

Modelling equilibrium adsorption of single, binary, and ternary combinations of Cu, Pb, and Zn onto granular activated carbon

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Abstract

Elevated concentrations of heavy metals in water can be toxic to humans, animals, and aquatic organisms. A study was conducted on the removal of Cu, Pb, and Zn by a commonly used water treatment adsorbent, granular activated carbon (GAC), from three single, three binary (Cu-Pb, Cu-Zn, Pb-Zn) and one ternary (Cu-Pb-Zn) combination of metals. It also investigated seven mathematical models on their suitability to predict the metals' adsorption capacities. Adsorption of Cu, Pb, and Zn increased with pH with an abrupt increase in adsorption at around pH 5.5, 4.5, and 6.0, respectively. At all pHs tested (2.5 – 7.0) the adsorption capacity followed the order Pb > Cu > Zn. The Langmuir and Sips models fitted better than the Freundlich model to the data in the single metal system at pH 5. The Langmuir maximum adsorption capacities of Pb, Cu, and Zn (mmol/g) obtained from the model's fits were 0.142, 0.094, and 0.058, respectively. The adsorption capacities (mmol/g) for these metals at 0.01 mmol/L equilibrium liquid concentration were 0.130, 0.085 and 0.040,

respectively. Ideal Adsorbed Solution (IAS)-Langmuir and IAS-Sips models fitted well to the binary and ternary metals adsorption data, whereas the Extended Langmuir and Extended Sips models' fits to the data were poor. The selectivity of adsorption followed the same order as the metals' capacities and affinities of adsorption in the single metal systems.

Keywords: adsorption modelling, heavy metals adsorption, ideal adsorption solution theory, granular activated carbon, metal adsorption competition

Introduction

Elevated concentrations of heavy metals such as Cu, Pb, and Zn in water pose a great risk to humans, animals, and aquatic flora and fauna (Ahmaruzzaman 2011; Fu and Wang 2011). Furthermore, heavy metals are not biodegradable and therefore persist and accumulate in the water and have a cumulative effect. Consequently, these metals must be removed from water. Several methods are available for the removal of heavy metals from water, for instance chemical precipitation, ion exchange/adsorption, membrane filtration and electrochemical methods (Ahmaruzzaman 2011; Baily et al. 1999; Fu and Wang 2011). Of these, adsorption is generally preferred because of its simplicity, effectiveness at low concentration, low waste production and low cost (Hua et al. 2012). Granular activated carbon (GAC) is a widely used and versatile adsorbent in water reclamation plants as it can remove many contaminants such as organic carbon, turbidity, micropollutants, and nutrients (Shanmuganathan et al. 2017; Sountharajah et al. 2015b; Yin et al. 2007). It can also effective in removing heavy metals (Genc-Fuhrman et al. 2007; Minceva et al. 2007; Sountharajah et al. 2015a). GAC's high efficiency in removing pollutants is because of its high surface area (500-1500 m²/g), internal porosity and the presence of different types of functional groups, low cost and easy availability (Cougnaud et al. 2005; Pawluk et al. 2015; Shanmuganathan et al. 2017).

Although GAC has been shown to remove heavy metals from single metal systems in many studies (An et al. 2001; Lakherwal et al. 2016; Sounthararajah et al. 2015b), only a few studies have been reported on removing metals when they are present together in water (Gabaldon et al. 1996; Pawluk et al. 2015;). Studies on simultaneous removal of metals from mixed metals systems are important because most wastewaters contain more than one heavy metal and there can be competitive adsorption between metals. For this reason, it is important to study the adsorption behaviour of mixtures of metals and to determine the effect of one metal on the adsorption of another metal. This can be done only by conducting experiments on multicomponent systems. If the experimental data obtained in these systems can be mathematically modelled, the models can be used to predict the adsorption behaviour of mixtures of metals. The main advantage of a model is that it can in principle be used to simulate the process in other experimental conditions; not just those used to estimate the model parameters. Heavy metals adsorption modelling has been reported for mixtures of metals adsorption mainly in binary metals systems on many adsorbents such as Cu-Cd, Cu-Ni, Cd-Ni on pine bark (Al-Asheh et al. 2000), Cu-Zn, Cu-Cd, Cd-Zn on bone char (Ko et al. 2004), Pb-Hg on bentonite-alginate composite (Sellaoui et al. 2018), Pb-Cu, Pb-Cd, Cu-Cd on zeolite (Lee and Moon 2001), Cu-Pb on sea mango shell (Sellaoui et al. 2017) and Cd-Zn, Zn-Ni, Cd-Ni on tourmaline (Liu et al. 2013). Adsorption of binary metals was mostly described using extended Langmuir (E_L) and extended Sips (E_S) models and models based on Ideal Adsorbed Solution (IAS) theory.

Modelling of binary metals adsorption is limited for adsorption on GAC, which is a versatile adsorbent used extensively in the water treatment process for many decades. Erto et al. (2015) studied the adsorption of Cd and Zn on a GAC and reported that Cd in solution, irrespective of its concentration, did not influence the Zn adsorption capacity. In contrast, increase of Zn concentration decreased Cd adsorption capacity. The results were successfully described by E_L and vacancy solution theory models. In another study on the adsorption of

Cu and Ni on coconut shell activated carbon, E_L model was found to describe the binary adsorption of these metals very well (Wu et al. 2013).

Compared to binary metals adsorption, modelling of ternary heavy metals adsorption is rare for most adsorbents. Lee and Moon (2001) reported that the model based on IAS theory successfully described the data on adsorption of Pb, Cd, and Cu on a zeolite. We are not aware of any studies on modelling of metals adsorption on GAC in ternary system. The study reported in this paper is the first one of this nature. Here, we compare E_L and E_S models with two IAS models for the adsorption of three heavy metals in a ternary system.

The objectives of this study were to: (1) mathematically model the adsorption of heavy metals on GAC in single, binary, and ternary systems; and (2) determine the effect of pH on the adsorption of Cu, Pb, and Zn and zeta potential of GAC suspensions and explain the mechanism of adsorption behaviour in the different metals adsorption systems.

Materials and methods

GAC and chemicals

A wood-based granular activated carbon (GAC) obtained from James Cummins P/L, Australia was sieved to a particle size range of 0.3–0.6 mm and used in the study. The GAC had a BET surface area of 950 m²/g and ash content of 6.9%. Analar grade (laboratory analytical grade, 99% purity) nitrate salts of heavy metals (Pb, Cu, and Zn) were employed in the study to prepare the heavy metals solution. These salts were supplied by Sigma-Aldrich (USA).

Equilibrium adsorption experiments

Equilibrium adsorption isotherms for each metal ion were obtained in batch experiments by shaking GAC at doses of 0.1 to 5 g/L with 100 mL of 0.1 mM and 0.2 mM solutions containing Cu, Pb and Zn in 200 mL flasks for 24 h at room temperature ($24 \pm 0.5^\circ\text{C}$). Initial pH of the suspensions was kept at 5.0 to avoid any precipitation from metals. The pH decreased during adsorption due to release of H^+ from the surface of GAC. This decrease of pH occurred mostly during the initial period of adsorption when majority of the adsorption took place. To measure the heavy metals adsorption at a constant equilibrium pH of 5.0, the pH was adjusted back to the initial value after 4 h shaking period. The final pH was 5.0 ± 0.1 . The background ionic strength was maintained at 0.001 M NaNO_3 . After 24 h of agitation the adsorbent was separated from the liquid by filtration through a 1.2 μm filter, the filtrates were acidified and analysed for metal concentration using a Microwave Plasma-Atomic Emission Spectrometer (Agilent 4100 MP-AES). The amount of metals adsorbed was determined by subtracting the respective amounts of metals in the filtrate from the amounts initially added.

Equimolar concentration of 0.2 mM of Zn-Cu, Zn-Pb, Cu-Pb binary mixtures and Zn-Cu-Pb ternary mixture at pH 5.0 ± 0.1 served as a feed solution for multicomponent metals. The adsorption experiments were conducted in a flat shaker using 200 mL Pyrex flasks containing 100 ml mixed metals solutions and a range of GAC doses and agitated at 120 rpm for 24 h at room temperature ($24 \pm 0.5^\circ\text{C}$). The amounts of metals adsorbed were calculated as before.

Modelling adsorption

For the single metals, three adsorption models, specifically Langmuir (equation 1), Freundlich (equation 2), and Sips (or sometimes known as Langmuir-Freundlich) (equation 3)

were employed to study the adsorption process (Ahmaruzzaman 2011; Freundlich 1932; Langmuir 1918; Oh et al. 2009; Papageorgiou et al. 2009; Sips 1948).

The Langmuir model (Langmuir 1918), which was derived based on a monolayer homogeneous surface adsorption process, is one of the most commonly used models for equilibrium adsorption studies. The model assumes that the adsorption sites have the same energy of adsorption and are equally available to all the adsorbing ions and there is no interaction between adsorbed ions (Erto et al. 2015). The equation for this model can be expressed as

$$q = \frac{q_m bC}{1 + bC} \quad (1)$$

where q is the equilibrium solid-phase concentration (mmol/g), q_m is the maximum adsorption capacity (mmol/g), b is the Langmuir isotherm constant (1/mmol) and C is the equilibrium liquid-phase concentration (mmol/L). On the other hand, the Freundlich model equation (Freundlich 1932) is characterised by the heterogeneity factor, n , and it can be employed to describe the heterogeneous surface adsorption sites with different affinities for adsorption.

The Freundlich model can be expressed as

$$q = k_F C^{1/n} \quad (2)$$

where C = equilibrium concentration (mmol/L), q = amount adsorbed per unit mass of GAC (mmol/g), and K_F ((mmol/g)/(mmol/L) ^{n}) and n are Freundlich constants. The Sips (or Langmuir-Freundlich) model (Sips 1948) is a combination of the Langmuir and Freundlich models, which can be given as

$$q = \frac{q_m bC^{1/n}}{1 + bC^{1/n}} \quad (3)$$

In order to properly express the competitive multicomponent adsorption behavior, many approaches have been introduced with different advantages and disadvantages. The extended Langmuir (E_L) model, which was a simple extension of the Langmuir equation (1), has been widely used to predict the multicomponent adsorption isotherm data (Ahmaruzzaman 2011; Al-Asheh et al. 2000; Oh et al. 2009; Papageorgiou et al. 2009; Tien 1994). The main advantage of the E_L model is its simplicity in calculation but this equation, in some cases, is inappropriate to describe the multicomponent experimental data. Utilising this model to estimate multicomponent equilibrium data is reasonable only when the q values for each adsorbate obtained from single metal isotherm model are close to each other. The E_L model can be given as

$$q_i = \frac{q_{mi} b_i C_i}{1 + \sum_{j=1} b_j C_j} \quad (4)$$

where q_i is the amount adsorbed of component i in the multicomponent system (Cu, Pb, and Zn) and C_i is the equilibrium concentration of each component in the system, and q_{mi} and b_i are Langmuir constants obtained from the single metal isotherm for each metal and substituted in the above equation to predict the uptake of particular metal ions in the multicomponent system.

The extended Sips (E_S) model, which is also called loading ratio correlation, is an extension of the Sips equation (Al-Asheh et al. 2000; Papageorgiou et al. 2009; Tien 1994). In general, E_S model is expected to have a better data-fitting ability than E_L model in the multicomponent experimental system because it has the additional heterogeneity parameter.

The E_S model can be expressed as

$$q_i = \frac{q_{mi} b_i C_i^{1/n_i}}{1 + \sum_{j=1} b_j C_j^{1/n_j}} \quad (5)$$

where q_i is the amount adsorbed of component i in the multicomponent system (Cu, Pb, and Zn) and C_i is the equilibrium concentration of each component in the system and q_{mi} and b_i are Sips constants obtained from the single metal isotherm for each metal and substituted in the above equation to predict the uptake of a particular metal ion in the multicomponent system. n_i (or n_j) is the exponent of the i th (or j th) adsorbate of the Sips equation representing the system heterogeneity.

Myers and Prausnitz (1965) proposed the IAS theory based on the interfacial thermodynamics to predict the multicomponent gas mixtures using single component isotherms. This IAS theory was then extended by Radke and Prausnitz (1972) for application to multicomponent liquid phase adsorption systems. The major theoretical advantages of the IAS theory are that: firstly, it has a sound thermodynamic basis; and secondly, it requires only single-component isotherm parameters to predict the adsorption equilibrium for the multicomponent system. IAS theory is based on the assumption that the adsorbed phase can be treated as an ideal solution of the adsorbed components. Also, IAS theory uses several equations to calculate the mole fraction of adsorbed phase concentrations. The use of these equations is shown and discussed below (Cheung et al. 2003; Ko et al. 2004; Lee et al. 2001; Tien 1994).

The general calculation procedure is as follows:

$$c_i = c_i^0(\pi_i, T)x_i \quad (6)$$

$$\pi_i = \frac{RT}{A} \int_0^{c_i^0} \frac{q_i^0}{c_i^0} dc_i^0 \quad (7)$$

$$\Pi = \frac{\pi_i A}{RT} = \int_0^{c_i^0} \frac{q_i^0}{c_i^0} dc_i^0 \quad (8)$$

$$q_t = \left[\sum_{j=1}^n \frac{x_j}{q_j^0} \right]^{-1} \quad (9)$$

$$q_i = x_i q_t \quad (10)$$

$$\sum x_i = 1 \quad (11)$$

where c_i is the concentration of the i th adsorbate in the liquid phase, c_i^0 is the concentration of the liquid phase in the single component adsorption of the i th adsorbate, π_i is the spreading pressure which is equal for each component in a given system ($\pi_i = \pi_j A = \pi_N = \pi$), R is the gas law constant, T is the temperature, A is the surface area per unit mass of adsorbent, q_i^0 is the concentration of the adsorbed phase in the single component adsorption of the i th adsorbate, Π is the modified spreading pressure, x_i is the mole fraction of the i th adsorbate in the adsorbed phase, q_i is the concentration of the i th adsorbate in the adsorbed phase, and q_t is the total concentration of the adsorbate in the adsorbed phase. The modified spreading pressures for the single component isotherms are:

$$\text{Langmuir: } \Pi = q_{mi} \ln(1 + b_i c_i^0) \quad (12)$$

$$\text{Sips: } \Pi = n_i q_{mi} \ln(1 + b_i (c_i^0)^{1/n_i}) \quad (13)$$

The Newton–Raphson method (Riggs 1988) was used to identify values of Π and x_i that minimise the error between the experimental initial liquid-phase adsorbate concentrations, which are predicted by IAS models. In this work IAS models for binary and ternary component calculations using Langmuir and Sips equations are named as IAS_L and IAS_S, respectively.

Assessing models' fits to experimental data

Assessments of the closeness of the models' fits to experimental data were determined by calculating the coefficient of determination (R^2) and error values based on the differences between model predicted values and experimental values according to the following equation:

$$Error = \frac{100}{N} \sum_{i=1}^N \left(\frac{Q_{exp} - Q_{cal}}{Q_{exp}} \right) \quad (14)$$

where Q_{exp} and Q_{cal} are the metal adsorption capacity values obtained from the experiment and models, respectively, and N represents the number of data points.

Zeta potential measurement

The zeta potential values were measured on 1.0 g/L of GAC with a particle size of 0.075 – 0.150 mm suspensions in the presence of 0.2 mM solutions of Cu, Pb and Zn in the pH range of 2.5-9.0. A Zetasizer nano instrument (Nano ZS Zen3600, Malvern, UK) was used for this measurement, specifically at 10^{-3} M NaNO₃ to maintain a constant ionic strength. The suspensions were agitated for 18 h in a flat shaker at a shaking speed of 120 rpm at room temperature ($24 \pm 0.5^\circ$ C). Because the pHs changed during adsorption, they were adjusted back to their initial values after a 4 h shaking period to keep the pHs as close as possible to

the initial values and the final pHs at the end of 18 h were measured. A HQ40d portable pH Meter was used for all pH measurements. Duplicate measurements were made to minimise undesirable biases (with differences between replicates always being less than 5%) and the average value was used for data analyses.

Effect of pH on heavy metals adsorption

The effect of pH on heavy metals adsorption was investigated by adding 1.0 g GAC with a particle size of 0.3 – 0.6 mm to 100 mL solution containing 0.2 mM Cu, Pb and Zn separately. Then the suspension was shaken in a flat shaker with a shaking speed of 120 rpm at room temperature (24 ± 0.5 °C) for 24 h. The pH values of the solutions were initially set at a range of 2.5 – 10.0 using 0.1 M HCl and 0.1 M NaOH. They were adjusted back to their initial values after a 4 h shaking period. The final pHs at the end of the shaking period were measured.

Results and discussion

Adsorption isotherms

Fig. 1 shows the adsorption isotherms for Cu, Pb, and Zn on GAC at 298 K. As shown in this figure, all adsorption isotherms follow the H-type with steep slope behaviour at low concentration range. This indicates the strong affinity of the adsorbent towards the metals (Tien 1994). The adsorption capacity is in the order of $Pb > Cu > Zn$. As expected, the order of the binary adsorption capacity ($Pb > Cu$, $Cu > Zn$, and $Pb > Zn$) is the same as that of the single component isotherm data (Fig. 2).

The adsorption capacities of the metals in the ternary metals system also followed the adsorption capacity order of the respective metals determined from the single component isotherm data. As in the binary metals system, due to competition for adsorption, the amount of metal adsorbed was less than in the single metal system for all three metals in the ternary metals system (Figs. 1 and 3). The metal with the lowest adsorption affinity in the single metal system (Zn) showed the highest reduction in the amount adsorbed in the ternary system, while the metal which had the highest adsorption affinity (Pb) had the lowest reduction in the amount adsorbed. Another interesting observation in the ternary system is that the adsorption of the highest affinity metal, Pb, increased with equilibrium concentration whereas the less affinity metals, Cu and Zn, decreased with equilibrium concentration (Fig. 3). This is due to insufficient adsorption sites available for the metals at high solution concentrations to accommodate all metals. Pb which had the highest affinity to the sites was preferentially adsorbed at the expense of Cu and Zn.

Zeta potential

Zeta potential analysis showed that the negative zeta potential of GAC in deionised water at an ionic strength of 10^{-3} M NaNO_3 increased with pH (Fig. 4), indicating that the surface negative charge on GAC increased with pH. The zeta potential was zero at approximately pH 3, indicating that the zero point of charge (ZPC, the pH at which the net surface charge is zero) was 3. The low ZPC suggests that the GAC surface had mainly acidic functional groups favouring adsorption of the positively charged metal ions. Noh and Schwarz (1990) reported that oxidation of a coconut based activated carbon using HNO_3 increased the surface acidity thereby decreased the ZPC from 10 to 3.5.

The negative zeta potential of GAC in the presence of Cu, Pb, and Zn at 10^{-3} M NaNO_3 also increased with pH but the rate of increase was much lower than that of GAC in

distilled water (Fig. 4). The difference between the zeta potentials of GAC with and without the presence of heavy metals increased with pH suggesting that the heavy metals were specifically adsorbed by inner-sphere complexation providing surface positive charges (Loganathan et al. 2012). Specific adsorption of heavy metals at high pHs has been reported for several adsorbents and this was explained as being due to adsorption of hydroxy complexes of metals and surface precipitation of metal hydroxides (Karapinar et al. 2016; Nguyen et al. 2017; Sounthararajah et al. 2015a). The zeta potential differences for GAC suspensions with and without heavy metal increased in the order of $Zn < Cu < Pb$, at pHs 4-6 which followed the order of the first hydrolysis constant (pK_1) and solubility product of hydroxide precipitate (pK_{so}) of the metals (Karapinar 2016; Nguyen et al. 2017).

pH effect on adsorption

In agreement with the zeta potential results, the heavy metals adsorption increased with pH (Fig. 5). This is due to the increased number of negative charges on the GAC helping in electrostatic adsorption (outer-sphere complexation) and increased concentration of hydroxy complexes of the metals at higher pHs which were adsorbed specifically by inner-sphere complexation (Huang et al. 2001; Karapinar 2016). James and Healy (1972) using thermodynamic analysis suggested that though the concentrations of hydroxy complexes are lower than that of the divalent metal ions the ion-solvent interactions present a barrier for close approach of the divalent metal ions to the interface between a low dielectric constant solid and water. When the ionic charge is lowered by hydrolysis, the ion-solvent interaction is decreased to reduce the energy barrier to produce a more favourable adsorption. Other reasons for the higher affinity of the much lower solution concentrations of hydroxyl species than the simple divalent metals for adsorbents are: hydrogen-bonding formation between the hydroxyl species and surface oxygen atoms, reduction of free energy requirement for adsorption as a

result of replacement of water of hydration in divalent metal ions by OH⁻ group, hydroxyl species being more hydrophobic than simple metal ions making it more susceptible to chemical bond formation with activated carbon (Elliott and Huang 1979). Corapcioglu and Huang (1987) explained the abrupt increase of adsorption of Cu, Ni, Pb, and Zn at narrow pHs using surface complex formation model involving metal hydroxy species. They stated that specific chemical bonding probably H-bonding provided the sole energy needed for the adsorption.

Another reason for the increased adsorption of metals at high pHs is that the metals might have formed surface hydroxide precipitation on the GAC surfaces at pHs lower than the pHs required for precipitation in pure solutions (Dzombak et al. 1986; Karapinar 2016; Scheidegger et al. 1997; Sparks 2000). Scheidegger et al. (1997) reported that the possible causes for this surface precipitation were the enhanced surface concentration, reduction of the dielectric constant of water near the surface and solid solution formation. Surface precipitation has been convincingly demonstrated by combining kinetic studies and in-situ molecular-scale techniques (Sparks 2000).

The above explanations have been reported for increased adsorption of Pb, Cu and Zn at high pHs on other adsorbents (Karapinar 2016; Sountharajah et al. 2015b). Karapinar (2016) found a linear relationship between the pH at which 50% of Pb, Cu, and Zn adsorption and the metal hydrolysis constant as well as solubility products of metals hydroxide precipitate. In the present study, abrupt increase in metals adsorption occurred at 50% adsorption (adsorption edge) and this occurred at pHs 4.5, 5.5, and 6.0 for Pb, Cu, and Zn in the same order as their order of hydrolysis constants (pK_1) and solubility products (pK_{so}) (hydrolysis constants of 7.71, 7.96, and 8.96 and solubility products of 19.9, 19.3, and 16.5 for Pb, Cu, and Zn, respectively (Sountharajah et al. 2015a)).

Modelling single metal adsorption

Adsorption data for all three metals in the single metal system fitted well to the Langmuir, Sips, and Freundlich isotherm models with the fits being more satisfactory for the first two models (Fig. 1, Table 1). The data fits for these models were better for Cu and Zn ($R^2 = 0.94-0.96$) than Pb ($R^2 = 0.84-0.85$). Good data fit to the Langmuir model suggests that the metals' adsorption on the GAC surface was homogeneous with monolayer coverage. In the Langmuir model, a dimensionless constant called a separation factor R_L that describes the type of adsorption isotherm is calculated from the following formula,

$$R_L = 1 / (1 + bC_m) \quad (15)$$

where C_m is the maximum initial concentration of adsorbate. R_L indicates the favourability of the adsorption process, such as unfavourable ($R_L > 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Ko et al. 2004; Naidu et al. 2016). The calculated R_L values for Cu, Pb, and Zn were in the 0.006–0.010 range, indicating that the adsorption process is favourable for all three metals.

The Langmuir maximum adsorption capacities (mmol/g) for Pb, Cu, and Zn were 0.142, 0.094, and 0.058, respectively (Table 1). This order is consistent with the amount of negative zeta potential reduction caused by these metals which was explained in the earlier section as due to inner-sphere complexation caused by the adsorption of metal hydroxide complexes and surface precipitation of metal hydroxides. Minceva et al. (2007) also reported a larger amount of Pb adsorption (0.12 mmol/g) than Zn adsorption (0.061 mmol/g) on a GAC. However, they explained this difference in adsorption as due to Pb having a higher Pauling electronegativity (2.33) and lower hydrated ionic radius (4.01 Å) than Zn (1.65 and 4.30 Å) (Table 2). Their experiment was conducted in natural water pH without any control of pH during adsorption. The current experiment was conducted at pH 5 and therefore there

could have been a higher proportion of divalent simple metal concentration in solution which would have contributed significantly to the metals' adsorption. Therefore, it is possible that the electronegativity and hydrated ionic radius of the divalent metal ions, as explained by Minceya et al. (2007), would have also contributed to the adsorption in addition to the metal hydroxyl ions and surface precipitation explained earlier. Copper has electronegativity (1.90) (Kang et al. 2016) and hydrated ionic radius (4.19 Å) between Pb and Zn, and therefore produced Langmuir adsorption capacity between Pb and Zn (Table 2). Ion with smaller hydrated ionic radius is able to move closer to the GAC surface as well as easily enter the channels in the GAC for preferential adsorption. Ion with low hydration energy can easily become dehydrated and shrink in size for greater adsorption. The order of adsorption of the metals followed that of hydrated ionic radius but Zn having a slightly lower negative hydration energy than Cu had lower adsorptive capacity than Cu. Probably other factors such as hydrated ionic radius, electronegativity and hydrolysis constant would have had more influence on the adsorption process of these two metals (Table 2).

Modelling binary metals adsorption

Since the Langmuir and Sips models fitted the single metals adsorption data better than the Freundlich model, extended versions of these models (i.e., E_L and E_S) and the IAS theory applied to these models (i.e., IAS_L and IAS_S) were used in the multicomponent adsorption analyses. Adsorption of metals in the binary system, where metals' competition for adsorption occurs, is consistent with the results obtained in the single metal adsorption system. The selectivity of adsorption between metals was in the order Pb > Cu > Zn (Fig. 2). Both the capacity (q_m) and affinity (b) of adsorption of the metals in the single metal systems were in the order Pb > Cu > Zn (Table 1). This means that the metals would preferentially adsorb according to this order when they are present together as pairs. The reasons for this

order of preference were explained in the previous section in terms of the metals' electronegativity, hydrated ionic radius, hydrolysis constant and solubility product. Due to competitive adsorption, the amount of metal adsorbed in the binary systems was lower than in the single metal system for all three metals. The metal with the lower adsorption affinity in the single metal system had higher reduction in adsorption capacity in the binary system (Zn in both the Cu-Zn and Pb-Zn systems and Cu in the Pb-Cu system) (Fig. 2). A similar adsorption reduction pattern was found by Oh et al. (2009) for Pb-Cd adsorption on coastal sediment samples.

Of the various models tested to predict the adsorption behaviour of metals in the binary system of metals, IAS_S and IAS_L emerged as the best for all three combinations of metals (Cu/Pb, Cu/Zn, Pb/Zn) (Fig. 5). These two models predict the binary systems reasonably on the whole (Fig. 2) and had the lowest error values for all three combinations of metals compared to those of simple extension models (i.e., E_L and E_S) (Table 3). Since IAS theory is based on thermodynamics principles and derived for dilute solutions, introducing activity coefficients into IAS theory may help to reduce the errors as Ko et al. (2004) suggested.

Modelling ternary metals adsorption

As in the case of the binary metals systems, it is clear that the IAS approaches (IAS_L and IAS_S) were more suitable for predicting the ternary adsorption system over the range tested than the simple models-extension approaches (E_L and E_S) (Fig. 7). The error values were also the lowest for these two models' fit to the data (Table 3).

Conclusions

Batch adsorption of Cu, Pb, and Zn on GAC was studied in single, binary and ternary metals systems. In the single metals system, all adsorption isotherms followed the H-type with steep slope behaviour at low concentration range. This indicates the strong affinity of the adsorbent towards the metals. The adsorption capacity of Cu, Pb, and Zn increased with pH and an abrupt increase in adsorption (adsorption edge) occurred at around pH 5.5, 4.5, and 6.0, respectively. At all pHs tested (2.5 – 8.0) the adsorption capacity followed the order Pb > Cu > Zn. This is the same order as the solubility products of the metal hydroxides (pK_{so}), metals' electronegativity, and the amount of zeta potential reduction of GAC by the metals, and in the reverse order as the metals' hydrolysis constants (pK_1) and hydrated ionic radii. These properties/observations explained the metals' adsorption capacity differences. The mechanism of adsorption of the metals is mainly inner-sphere complexation (specific adsorption).

In the binary and ternary metals systems, the amount of metal adsorbed was less than in the single metal system for all three metals due to competition for metals' adsorption. The selectivity of adsorption followed the same order as the metals' capacities and strengths of adsorption. The metal with the lowest adsorption affinity in the single metal system (Zn) showed the highest reduction in the amount adsorbed in the ternary system, while the metal which had the highest adsorption affinity (Pb) had the lowest reduction in the amount adsorbed. Also, in the ternary system the adsorption of the highest affinity metal, Pb, increased with equilibrium concentration whereas the less affinity metals, Cu and Zn, decreased with equilibrium concentration

The Langmuir and Sips models fitted better than the Freundlich model to the metals' adsorption in the single metal system. The Langmuir maximum adsorption capacities and strength of adsorption were in the order Pb > Cu > Zn. The IAS_L and IAS_S models fitted well to the binary and ternary metals adsorption data, whereas the E_L and E_S models' fits to the data were poor. The predictions of the metal adsorption capacities by the IAS_L and

IAS_S models in both the binary and ternary metals systems were satisfactory with lowest error values. Since IAS theory is based on thermodynamics principles and derived for dilute solutions, introducing activity coefficients into IAS theory may help to further reduce the errors and this is recommended for future research.

Overall, the study provided new information on the modelling of binary and ternary heavy metals adsorption on GAC, which is a versatile adsorbent used extensively in the water treatment process.

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Figure captions

Fig 1. Adsorption isotherms for metals in single-metal systems and models fits to the data.

Fig 2. Adsorption isotherms of metals in binary metals systems and models fit to data (IAS-Ideal Adsorbed Solution theory, IAS-Langmuir (IAS_L) and IAS-Sips (IAS_S)).

Fig. 3. Adsorption isotherms of metals in the ternary metals system (IAS - IAS-Ideal Adsorbed Solution theory, S – Sips, L – Langmuir).

Fig. 4. Zeta potential of GAC in the presence of 10^{-3} M NaNO_3 and 0.2 mM nitrate salts of Cu, Pb, and Zn and deionised water.

Fig. 5. Effect of pH on Cu, Pb, and Zn (a) removal efficiency and (b) adsorption capacity (0.2 mM nitrate salts of Cu, Pb, and Zn in the presence of 10^{-3} M NaNO_3 and 1 g GAC/L).

Fig 6. Comparison of the models calculated values and experimental values of adsorption capacities in the binary metals systems (E_L-Extended Langmuir, E_S-Extended Sips, IAS-Ideal Adsorbed Solution theory).

Fig 7. Comparison of models' calculated values and experimental values of adsorption capacities in the ternary metals system (E_L-Extended Langmuir model, E_S-Extended Sips model, IAS-Ideal Adsorbed Solution theory).

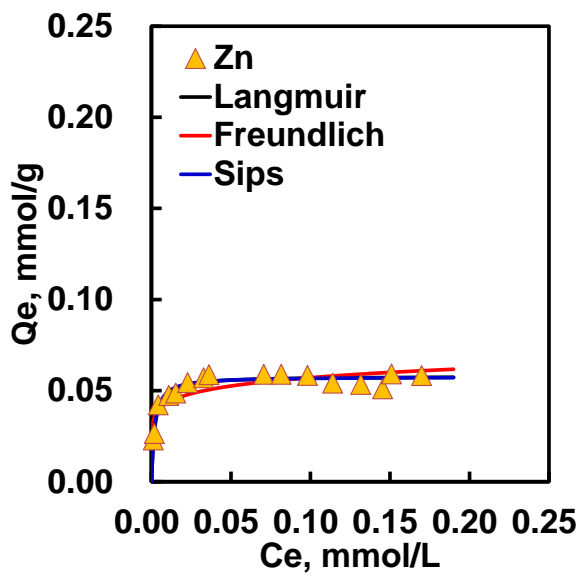
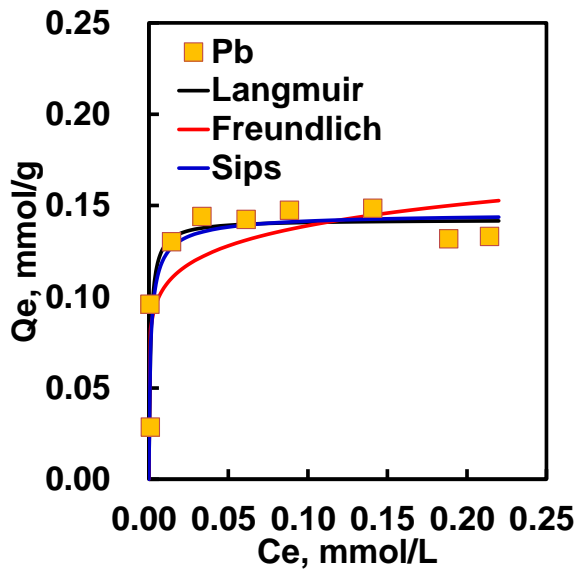
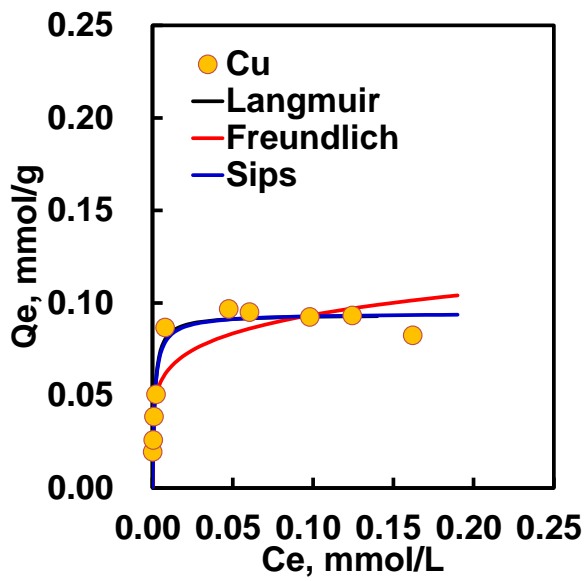


Fig. 1.

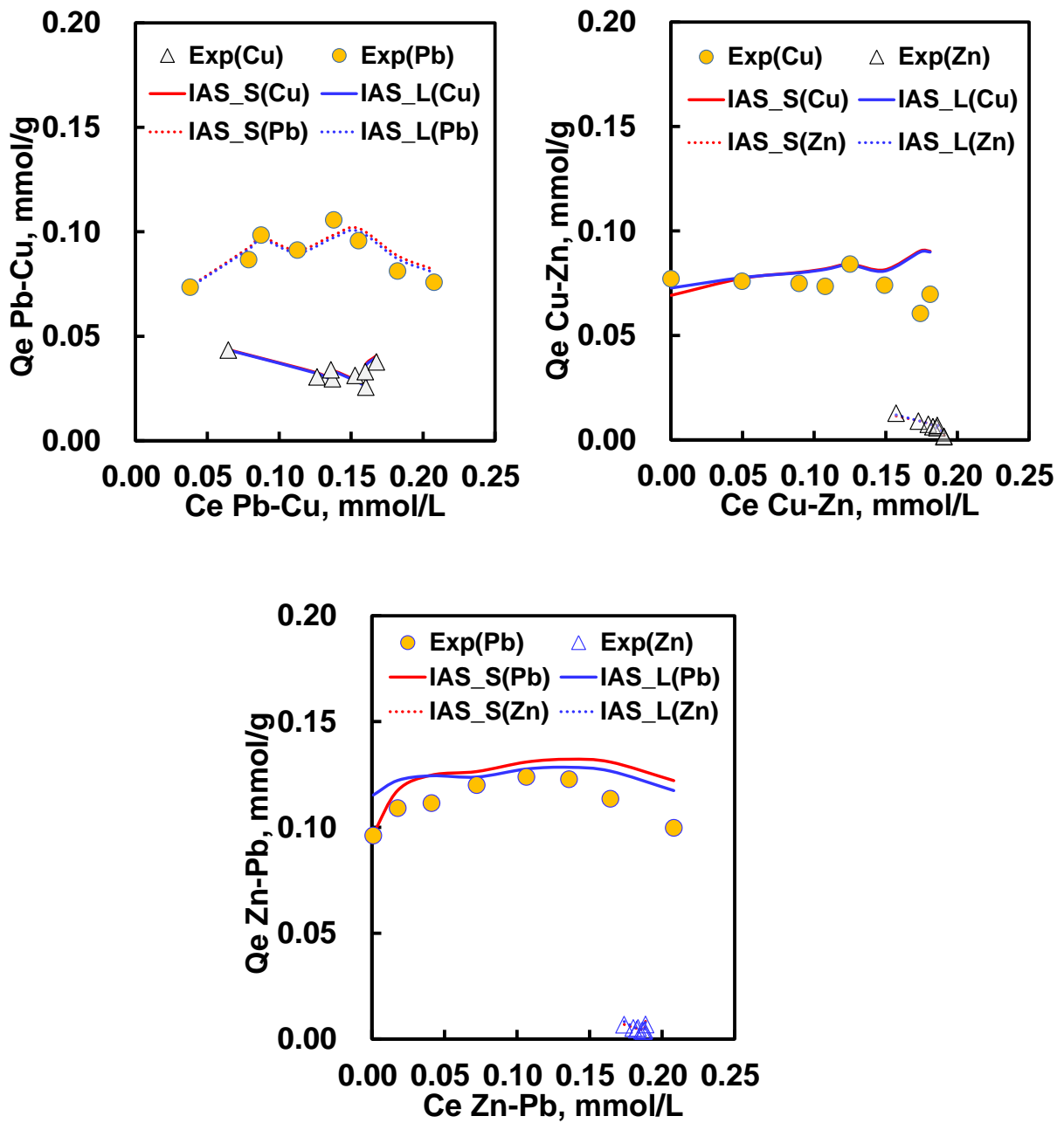


Fig. 2.

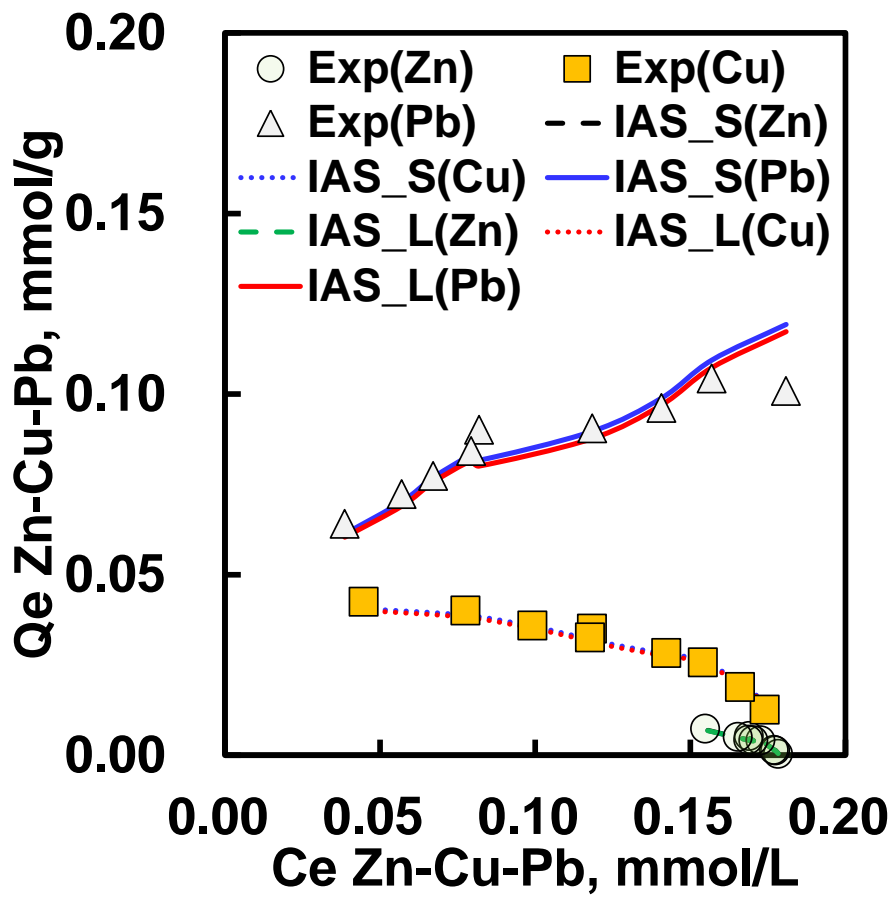


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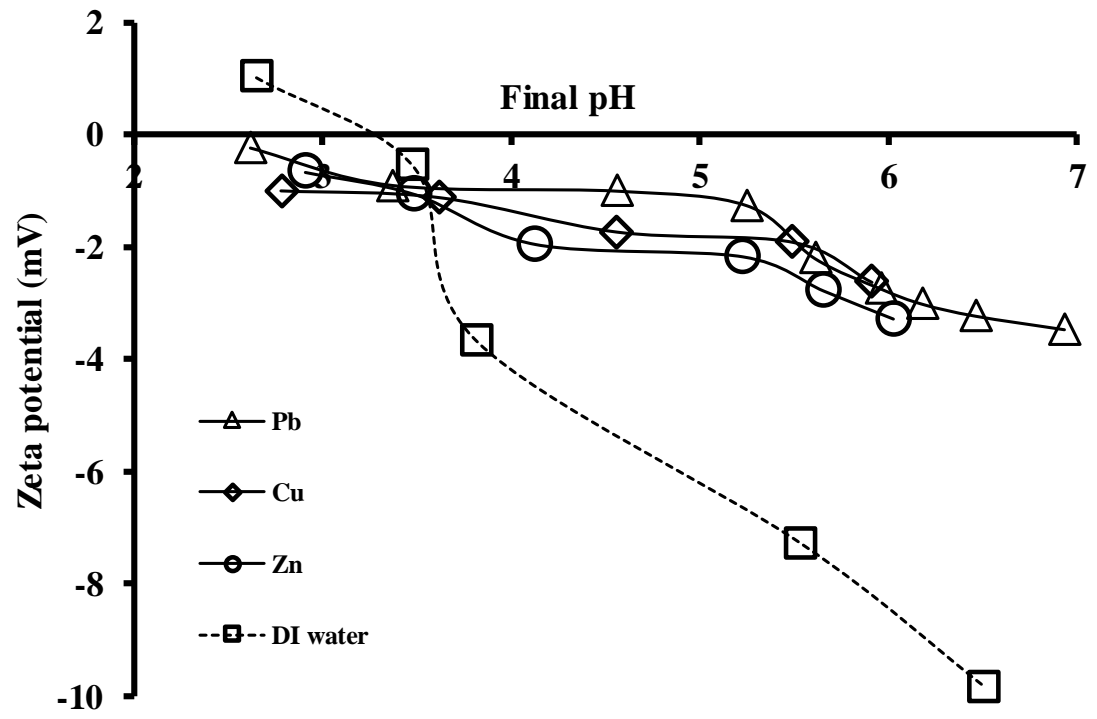


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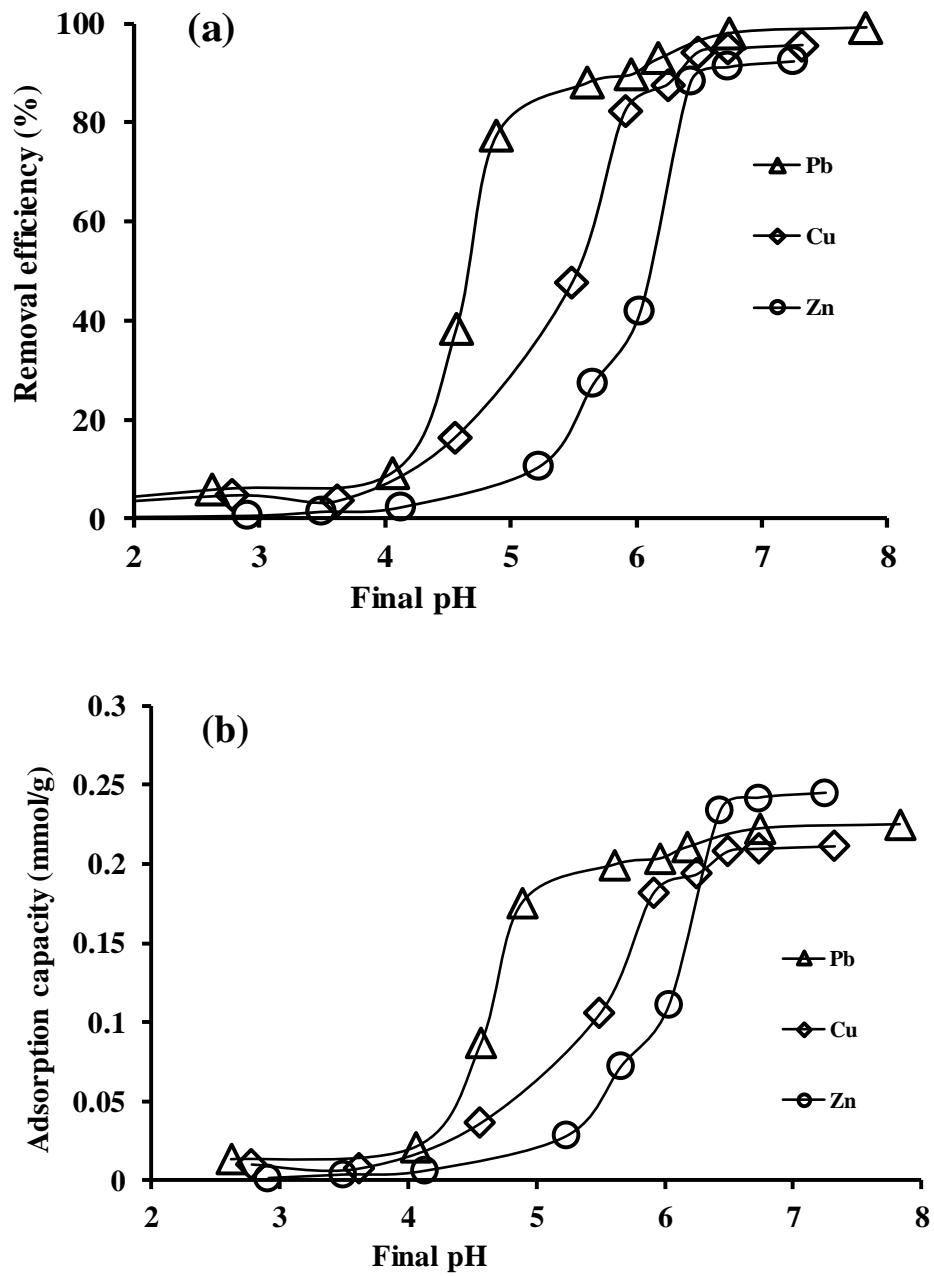


Fig. 5.

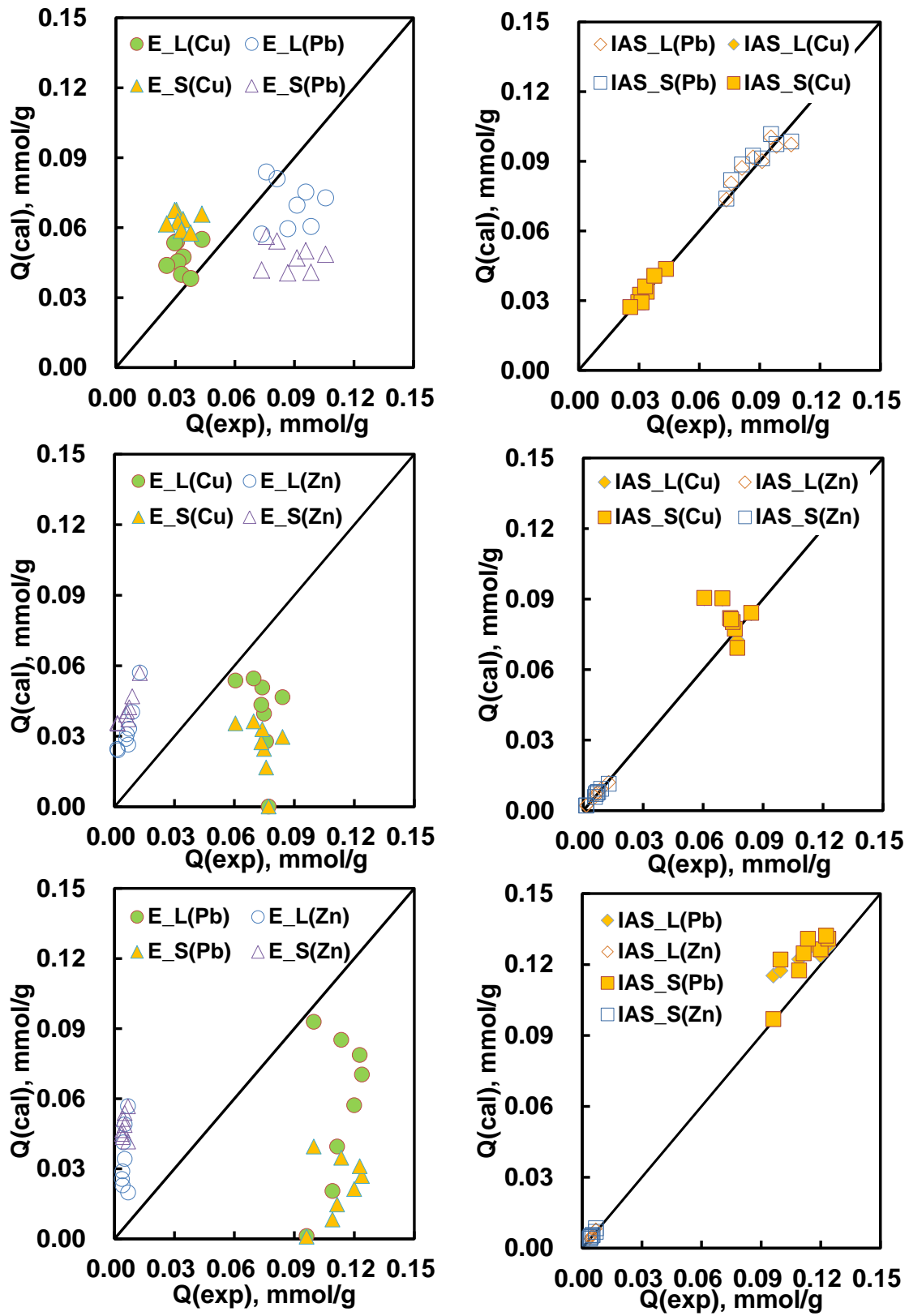


Fig 6.

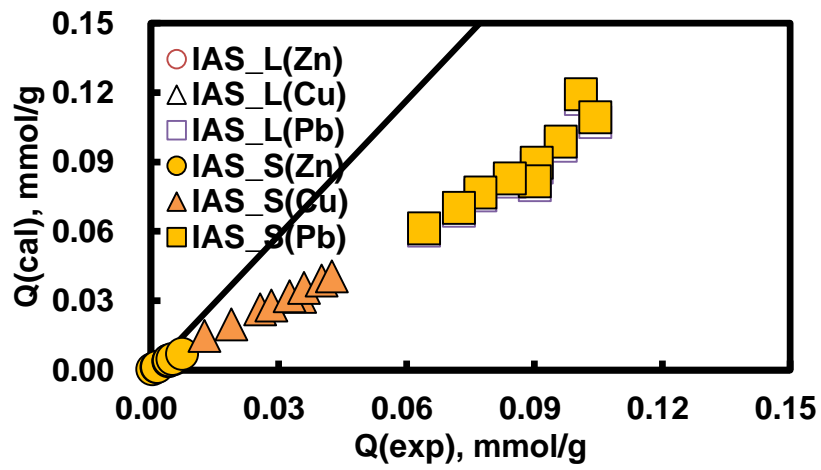
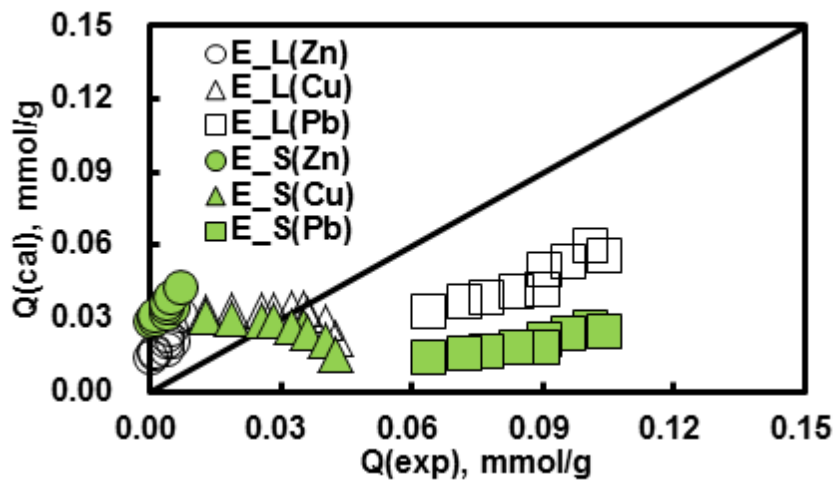


Fig 7.

Table 1

Parameters for the models fits to experimental data for Cu, Pb, and Zn adsorption on GAC in single metal systems.

Model	Parameters	Cu	Pb	Zn
Langmuir	q_m (mmol/g)	0.094	0.142	0.058
	b (L/mmol)	761	895	517
	R^2	0.960	0.840	0.937
Freundlich	K_F (mmol/g/(mmol/L) ⁿ)	0.137	0.183	0.075
	n	6.06	8.37	8.28
	R^2	0.812	0.817	0.712
	q_m (mmol/g)	0.095	0.146	0.058
Sips	b (L/mmol)	394	164	792
	n	1.11	1.32	0.94
	R^2	0.961	0.853	0.938

Table 2

Some properties of Cu, Pb, and Zn relevant to their adsorption characteristics

Metals	pK ₁	pK _{so}	Electronegativity	Hydrated	Hydration
	(Sounthararajah et al. 2015a)	(Sounthararajah et al. 2015a)	(Kang et al. 2016)	ionic radius (Å) (Minceva et al. 2007, Giraldo et al. 2013)	Energy (kJ/mol) (Sounthararajah et al. 2015a)
Pb	7.71	19.9	2.33	4.01	-1345
Cu	7.96	19.3	1.90	4.19	-1920
Zn	8.96	16.5	1.65	4.30	-1880

Table 3

Error values for models' fits to experimental data of metals adsorption on GAC in binary and ternary metals systems.

			E_L ^a	E_S ^b	IAS_L ^c	IAS_S ^d	
Binary	Cu/Pb	Cu	45.3	94.8	4.4	4.8	
		Pb	22.3	45.5	4.4	4.8	
	Cu/Zn	Cu	45.0	64.6	14.2	15.0	
		Zn	633.8	901.0	14.3	15.1	
	Pb/Zn	Pb	51.0	80.4	10.5	9.6	
		Zn	603.8	900.2	10.6	9.4	
	Ternary	Zn/Cu/Pb	Zn	874.8	1751.4	8.1	7.5
			Cu	41.6	44.6	5.5	5.1
Pb			48.1	77.7	5.6	5.1	

^aExtended Langmuir, ^bExtended Sips, ^cIAS-Langmuir, ^dIAS-Sips