mag-Ligand particles.^{47,48} These two metals (Hg²⁺ and Pb²⁺) also resulted in some of the highest sorption capacities. For metal ions with positive entropy changes, the metal Mag-Ligand interactions result from favorable enthalpy conditions ($\Delta H < 0$) and entropic gain ($T\Delta S > 0$), as shown in Table 1. Thus, for these metal ions, the metal Mag-Ligand complexations are most likely dominated by the weaker adsorption onto the porous structure, reflected in the binding energy ($\Delta H < -T\Delta S$).⁴⁹

Table 1 also indicates the sequence of the metal ion affinity to Mag-Ligand, which follows the pattern Cr³⁺ < Cu²⁺ < Zn²⁺ < Ga³⁺ < Ce³⁺ < Cd²⁺ < In³⁺ < Hg²⁺ < Pb²⁺. Cr³⁺ has the weakest interaction toward Mag-Ligand with a binding constant of 1.472×10^3 M⁻¹, while Pb²⁺ showed the highest affinity with a binding constant of 1.744×10^4 M⁻¹, which is more than a 10-fold difference. It should be noted that the binding constants reflect the entire interaction of Mag-Ligand with the metal ions, involving complexation reactions, adsorption onto porous structures and electrostatic

Table 1 ΔH , K_d and n derived using the MNIS model based on the ITC analysis of the integrated heats. ΔG and ΔS were calculated from K_d and ΔH values

Element	ΔH (kJ mol ⁻¹)	K_d (M ⁻¹)	ΔG (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)	$-T\Delta S$ (kJ mol ⁻¹)	n
Cr ³⁺	-3.334	1.472×10^3	-18.08	49.47	-14.75	2.554
Cu ²⁺	-12.82	1.825×10^3	-18.61	19.45	-5.799	1.171
Zn ²⁺	-10.96	1.934×10^3	-18.76	26.15	-7.795	1.162
Ga ³⁺	-7.416	2.693×10^3	-19.58	40.8	-12.16	2.800
Ce ³⁺	-8.732	3.684×10^3	-20.36	38.99	-11.62	1.051
Cd ²⁺	-8.828	5.691×10^3	-21.43	42.28	-12.61	1.319
In ³⁺	-8.272	6.282×10^3	-21.68	44.97	-13.41	1.707
Hg ²⁺	-45.74	7.819×10^3	-22.22	-78.87	23.52	0.360
Pb ²⁺	-26.43	1.744×10^4	-24.21	-7.457	2.223	0.181

interactions.^{10,50,51} The difference in magnitude of Mag-Ligand binding with different metal ions is likely the result of a combination of several factors, including the geometry of the metal coordination complexes, ionic radii of the metal cations and metal valence.^{52–54} Most of the stoichiometry (n) values are close to 1 (Table 1), suggesting the complexation between metal ions and the ligand (e.g. EDTA) associated on the surface of Mag-Ligand particles is the dominant process.^{55,56} However, for Hg^{2+} and Pb^{2+} , the stoichiometry (n) values are much lower than 1, and it may result from the conformational hindrance as Hg^{2+} and Pb^{2+} have larger ionic radii⁵⁷ (Fig. 4). These key thermodynamic data of the interaction between Mag-Ligand and nine different metal ions indicate promising applications in environmental remediation and metal recovery processes.

3.3. Sorption kinetics of individual metal ions

Time dependent removal of Pb^{2+} (initial concentration = 10 mg L^{-1}) by Mag-Ligand (0.2 g L^{-1}) showed rapid adsorption in the first 15 minutes, with >97% removal efficiency, and thereafter the rate decreased gradually and reached equilibrium, as shown in Fig. 3A. Since most of the sorption occurred in the first 30 minutes, the rest of the kinetic studies were conducted with mixing times of 1, 5, 10, 15 and 30 minutes. Both pseudo-first-order and pseudo-second-order kinetic models were used to investigate the adsorption rate (Fig. 3B), and were judged based on the regression coefficient (R^2). Sorption of Pb^{2+} by Mag-Ligand followed the pseudo-second-order model ($R^2 = 0.997$) better. The kinetic studies for the 8 other metal ions are presented in Fig. S6.† The calculated kinetic parameters are summarized in Table 2, indicating very good fit with the pseudo-second-order model ($R^2 > 0.990$), compared to a pseudo-first-order model.

The effective ionic radius of each metal ion serves to determine the adsorption rate,⁵⁸ as generally reflected by the relation between ionic radius and k_2 (Fig. 4, data for ionic radii from Shannon, 1976 (ref. 59)). Smaller metal ions such as Cr^{3+} and Cu^{2+} have much faster equilibrium rates than larger ions (e.g. Cd^{2+} and Pb^{2+}). This result can be expected because the adsorption is controlled either by diffusion onto Mag-Ligand's porous structure or by a second-order chemical reaction⁶⁰ with the chelating functional groups present on the surface of Mag-Ligand,¹⁰ both of which are influenced by metal ion size.

3.4. Sorption isotherms of individual metal ions

Fig. 5 presents the experimental results of the non-competitive sorption for each metal ion (Cr^{3+} , Cu^{2+} , Ce^{3+} , Zn^{2+} , In^{3+} , Ga^{3+} , Hg^{2+} , Cd^{2+} and Pb^{2+}) for the range of concentrations studied, as well as the fit of the Langmuir isotherm model (fitted parameter values are summarized in Table 3). Overall the Langmuir model provides excellent fit to the data (results for Freundlich model not shown).

Pb^{2+} exhibited the highest adsorption capacity onto Mag-Ligand (112.4 mg g^{-1}) while Cr^{3+} exhibited the lowest sorp-

Fig. 3 (A) Pb^{2+} sorption uptake versus time at pH 7; and (B) sorption kinetics fitted by pseudo-first order (regression coefficient factor $R^2 = 0.864$) and pseudo-second order (regression coefficient factor $R^2 = 0.997$) models onto Mag-Ligand at pH 7.

Fig. 4 Equilibrium rate constants of kinetics k_2 (red dots) versus effective ionic radii (blue bars) (in pm, $1 \text{ pm} = 10^{-12} \text{ m}$), data for ionic radii from Shannon, 1976.⁵⁹

tion capacity (18.17 mg g^{-1}). These differences reflect the different interaction strengths (e.g. binding affinity constant and Gibbs free energy) between the individual metal ions and

Table 2 Adsorption kinetics of metal ions onto Mag-Ligand. Based on pseudo-second-order model for the adsorption kinetics of each individual metal

Element	q_e (mg g ⁻¹)	k_2 (g h ⁻¹ mg ⁻¹)	R^2
Cr ³⁺	5.084	17.59	0.995
Cu ²⁺	25.71	7.566	0.997
Zn ²⁺	23.26	1.027	0.999
In ³⁺	16.50	4.590	0.998
Ga ³⁺	13.64	5.373	0.990
Ce ³⁺	22.37	2.220	0.996
Cd ²⁺	34.84	2.746	0.991
Hg ²⁺	42.02	2.832	0.999
Pb ²⁺	55.87	1.602	0.999

Table 3 Langmuir isotherm model fitted parameters for sorption of each individual ion onto Mag-Ligand

Element	q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2
Cr ³⁺	18.17	3.154	0.999
Cu ²⁺	23.09	-2.221	0.937
Zn ²⁺	33.28	4.645	0.973
In ³⁺	34.21	4.684	0.967
Ga ³⁺	36.91	3.229	0.990
Ce ³⁺	27.56	14.69	0.988
Cd ²⁺	79.37	7.200	0.980
Hg ²⁺	74.97	12.83	0.961
Pb ²⁺	112.4	12.30	0.769

Mag-Ligand particles. Notably, the sequence of maximum sorption capacity predicted by the Langmuir isotherm sorption model agreed with the trend of metal ion binding affinity to Mag-Ligand (Fig. 6), with a correlation coefficient, $r = 0.72$, indicating a strong positive relationship. Furthermore, the similar trend among sorption capacity, kinetic rate and binding constants indicated that the most likely mechanisms of interactions between metal ions and Mag-Ligand are complexation reactions and adsorption onto porous structures.⁶¹

Interestingly these results do not follow the sequence in conventional formation constants for metal-EDTA complexes⁶² ($\log K$, 298 K) strictly, which are 23.40 for Cr³⁺ and 18.04 for Pb²⁺, and the order of magnitude of the affinity constants we obtained in the current study are much lower. As indicated in our previous study,¹⁰ EDTA was covalently attached to the APTES coated maghemite nanoparticles by the formation of amide bonds between the carboxylic acid groups of the complexing agent and amino groups provided by the APTES coating. This covalent attachment requires that at

Fig. 5 Adsorption of individual metal ions (Cr³⁺, Cu²⁺, Ce³⁺, Zn²⁺, In³⁺, Ga³⁺, Hg²⁺, Cd²⁺ and Pb²⁺) onto Mag-Ligand with Langmuir adsorption isotherms fit at pH 7, symbols represent experimental data, error bars represent standard deviation from the mean ($n = 3$), and red line represents model prediction.

Fig. 6 Predicted maximum adsorption capacity (using Langmuir model) of metal ions onto Mag-Ligand in individual sorption (blue bars) versus the binding constant $\log K_d$ (red dots).

least one of EDTA's carboxylic acid groups be bound, which influences its complexing ability.⁶³ Therefore, the binding capacity of EDTA attached to Mag-Ligand particles is different from the unbound EDTA. The thermodynamic data is also different, which needs to be determined, for example *via* ITC.

The Visual MINTEQ model was used to simulate metal species distribution at pH 7 (Table S2†), the pH at which we conducted the sorption studies. Most of the metals have free ions as the dominant species (>96%), although all the metals form aqueous hydroxide species at pH 7. Cr³⁺ and Cu²⁺ have the smallest fraction of free ions, and a lower removal efficiency (Table 3), suggesting that forming hydroxide species may hinder the removal efficiency *via* conformational resistance and/or reduced electrostatic binding or even repulsion.

Furthermore, the sorption studies were conducted under different environmental conditions by adjusting the pH (Fig. S7†) and the water hardness (*i.e.* the concentration of Ca²⁺ and Mg²⁺ present in the water matrices) (Fig. S8†). The results indicate stable and good performance across a wide range of Ca²⁺ or Mg²⁺ concentrations (1–100 mg L⁻¹) and pH (3–7). In our previous study,¹⁰ Mag-Ligand also exhibited high regenerability and reusability.

3.5. Competitive equilibrium of multiple metal ions

Since wastewater usually contains a wide variety of dissolved metal ions we conducted competitive sorption with three groups of metal ions, with equal initial metal ion concentrations ranging from 1 to 20 mg L⁻¹. In group 1 (Cd²⁺ and Pb²⁺) removal efficiency of both metal ions increased first and then decreased with increasing initial ion concentration, once the maximum adsorption capacity was reached (Fig. 7A). In group 2 (Ga³⁺, In³⁺ and Ce³⁺) and group 3 (Cd²⁺, Pb²⁺, Cu²⁺, Zn²⁺, Hg²⁺ and Cr³⁺), the removal efficiency of all the metal ions decreased with increasing initial ion concentration, as shown in Fig. 7B and C, respectively.

Fig. 7A indicates that Mag-Ligand has stronger affinity for Pb²⁺ than Cd²⁺ in competitive sorption, with a maximum ad-

Fig. 7 Competitive sorption of multiple metal ions (A) group 1: Cd²⁺ and Pb²⁺; (B) group 2: Ce³⁺, In³⁺ and Ga³⁺; and (C) group 3: Cr³⁺, Zn²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Cu²⁺ onto Mag-Ligand at pH 7 as a function of initial ions concentration with a fixed adsorbent concentration of 4 g L⁻¹.

sorption capacity of 49.6 mg g⁻¹ for Pb²⁺ and 19.3 mg g⁻¹ for Cd²⁺ (Table S4†), which agreed with the trend in individual

sorption (Table 3). A similar trend was observed in group 2 (Fig. 7B), where the affinity was $\text{Ga}^{3+} > \text{In}^{3+} > \text{Ce}^{3+}$, following individual sorption sequence (Table 3).

However, in group 3 Cu^{2+} was sorbed to a greater extent (21.4 mg g^{-1}) than other metal ions, especially at the higher initial concentration range (Fig. 7C). This was unexpected, since Cu^{2+} exhibited relatively lower sorption capacity in individual sorption compared to other metal ions (Table 3). At low initial metal concentrations all metals are adsorbed, since the sorption capacity of Mag-Ligand is not exceeded. However, at high initial metal concentrations, the sorption capacity is exceeded. Since Cu^{2+} is one of the smallest ions,⁵⁹ it is likely that it can find certain sites which cannot be reached by other metal ions, explaining the behavior.

The competitive isotherm sorption data was analyzed using the Langmuir isotherm model (Fig. S9A–C†), and the fitted parameters are listed in Table S4.† The maximum adsorption capacities of all metal ions onto Mag-Ligand in competitive sorption (Table S4†) are noticeably lower than that in individual sorption (Table 3). This is expected since there are a fixed number of adsorption sites on the Mag-Ligand particles which are shared by the various metal ions.¹⁰ We also conducted an equi-molar concentration competitive sorption study (Fig. S10A–C†), and the results generally agree with the outcome of the equi-mass concentration study (Fig. 7A–C), suggesting the molar gradient of the metal ion did not play a key role in the competitive adsorption.

As shown in Fig. 8, the trend in maximum adsorption capacity of metal ions onto Mag-Ligand in competitive sorption (based on the Langmuir model) generally agreed with the sequence of k_2 (equilibrium kinetic rate constant). Thus, in competitive sorption, as the number of binding sites on Mag-Ligand particles is limited, metal ions with higher adsorption rate occupy the sites first, leading to higher removal rate, regardless of the affinity. This also explains the fact that Cu^{2+} showed slightly lower removal efficiency than other metal

ions at low initial concentration (Fig. 7C), as there were sufficient absorption sites and Cu^{2+} has lower affinity to Mag-Ligand.

4. Conclusion

We investigated the thermodynamics, kinetic and competitive equilibrium of sorption using Mag-Ligand to remove several different metal ions from aquatic systems. Using isothermal titration microcalorimetry we determined the sequence of selectivity as $\text{Cr}^{3+} < \text{Cu}^{2+} < \text{Zn}^{2+} < \text{Ga}^{3+} < \text{Ce}^{3+} < \text{Cd}^{2+} < \text{In}^{3+} < \text{Hg}^{2+} < \text{Pb}^{2+}$. The interactions are enthalpically driven and energetically favorable with exothermic binding reactions. Given their large surface area relative to volume, these magnetic adsorbents result in fast kinetics, with >97% removal in 15–30 min. The removal capacity remains high for a significant range of aqueous chemistries, over a range of pH (Fig. S7†) and water hardness (Fig. S8†) conditions. The magnetic behavior of Mag-Ligand results in fast and efficient solid–liquid separation after the sorbent has extracted the metal ions from the contaminated waters. Mag-Ligand showed high sorption capacity (average $\sim 50 \text{ mg g}^{-1}$) for these nine metal ions, typically in less than 15 min. We demonstrate that Mag-Ligand can be regenerated for reuse, providing a more sustainable, fast, convenient, and efficient approach for heavy metal remediation.

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Fig. 8 Langmuir model predicted maximum adsorption capacity (q_e) of metal ions onto Mag-Ligand in group competitive sorption (blue bars) versus the equilibrium kinetic rate constant, k_2 (red dots).

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