On the dominance of Pb during competitive biosorption from multi-metal systems: A review

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Abstract: Biosorption, despite being initially heralded as a technology offering great potential for detoxification, is still yet to be commercialized. One of the reasons given is the lack of universal understanding of the mechanisms involved. This review focused on the removal of heavy metals from solutions in which Pb(II) co-existed with other metals in binary, ternary and quaternary systems. Trends in sorption capacities were analysed using ratios of maximum adsorption capacities: $q^0_{m,X}/q^0_{m}$, $q^0_{Pb}/q^0_{m,X}$, and $q^0_{Pb}/q^0_{m}$, where $q^0_{m}$ and $q^0_{m,X}$ represent the adsorption capacity in the presence and absence of the interfering metal ion, respectively, and $X$ is the metal ion co-existing with Pb(II). The data in literature were analysed for selected metal ions Pb(II), Cu(II), Zn(II), Cd(II), Ni(II) and Cr(III). It was shown that for all systems analysed, the ratio: $(q^0_{m,X}/q^0_{m}) < 1$, thus confirming that the simultaneous presence of metal ions in solution reduced their adsorption capacities. For the selected Pb/Cu system it was shown that generally $(q^0_{m,Pb} + q^0_{m,Cu}) > (q^0_{m,Pb} + q^0_{m,Cu})$, $q^0_{m,Pb}/q^0_{m,Cu} > 1$ and $q^0_{m,Cu}/q^0_{m,Cu} > 1$, thus confirming antagonistic effects for the system. It was further
shown that Pb(II) contributed to 70–77% of the total adsorption capacity, and the % change in adsorption capacity ($\Delta q_m$) was negative. In conclusion, these findings confirmed the superiority of Pb(II) adsorption across several metal-biosorbent systems, which has implications on the designing of model biotechnologies for possible practical applications.

**Subjects:** Environmental Chemistry; Materials Chemistry; Chemical Engineering; Clean Tech

**Keywords:** competitive adsorption; lead; binary; ternary; quaternary; multi-metal system; surface response methodology

1. **Introduction**

Research and development focusing on biosorption phenomena provides a springboard for a whole new environmental technology targeting the removal of various toxic substances or the recovery of precious metals from aquatic systems. It is therefore not surprising that numerous articles (in excess of 13 000) have been produced on biosorption in the past 60 years (Abdulaziz & Musayev, 2017). However, despite the significant progress in understanding of this complex phenomenon, commercialization of biosorption technologies has been elusive so far (Fomina & Gadd, 2014). In recent times, research has therefore sought to align biosorption technology towards more practical application to detoxification of environmental systems by enhancing physicochemical characteristics of the biosorbents, optimizing the biosorption processes, and applying the technology to more complex systems, e.g., multi-metal systems. More recently, research has focused on harnessing the capabilities offered by nanotechnology to develop biosorbents which are cost-effective, have high adsorption capacity, capable of adsorbing pollutants at lower concentrations (ppb) and can be regenerated in several sorption-desorption cycles (Khajeh, Laurent, & Dastafkan, 2013).

Focusing on the removal of metals from aquatic systems, biosorption has mainly been applied for the uptake of toxic metals (e.g., Hg, Pb, Cr, Cu, Zn, Cd, As, Co etc.), radionuclides (e.g., U, Th, Ra, Am etc.) and valuable metals (e.g., Au, Pt, Pd, Ru etc.) (Wang & Chen, 2006, 2009). It has since been established that factors which significantly influence biosorption include solution pH, ionic strength, initial sorbate concentration, biosorbent nature and the availability of binding sites, temperature, and agitation rate (Fomina & Gadd, 2014). Solution pH is a very important variable as it determines the solution chemistry of the sorbate and the functional activity of the biosorbents (Vijayaraghavan & Yun, 2008). Whereas the increase in ionic strength reduces biosorptive removal of pollutant species due to competition for binding sites, increase in initial pollutant concentration increases the quantity of biosorbed pollutant per unit weight of biosorbent (Fomina & Gadd, 2014). However, the removal efficiency decreases with an increase in initial metal concentration. The advent of nano-biosorbents has shown that the method of synthesis, surface modifications, and dosage play a pivotal role in determining the performance characteristics (Krstić, Urošević, & Pešovski, 2018; Shirsath & Shirivastava, 2015; Wang et al., 2012; Yu et al., 2013). Although the temperature has been shown to enhance the biosorption of pollutants, the effect is not significant for metal sorption between 20°C and 35°C. The presence of other pollutants generally lowers individual pollutant removal through competition for adsorption sites in multi-metal systems (Fomina & Gadd, 2014).

Motivated by the need to develop models applicable to real industrial samples, researchers have reported on the performance of biosorption technology when applied to multi-metal systems, mainly focusing on binary, ternary, and quaternary systems. Although these systems may not exhaustively resemble the composition of real industrial effluents, they at least give information useful in determining how adsorption capacity will be affected when metal ions co-exist in solution. Preliminary findings indicated that when Pb was removed from aqueous solution in the presence of other heavy metals, it mostly dominated the adsorption process (Al-Rub, El-Naas, Ashour, & Al-Marzouqi, 2006; Chong & Volesky, 1995; Hammaini, Ballesta, Blázquez, González, & Munóz, 2002;
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Maity & Ray, 2018; Wang, Vincent, Faur, & Guibal, 2017). In real practice, this means that when Pb is co-existing with other metal ions in solution, removal of the other ions would be suppressed until the Pb ions have been depleted to sufficiently low levels. Such sorption dynamics would, therefore, be important in understanding how the degree of tolerance of a biosorbent to multi-metal sorption and relative selectivity to individual metals vary with a combination of the metals in solution. However, a survey of the literature does not indicate that a systematic review was carried out on the apparent dominance of Pb during competitive biosorption from multi-metal systems.

The current study, therefore, sought to explore the above findings based on published equilibrium sorption data for several biosorbent systems. In particular, the study reviewed the sorption behaviour of multi-metal systems consisting of Pb, Cu, Cd, Zn, Ni, and Cr in binary, ternary, and quaternary systems. The sorption behaviour of the heavy metals was probed using ratios of maximum adsorption capacities: $q'_{m,X}/q^o_{m,X}$, $q'_{Pb}/q^o_{m,X}$, and $q'_{Pb}/q^o_{Pb}$, where $q^o_m$ and $q^o_{m,X}$ represent the adsorption capacity in the presence and absence of the interfering metal ion, respectively, and $X$ is the metal ion co-existing with Pb(II). Furthermore, equilibrium sorption data from multi-metal sorption were compared to that from monocomponent systems. The Pb-Cu system was selected as a typical binary system for an in-depth study whereas ternary and quaternary sorption systems were analysed for varying combination of the metals.

2. Competitive sorption from multi-metal systems

Although most industrial and municipal effluents are typically composed of a complex matrix of pollutants, relatively fewer studies have been conducted on competitive or simultaneous removal of metals from multi-metal systems compared to single-metal sorption. A scan of the literature shows that more than 500 papers have been published on biosorption in multi-component systems over the past few years, mainly in the fields of chemistry, environmental science and chemical engineering. These include studies on binary (Muthusamy & Venkatachalam, 2015; Suzaki et al., 2017; Xie, Hao, Mohamad, Liang, & Wei, 2013), ternary (Al-Rub et al., 2006; Costa, Da Silva, & Vieira, 2018; Ray, Jana, Bhanja, & Tripathy, 2018) and quaternary systems (Ahmad & Haseeb, 2017; Sulaymon, Mohammed, & Al-Musawi, 2013; Vijayaraghavan, Rangabhashiyam, Ashokkumar, & Arockiaraj, 2016). Table 1 shows the top 10 most cited articles and Figures 1 and 2 present number of papers and number of citations by the field for papers appearing with “lead” or “Pb” and “biosorption” in the topic listed in the Scopus database for period 2000–2017 (database searched on 23.10.18). Figure 2 shows that the number of citations generally increased from the year 2000, reaching a maximum in 2008 before declining in subsequent years. From the top 10 most cited papers, it is clear that most of the biosorbents studied showed greater affinity for Pb adsorption in both single and multi-metal systems. In these studies, whilst Pb effectively suppressed adsorption of competing metal ions, its uptake was not significantly reduced by the presence of the other metal ions. However, among authors with divergent findings, Saeed, Iqbal, and Akhtar (2005) reported that the presence of Pb did not affect the efficiency of removal of other metals when they were removed in binary and ternary solutions. Similar observations were made by Fiol et al. (2006) who reported that sorption of Cd was not significantly affected by the presence of Pb, and their results show that sorption of Cu and Ni was actually enhanced in the presence of Pb. However, one major challenge that arises on the interpretation of the findings from multi-metal studies is the difficulty in drawing meaningful and universal conclusions due to the different methodologies used. The several papers reported in the literature present sorption studies carried out under varying conditions of solution pH, ionic strength, initial pollutant concentration, agitation rate, and temperature.

2.1. A critical analysis of initial metal concentration as an experimental design parameter

Among the experimental conditions discussed earlier, the variation of initial metal concentration is key in characterizing sorption behaviour of a given sorbate-biosorbent system. In both batch and continuous flow systems, useful data are generated when the adsorption capacity of the biosorbent is determined as a function of initial metal concentration. In batch systems, such studies can generate equilibrium sorption data which can be modelled using various adsorption isotherms. The published material shows that it is possible to classify the experimental conditions based on how the initial metal concentration...
Table 1. The top 10 most cited articles in the Scopus database appearing with “lead” or “Pb” and “biosorption” in the topic (out of a total of 844 articles appearing: database searched 23.10.18)

| Article | Number of times article cited | Summary of conclusions |
|---------|-----------------------------|------------------------|
| Fourest and Roux (1992) | 599 | Adsorption of metal ions from mono-component systems by Rhizopus arrhizus followed the order: Pb(55.6 mg/g) > Cd(26.8 mg/g) > Zn(13.5 mg/g) > Ni(18.7 mg/g). Trend indicates that biosorbent had the highest affinity for Pb. |
| Kapoor and Viraraghavan (1995) | 586 | Fungal biosorption generally depended on pH, metal ion concentration, biomass concentration, and presence of various ligands in solution. |
| Gupta and Rastogi (2008) | 384 | Maximum adsorption capacity for the removal of Pb from single metal solution using Spirogyra sp. was found to be 140 mg/g. Basing on this value, it was concluded that the adsorbent was effective in Pb adsorption. |
| Chang, Law, and Chang (1997) | 364 | Adsorption of metals from mono-component systems by P. aeruginosa followed the order: Pb(110 mg/g) > Cd(58 mg/g) > Cu(23 mg/g). Increase in Hg concentration (from 0 to 50 mg Hg\(^{2+}\)/litre) in the growth media had no significant effect on metal adsorption. |
| Holan and Volesky (1994) | 356 | Adsorption of Pb and Ni by marine algae followed the order: Pb(370 mg/g) > Ni(74 mg/g). The lower adsorption capacity for Ni was explained in terms of its lower selectivity coefficient for alginates when compared to Pb. |
| Saeed et al. (2005) | 349 | Adsorption capacities for the removal of metals by crop milling waste followed the order: Pb(4.97 mg/g) > Cd(39.99 mg/g) > Zn(33.81 mg/g) > Cu(25.73 mg/g) > Ni(19.56 mg/g). The presence of Pb did not affect the efficiency of removal of other metals in binary and ternary solutions. |
| Krishnani, Meng, Christodoulatos, and Boddu (2008) | 331 | Adsorption capacities for the removal of metals followed the order: Pb(58.02 mg/g) > Hg(36.61 mg/g) > Cd(16.75 mg/g) > Cu(10.93 mg/g) > Mn(8.30 mg/g) > Zn(8.11 mg/g) > Ni(5.52 mg/g) > Co(4.54 mg/g) |

(Continued)
| Article                      | Number of times article cited | Summary of conclusions                                                                                                                                 |
|-----------------------------|------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|
| Fiol et al. (2006)          | 330                          | Removal of metals from single component systems using olive stone waste followed the order:                                                                 |
|                             |                              | Pb(9.26 mg/g) > Cd(7.74 mg/g) > Ni(2.13 mg/g) > Cu(2.03 mg/g)                                                                                         |
|                             |                              | For binary systems:                                                                                                                                     |
|                             |                              | Pb(10.90 mg/g) > Cu(3.22 mg/g)                                                                                                                        |
|                             |                              | Pb(10.24 mg/g) > Ni(3.10 mg/g)                                                                                                                        |
|                             |                              | Pb(9.84 mg/g) > Cd(7.61 mg/g)                                                                                                                         |
|                             |                              | Comparison of adsorption capacities for single and binary sorption systems shows that sorption of Cd was not significantly affected by the presence of Pb, and sorption of Cu and Ni was actually enhanced in the presence of Pb. |
| Yan and Viraraghavan (2001) | 325                          | For single metal adsorption using M. rouxi, the adsorption capacities were: Pb(4.06 mg/g) > Cd(3.76 mg/g) > Zn(1.36 mg/g) > Ni(0.36 mg/g)     |
| Sari and Tuzen (2009)       | 295                          | Maximum adsorption capacities of A. rubescens for Pb and Cd was found to be: Pb(38.4 mg/g) > Cd(27.3 mg/g).                                            |
concentration is varied during biosorption studies. It emerges from performing an in-depth analysis
that three conditions can be proposed, namely: Condition (I), where the initial concentrations \( C_{o} \) of the metals \( X_{1} \) and \( X_{2} \) are varied simultaneously, with \( C_{o, X_{1}} = C_{o, X_{2}} \); Condition (II), where initial concentrations of both components are varied simultaneously with \( C_{o, X_{1}} \neq C_{o, X_{2}} \); and Condition (III), where the initial concentration of one of the components is varied while keeping the other constant. The initial metal conditions used by several authors are shown in Table 2.

It was observed that for most of the studies, the initial concentration, \( (C_{o}) \), is measured in mg/L. Therefore, due to differences in molecular weight, the molar concentration would be different even for the same initial concentration (condition (I)). Since it has already been noted that the removal efficiency decreases with increasing initial concentration, comparison of findings obtained under conditions (I)–(III) would reveal the level of competition between the sorbates. Furthermore, some authors have reported on biosorption studies carried out under a combination of the conditions, e.g., under conditions (I) and (II) (Jiang, Zhou, Liu, Liu, & Wang, 2017), conditions (I) and (III) (Ronda, Martín-Lara, Dionisio, Blázquez, & Calero, 2013; Yan, Li, Xue, Wei, & Li, 2010), and conditions (I), (II) and (III) (Wang et al., 2017). Some authors have expanded the multicomponent system to study competitive biosorption in ternary and quaternary systems (Mahamadi & Nharingo, 2010; Saeid & Chojnacka, 2015; Sulaymon et al., 2013).
### Table 2. Classification of initial concentration variations

| Variation of initial concentration | Summary of conclusions                                                                 | References                                                                                     |
|-----------------------------------|----------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| **Condition (I)**                 | Simultaneously varying the initial concentrations \( C_0 \) of the pollutants \( X_1 \) and \( X_2 \), where \( C_{0,X_1} = C_{0,X_2} \) |                                                                                                 |
| Binary sorption capacities obtained using pine cone shell biosorbent followed the order: \( \text{Pb}(17.41 \text{ mg/g}) > \text{Cu}(6.52 \text{ mg/g}) \). However, the single-metal uptake capacities of the biomass for copper and lead were slightly inhibited by the presence of either metal ion. | Martin-Lara, Blázquez, Calero, Almendros, and Ronda (2016)                                      |
| Chitosan-pyromellitic dianhydride (PMDA)-modified biochar had strong selective adsorption of Cu(II) compared to Cd(II) and Pb(II). | Deng et al. (2017)                                                                            |
| The affinity between metals and biosorbent calculated by the separation factor in binary metals systems followed the order: \( \text{Pb} > \text{Cd} > \text{Zn} \). | Jang et al. (2017)                                                                            |
| Chitosan-based nano composite showed higher adsorption of Pb(II) than Cd(II). Decrease in adsorption of Cd(II) in the presence of Pb(II) was more than decrease in Pb(II) adsorption in the presence of Cd(II). | Maity and Ray (2018)                                                                          |
| Calcium alginate, algal biomass and algal/glutaraldehyde-crosslinked polyethyleneimine showed a greater affinity for Pb(II) compared to Cu(II) regardless of the molar ratio of competitor ions. | Wang et al. (2017)                                                                           |
| Myriophyllum spicatum had no preference for Cu(II) and Pb(II) in spite of their differences in physicochemical properties. | Yan et al. (2010)                                                                            |
| Maximum adsorption capacities for single metal removal of Cu(II) and Pb(II) using activated carbon from Eucalyptus camaldulensis Dehn bark were 109.8 and 28.6 mg/g, respectively. Trend also observed for binary metal systems. | Kangsuwan, Patrukaa, and Pavasant (2009)                                                     |
| The affinity of Pb(II) for almond shell was higher than that of Cu(II), with maximum adsorption capacities of 13.7 and 9.0 mg/g obtained, respectively. | Ronda et al. (2013)                                                                          |
| Compared to single metal sorption using Pithophora oedogonia, the adsorption capacities for the removal of Cu(II) and Pb(II) were reduced in binary system. However, the adsorbent showed a greater affinity to sorb Cu(II) than Pb(II) from binary solution. | Kumar et al. (2008)                                                                          |
| Affinity of Pb(II) for Industrial chili seeds (Capsicum annuum) waste was more than 5 times higher than that of Cd(II). | Medellin-Castillo et al. (2017)                                                               |
| The presence of Cu(II) adversely affected Pb(II) adsorption onto Chlorella vulgaris, whereas Zn(II) ions seemed to have negligible effect on the process. | El-Noas et al. (2007)                                                                        |
| Ni(II) and Zn(II) had lower interference effect on Pb(II) sorption by Arthrosira (Spirulina) platensis and Chlorella vulgaris than the contrary, hence biosorbents had greater preference to Pb(II). | Rodrigues et al. (2012)                                                                      |
| The affinity order of calcium-saturated anaerobic sludge biosorbent was established as: \( \text{Pb} > \text{Cu} > \text{Ni} > \text{Cd} \). The single-metal sorption for Pb was slightly inhibited by the presence of Cu and Cd cations (by 6%) and by the presence of nickel (by 11%). | Hawari and Mulligan (2007)                                                                    |
| Variation of initial concentration | Summary of conclusions | References |
|-----------------------------------|------------------------|------------|
| Condition (II) Simultaneously varying the initial concentrations of both components with \( C_{o,X1} \neq C_{o,X2} \) | As summarized under Condition (I) above | El-Naas et al., 2007; Yan et al., 2010; Randa et al., 2013; Wang et al., 2017 |
| Condition (III) Varying the initial concentration of one of the components whilst keeping the other constant | Adsorption capacities were 11.76 and 27.47 mg/g, for Cd(II) and Pb(II), respectively. Competition, interaction or displacement effect observed between Cd(II) and Pb(II) ions. | Módenes, Espinoza-Quiones, Colombo, Geraldi, & Trigueros, 2015 |
| | As described above under Condition (I) | Wang et al., 2017 |
The findings from these studies confirm the general conclusions made earlier, that most of the biosorbents had strong selective adsorption of Pb compared to other heavy metals. However, as also noted in the earlier discussion, a few authors also reported conflicting observations. Deng et al. (2017) reported that chitosan-pyromellitic dianhydride (PMDA)-modified biochar had strong selective adsorption of Cu(II) compared to Cd(II) and Pb(II). In another study, it was observed that Myriophyllum spicatum had no preference for Cu(II) and Pb(II) in spite of their differences in physicochemical properties (Yan et al., 2010). Elsewhere, Pithophora oedogonia biosorbent showed a greater affinity to sorb Cu(II) than Pb(II) from binary solution (Kumar, Singh, & Gaur, 2008) and presence of Cu(II) adversely affected Pb(II) adsorption onto Chlorella vulgaris, whereas Zn(II) ions seemed to have negligible effect on the process (El-Naas, Al-Rub, Ashour, & Al Marzouqi, 2007). These differences could be a result of variations in physicochemical characteristics of the biosorbents which affect metal sorption preferences. For example, it was observed that the types of effective functional groups involved in the sorption of Cd, Cu, and Pb by chitosan-pyromellitic dianhydride were different, with N-C = O playing a significant role in the process of Pb(II) removal, while C = C and N-containing functional groups were important in the removal of Cd(II) (Deng et al., 2017).

2.2. Biosorption isotherms

Applied at a constant temperature, biosorption isotherms describe metal sorption as a function of metal concentration in the solution at equilibrium. Some of the isotherms which are commonly used to describe single-metal sorption on biosorbent include Freundlich, Langmuir, Redlich-Peterson and Sips models. Since these models were primarily developed for monocomponent systems, they fail to adequately describe sorption behaviour for multi-component systems (Kumar et al., 2008). Researchers have therefore developed several empirical and mechanistic models to describe sorption for these complex systems. These include three and five-parameter extended Freundlich model (Fritz & Schluender, 1974; Kumar et al., 2008; Sheintuch & Rebhun, 1988), Competitive Hill model (Sellaoui, Franco, Dotto, Lima, & Lamine, 2017), and competitive Langmuir model (Ofomaja, Unuabonah, & Oladoja, 2010b). Among these models, the Langmuir competitive model is the most tested, probably because of the relative simplicity in application and interpretation of data. Mostly, the model has been applied in the determination of the maximum equilibrium capacity of the biosorbents for the various sorption systems.

2.2.1. Monocomponent Langmuir isotherm

The Langmuir isotherm is described assuming that the receptor sites on the biosorbent are energetically identical regardless of adsorbate under study. Furthermore, it is assumed that a localized adsorbent site accommodates one adsorbate species per active site. The model further assumes that interactions among adsorbates are negligible.

For a monocomponent system, mathematical expression of the Langmuir isotherm can be expressed as below:

\[
q_e = \frac{q_m b C_{eq}}{1 + b C_{eq}}
\]

(1)

and linearized as:

\[
\frac{C_{eq}}{q_e} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m}
\]

(2)

where \(q_m\) (mg/g) is the maximum amount of adsorbate per unit weight of the biosorbent required to form a complete monolayer on the surface at equilibrium, and \(b\) is a constant reflecting the affinity of the binding sites for the metal ion (1 mg\(^{-1}\)).

2.2.2. Competitive Langmuir isotherm

For competitive adsorption, the model is similar to the single sorption model in that the rate of adsorption still depends on only the adsorbing component (Mahamadi & Nharingo, 2010).
However, the rate of adsorption must account for available sites only (i.e., \( \sum_{i=1}^{n} q_{m,i}^{o} \)). After setting the adsorption and desorption rates equal, it can be shown that the extent of adsorption is given by:

\[
q_{e,i} = q_{m,i}b_iC_{eq,i}(1 + \sum_{j=1}^{n} b_jC_{eq,j})^{-1}.
\]

were \( q_{m,i} \) and \( b_i \) are physical parameters, and \( C_{eq,i} \) represent the equilibrium concentrations in the mixture of the sorbates. Assuming that the concentrations of the sorbates are sufficiently large that surface coverage is substantially complete, the unit term in Equation (4) may be neglected, and after some rearrangements, the expression can be expressed in a linear form as shown in Equations (1) and (2) for binary and ternary systems, respectively:

\[
\frac{C_{eq,1}}{C_{eq,2}q_{e,1}} = \frac{C_{eq,1}}{q_{m,1}C_{eq,2}} + \frac{b_2}{b_1q_{e,1}}
\]

\[
\frac{C_{eq,1}}{q_{e,1}(b_2C_{eq,2} + b_3C_{eq,3})} = \frac{C_{eq,1}}{(b_2C_{eq,2} + b_3C_{eq,3})q_{m,1}} + \frac{1}{q_{m,1}b_1}
\]

By plotting \( C_{eq,1}/C_{eq,2}q_{e,1} \) as a function of \( C_{eq,1}/C_{eq,2} \) and \( C_{eq,1}/C_{eq,2}(b_2C_{eq,2} + b_3C_{eq,3}) \) as a function of \( C_{eq,1}/C_{eq,2}(b_2C_{eq,2} + b_3C_{eq,3}) \) would give intercepts of \( b_2/b_1q_{e,1} \) and \( 1/q_{m,1}b_1 \), slope of \( 1/q_{m,1} \) for binary and ternary systems, respectively.

2.3. Analysis of competitive Langmuir equilibrium sorption data

2.3.1. Binary sorption systems

For binary systems, the equilibrium data can be analysed using the ratio of biosorption capacity of one metal ion in the presence of the other metal ion (\( q'_{m,x} \)) to biosorption capacity for the same metal when it is present alone (\( q_{m,x}^{o} \)) (Ofomaja et al., 2010b). The following scenarios thus can be encountered:

\[
\frac{q'_{m,x}}{q_{m,x}^{o}} > 1
\]

Synergism: the biosorption is promoted in the presence of the other metal ion.

\[
\frac{q'_{m,x}}{q_{m,x}^{o}} = 1
\]

Non-interaction: there is no observable net effect

\[
\frac{q'_{m,x}}{q_{m,x}^{o}} < 1
\]

Antagonism: biosorption is suppressed, i.e., the effect of the mixture is less than that of the individual adsorbates in the mixture.

2.3.1.1. Pb-cu system

Various binary systems in which Pb co-exist with other metals in solution have been reported, and these include: Pb-Cd, Pb-Zn, Pb-Cu, Pb-Ni, and Pb-Cr. The Pb-Cu system was selected as a typical binary system for an in-depth probing of equilibrium sorption data using the adsorption capacity ratios. Data showing maximum equilibrium adsorption capacities (\( q_{m} \)), obtained from selected publications is shown in Table 3. It can be seen that in most cases, Condition (I) was used, i.e., equal initial concentrations of Pb(II) and Cu(II) (mg/L) \( (C_{o,Pb} = C_{o,Cu}) \). An analysis of the data shows that except for the sorption of Pb(II) and Cu(II) ions using alginate and alginate-immobilized Trichoderma asperellum which gave a values of 2.967 and 1.258 for the ratio \( q'_{m,x}/q_{m,x}^{o} \), respectively, the values computed for the rest of the biosorbents were less than unity, indicating that biosorption of both metals was largely suppressed in the binary system. This
| Adsorbent                                      | Solution component | Metal ions          | $q_m$ (mg/g) | $q_{m,2}/q_{m,1}$ | $q_{m,Pb}/q_{m,Cu}$ | $q_{m,Pb}/q_{m,Cu}$ | Reference                  |
|-----------------------------------------------|--------------------|---------------------|--------------|-------------------|---------------------|---------------------|----------------------------|
| Chitosan based nanocomposite                  | Single             | Pb(II)              | 357.4        | 341.6             |                     |                     | Maity and Ray (2018)       |
|                                               | Binary             | Pb(II) (Pb/Cd)      | 313.7        | 303.6             | 0.8778              | 0.8888              |                            |
|                                               |                    | Cd(III) (Pb/Cd)     |              |                   |                     |                     |                            |
|                                               | TEPA modified chitosan/CoFe$_2$O$_4$ | Single             | Pb(II)       | 168.067           | 228.311             |                     | Fan et al. (2017)          |
|                                               |                    | Cu(II) (Pb/Cu)      | 139.665      | 160.256           | 0.8310              | 0.7020              |                            |
|                                               |                    | Pb(II) (Pb/Cu)      |              |                   |                     |                     |                            |
|                                               | Alginato           | Single              | 414.4        | 113.1             |                     |                     | Wang et al. (2017)         |
|                                               |                    | Pb(II) (Cu)         |              |                   |                     |                     |                            |
|                                               |                    | Cu(II) (Cu)         |              |                   |                     |                     |                            |
|                                               | Alginato           | Binary              | Pb(II) (Cu/Pb)| 385.4-            | 0.9300-             |                     | Martin-Lara et al. (2016)  |
|                                               |                    |                     | Cu(II) (Cu/Pb)|                     |                     |                     |                            |
|                                               | Alginato-immobilized Trichoderma asperellum | Single             | Pb(II)       | 89.59             | 71.99               |                     | Chew and Ting (2016)       |
|                                               |                    | Cu(II)              |              |                   |                     |                     |                            |
|                                               | Alginato           | Binary              | Pb(II) (Cu/Pb)| 112.70            | 31.53               | 1.2580              |                            |
|                                               |                    |                     | Cu(II) (Cu/Pb)|                     |                     | 0.4380              |                            |
|                                               |                    | Pine cone shell     | Single        | 6.808             | 25.24               |                     | Martin-Lara et al. (2016)  |
|                                               |                    | Cu(II)              |              |                   |                     |                     |                            |
|                                               |                    | Pb(II)              |              |                   |                     |                     |                            |
|                                               |                    | Binary              | Cu(II) (Cu/Pb)| 6.522             | 174.07              | 0.958               | 2.669                     |
|                                               | Cabbage waste      | Single              | Cu(II)       | 10.315            | 60.568              |                     | Hossain et al. (2014)      |
|                                               |                    | Pb(II)              |              |                   |                     |                     |                            |
|                                               |                    | Binary              | Pb(II) (Pb/Cu)| 60.311            | 9.447               | 0.9958              | 6.384                     |
|                                               |                    |                     | Cu(II) (Cu/Pb)|                     |                     | 0.9159              |                            |

(Continued)
| Adsorbent                  | Solution component | Metal ions                  | $q_m$ (mg/g) | $q_{m, X} / q^n_{m, X}$ | $q_{m, Pb} / q_{m, Cu}$ | $q_{m, Pb} / q^n_{m, Pb}$ | Reference                          |
|---------------------------|--------------------|-----------------------------|--------------|--------------------------|--------------------------|---------------------------|-----------------------------------|
| Almond shell              | Single             | Pb(II) Cu(II)               | 26.546       | 2.8126                   |                          |                          | Ronda et al. (2013)               |
|                           | Binary (CŽ ratio 1:1) | Pb(II) (Pb/Cu) Cu(II) (Cu/Pb) | 13.712       | 0.5316                   | 1.5317                   |                          |                                   |
| Potassium hydroxide       | Single             | Pb(II) Cu(II)               | 32.26        | 1.2257                   |                          |                          | Ofomaja et al., (2010a)           |
| treated pine cone powder  | Binary (CŽ ratio 1:1) | Pb(II) (Pb/Cu) Cu(II) (Cu/Pb) | 30.12        | 0.9337                   | 1.3280                   |                          |                                   |
| Valonia tannin resin      | Single             | Pb(II) Cu(II)               | 98.55        | 2.513                    |                          |                          | Şengil and Ozacar (2009)          |
|                           | Binary (CŽ ratio 1:2) | Pb(II) (Cu/Pb) Cu(II) (Cu/Pb) | 78.2         | 0.7935                   | 2.514                    |                          |                                   |
|                           | (CŽ ratio 1:1)      |                            | 31.1         | 0.7932                   |                          |                          |                                   |
| Mansonia wood sawdust     | Single component   | Pb(II) Cu(II)               | 51.81        | 1.222                    |                          |                          | Ofomaja et al., (2010b)          |
|                           | (CŽ ratio 1:1)      |                            | 42.37        |                          |                          |                          |                                   |
|                           | Binary (CŽ ratio 1:1) | Pb(II) (Cu/Pb) Cu(II) (Cu/Pb) | 61.034       | 0.8356                   | 1.250                    |                          |                                   |
|                           |                    |                            | 48.84        | 0.8676                   |                          |                          |                                   |
| Myriophyllum spicatum     | Single             | Pb(II) Cu(II)               | 51.72        | 0.8928                   |                          |                          | Yan et al. (2010)                |
|                           | (CŽ ratio 1:8)      |                            | 46.18        |                          |                          |                          |                                   |
| Aspergillus flavus        | Single             | Pb(II) Cu(II)               | 11.30        | 1.1323                   |                          |                          | Akar and Tunali (2006)           |
|                           | (CŽ ratio 1:1)      |                            | 9.98         |                          |                          |                          |                                   |
|                           | Binary (CŽ ratio 1:1) | Pb(II) (Cu/Pb) Cu(II) (Cu/Pb) | 6.41         | 0.5672                   | 2.1086                   |                          |                                   |
|                           |                    |                            | 3.04         | 0.3046                   |                          |                          |                                   |
suggests that the simultaneous presence of both metals reduced their biosorption through competition for biosorbent binding sites. The results further show that except for Mansonia wood sawdust and Almond shell, \( q_{m, Pb}/q_{m, Cu}^0 > q_{m, Cu}/q_{m, Cu}^0 \) for the biosorbents, thus indicating that although competitive effect reduced the adsorption capacities for both metals, there was preferential adsorption for Pb(II). Valonia tannin resin biosorbent presented an interesting case in that \( q_{m, Pb}/q_{m, Pb}^0 = q_{m, Cu}/q_{m, Cu}^0 \), thus suggesting that there was no preferential sorption by the biosorbent for both metals, although the metals mutually experienced antagonistic effects reducing their individual adsorption capacities relative to single-component sorption.

From the adsorption capacities obtained for single-metal sorption systems, it can be seen that \( q_{m, Pb}^0/q_{m, Cu}^0 > 1 \) for all of the biosorbents investigated, thus indicating that the biosorbents had a greater affinity for Pb(II) than Cu(II). Further analysis shows that in single-metal systems, cabbage waste, pine cone shell, and alginate ranked highly as adsorbents for Pb(II). Further analysis of the equilibrium sorption data for binary removal of Pb(II) and Cu(II) can be done by comparing the ratio \( q_{m, Pb}^0/q_{m, Cu}^0 \) and \( q_{m, Pb}^0/q_{m, Cu}^0 \). From Table 3, it can be observed that for some of the biosorbents including alginate-immobilized Trichoderma asperellum, cabbage waste, Potassium hydroxide treated pine cone powder, and Aspergillus flavus, \( q_{m, Pb}^0/q_{m, Cu}^0 > q_{m, Pb}^0/q_{m, Cu}^0 \). This suggests that Pb(II) removal was enhanced relative to the removal of Cu(II) ions in the binary system compared to the single-metal system. Interestingly, however, the order was reversed for almond shell, pine cone shell, and TEPA modified chitosan/CoFe\(_2\)O\(_4\) although the individual \( q_{m}^0 \) values were higher for Pb(II) biosorption than Cu(II). Furthermore, the values obtained for \( q_{m, Pb}^0/q_{m, Cu}^0 \) and \( q_{m, Pb}^0/q_{m, Cu}^0 \) for Mansonia wood sawdust (1.222 and 1.250, respectively) and for Valonia tannin resin (2.513 and 2.514, respectively) suggest that the relative preference by the biosorbent for either metal was not affected by competitive effects. This suggests that the sorption sites available on Valonia tannin resin for Pb(II) and Cu(II) adsorption could be different (Wang & Sun, 2013).

A comparison of the sums: \( (q_{m, Pb}^0 + q_{m, Cu}^0) \) and \( (q_{m, Pb}^0 + q_{m, Cu}^0) \) gives further insights into how the total number of available binding sites were affected by the competitive effects. From Table 4, it can be seen that \( (q_{m, Pb}^0 + q_{m, Cu}^0) > (q_{m, Pb}^0 + q_{m, Cu}^0) \) for most of the biosorbents studies, including TEPA modified chitosan/CoFe\(_2\)O\(_4\), Pine cone shell, Alginate-immobilized Trichoderma asperellum, Almond shell, Valonia tannin resin, and Aspergillus flavus. These findings suggest that metal ion access to binding sites was reduced, probably as a result of mutual competitive effects. In related studies, Chew and Ting (2016) reported inferior biosorption in multi-metal systems, with cumulative means of total metals of 151.05 and 152.23 mg/g adsorbed compared to 233.96 and 209.25 mg/g in single-metal solutions using alginate-immobilized T. asperellum and plain-alginate beads, respectively. The authors attributed the lower metal sorption to competitive solute-solute (metal ion-metal ion) interaction as well as solute-surface (metal ion-surface of biosorbent) interaction for available binding sites.

It can also be observed that for all biosorbents analysed, ratios \( q_{m, Pb}^0/q_{m, Cu}^0 \) and \( q_{m, Pb}^0/q_{m, Cu}^0 \) were greater than unity. This suggests that all biosorbent studies showed higher adsorption for Pb(II) compared to Cu(II) in both single metal and binary component systems. This observation is very significant in that, despite the differences in experimental conditions (initial metal concentration, pH, biosorbent dosages, etc.), the findings confirm one major general observation: Pb(II) biosorption clearly dominated the process in the presence of Cu(II). From the data shown in Table 4, an average value of 70% can be computed for the contribution of Pb(II) to the total metal adsorption capacity for the binary Pb-Cu system. In related studies, Hammaini et al. (2002), showed that Cu(II) uptake decreased by 56% when Pb(II) was present at high concentration, whereas the interference of Cu(II) with Pb(II) uptake was much less pronounced and observed at much higher levels of Cu(II). Furthermore, the same authors reported that when the residuals of Pb(II) and Cu(II) were the same, about 97% of the total metal uptake was due to Pb(II) uptake. Generally, it
| Biosorbent                              | \( \left( q_{m,Pb} + q_{m,Cu} \right) \) | \( \left( q_{m,Pb} + q_{m,Cu} \right) \) | \( \frac{q_{m}}{\left( q_{m,Pb} + q_{m,Cu} \right)} \times 100\% \) | References                     |
|----------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|----------------------------------|
| TEPA modified chitosan/CoFe\(_2\)O\(_4\) | 396.378                                  | 299.921                                  | 76%                                      | Fan et al. (2017)                |
| Pine cone shell                         | 32.048                                   | 23.929                                   | 73%                                      | Martin-Lara et al. (2016)        |
| Alginate-immobilized Trichoderma asperellum | 161.58                                   | 144.23                                   | 78%                                      | Chew and Ting (2016)             |
| Cabbage waste                           | 70.883                                   | 69.758                                   | 86%                                      | Hossain et al. (2014)            |
| Almond shell                            | 35.984                                   | 22.664                                   | 61%                                      | Ronda et al. (2013)              |
| Potassium hydroxide treated pine cone powder | 58.58                                    | 52.80                                    | 57%                                      | Ofoimaja et al. (2010b)          |
| Valonia tannin resin                    | 137.76                                   | 109.3                                    | 72%                                      | Şengil and Özacar (2009)         |
| Mansonia wood sawdust                   | 94.18                                    | 109.874                                  | 56%                                      | Ofoimaja et al., (2010b)         |
| Aspergillus flavus                      | 21.28                                    | 9.45                                     | 68%                                      | Akar and Tunali (2006)           |
can be concluded that regardless of conditions used (Table 2), Pb(II) uptake was superior to that of Cu(II) for the various biosorption systems analysed.

It has been suggested that the extent to which metals bind to a biosorbent with different functional groups depends on their ionic properties. For metals, these include electronegativity, ionic radius, and redox potential (Naja, Vanessa, & Volesky, 2010; Sulaymon et al., 2013). For the current system, the differences in sorption affinities for these metals have been attributed to differences in the ionic radii and electronegativity of the atoms, which follow the order Pb(II) >Cu(II) (Al-Rub et al., 2006; Chong & Volesky, 1995).

2.3.2. Ternary system
As expected basing on the findings made for binary systems, the \( q_{m,X}/q_{m,X}^{0} \) ratios were all less than unity for the selected ternary systems shown in Table 5. This confirms that in all cases, antagonistic effects due to competitive adsorption were significant. Further insights into the competitive biosorption can be made by analysing the trends in the adsorption capacities for monocomponent and ternary systems. From Table 6, it can be seen that except for Date seed biochar and Casuarina equisetifolia where there were changes in the order of \( q_{m} \) for the Pb/Cu/Ni system, the rest of the metal combinations showed the same order for the monocomponent and ternary systems. For example, C. equisetifolia shows a preference for Pb(II) adsorption when compared to Cu(II) in the ternary system whereas \( q_{m,Cu}>q_{m,Pb} \) in the monocomponent system. This shows the complexity of the biosorption phenomenon as it depends not only on the physicochemical characteristics of the metal ions but also on the accessibility and energies of the binding sites on the biosorbent. However, it is very clear from Tables 5 and 6, that for all of the biosorbents, Pb(II) ions dominated the adsorption process in ternary systems. Furthermore, it can be shown that Pb(II) adsorption accounts for more than 77% of the total adsorption capacity for the ternary system. Again, these findings are very significant in that the trend demonstrates superior adsorption for Pb(II) despite the differences in experimental conditions used during the adsorption process.

The ability of Pb(II) to outcompete co-existing ions is further illustrated by the change in the order of adsorption capacities for single and multi-metal systems. Park and Chon (2016) reported the order: Cd≥Pb>Zn for single-metal sorption by Exiguobacterium sp. which changed to Pb(II) >Cd(II)>Zn(II) in a mixed metal solution. In similar studies, Engl and Kunz (1995) reported that the order of adsorption changed from Cu(II)>Cd = Pb>Zn to Pb>Cu>Zn = Cd for single and mixed metal systems, respectively. The differences in the sorption order were explained in terms of the higher electronegativity of Pb(II) resulting in more stable binding to the ligands on the biosorbent surface.

2.3.3. Quaternary system
Published work shows that limited research has been carried out on biosorption in quaternary systems, probably due to the greater experimental demands and complexity for such systems. However, it is important to study such systems as they represent the complex nature of most industrial effluents, e.g., from mining companies. Data obtained from typical quaternary systems is shown in Table 7. It is clear that except for the removal of Zn(II) from a Pb/Cu/Zn/Cd system using cabbage waste, \( q_{m,X}/q_{m,X}^{0} \) ratios were less than unity for all sorption systems. The data were further analysed by calculating the % change in adsorption capacity (\( \Delta q_{m} \)). If % \( \Delta q_{m} <0 \), then it would suggest that adsorption capacity was reduced due to competitive effects, % \( \Delta q_{m} = 0 \) would suggest no effect, and % \( \Delta q_{m} >0 \) would suggest enhancement of adsorption capacity in the presence of two or more metal ions. Except for cabbage waste biosorbent, % \( \Delta q_{m} \) negative for all of the systems confirming the mutual antagonistic effects experienced by the sorbate species. This means that the simultaneous presence of heavy metals in solution reduced their respective adsorption capacities.

2.4. Interpretation of multi-metal batch sorption data
The reviewed publications showed that most authors reported on the following: physical characterization of the biosorbent, optimum conditions, removal efficiency expressed as maximum
| Adsorbent                        | Solution component                  | Metal ions             | $q_m$ (mg/g) | $q_{m1}/q_{m2}$ | $\left(\frac{q_{m1}+q_{m2}+q_{m3}}{3}\right)$ x100% | Reference                                      |
|---------------------------------|-------------------------------------|------------------------|--------------|-----------------|--------------------------------------------------|------------------------------------------------|
| Date seed biochar               | Single component                    | Pb(II)                 | 14.77        |                 |                                                  | Mahdi, Yu, and El Hananadeh (2018)              |
|                                 |                                     | Cu(II)                 | 26.75        |                 |                                                  |                                                 |
|                                 |                                     | Ni(II)                 | 19.54        |                 |                                                  |                                                 |
|                                 | Ternary component (C$_3$ ratio 1:1:1) | Pb(II) (Pb/Cu/Ni)     | 4.51         | 0.292           | 72.0%                                            |                                                 |
|                                 |                                     | Cu(II) (Pb/Cu/Ni)     | 6.61         | 0.247           | 10.9%                                            |                                                 |
|                                 |                                     | Ni(II) (Pb/Cu/Ni)     | 10.33        | 0.529           | 17.1%                                            |                                                 |
| Aluminate treated Casurina equisetifolia leaves | Single component | Pb(II)                 | 28.60        |                 |                                                  | Rao and Khatoon (2017)                          |
|                                 |                                     | Cu(II)                 | 44.59        |                 |                                                  |                                                 |
|                                 |                                     | Ni(II)                 | 39.93        |                 |                                                  |                                                 |
|                                 | Ternary component (C$_3$ ratio 1:1:1) | Pb(II) (Pb/Cu/Ni)     | 21.73        | 0.76            | 51.1%                                            |                                                 |
|                                 |                                     | Cu(II) (Pb/Cu/Ni)     | 13.00        | 0.29            | 30.6%                                            |                                                 |
|                                 |                                     | Ni(II) (Pb/Cu/Ni)     | 7.80         | 0.20            | 18.3%                                            |                                                 |
| Cabbage Leaves Powder           | Single component                    | Pb(II)                 | 6.31         |                 |                                                  | Kamar, Nechifor, Nechifor, Al-Musawi, and Mohammed (2016). |
|                                 |                                     | Cu(II)                 | 5.75         |                 |                                                  |                                                 |
|                                 |                                     | Cd(II)                 | 5.07         |                 |                                                  |                                                 |
|                                 | Ternary component (C$_3$ ratio 1:1:1) | Pb(II) (Pb/Cd/Cd)     | 4.54         | 0.719           | 43.8%                                            |                                                 |
|                                 |                                     | Cu(II) (Pb/Cd/Cd)     | 3.35         | 0.583           | 32.3%                                            |                                                 |
|                                 |                                     | Cd(II) (Pb/Cd/Cd)     | 2.48         | 0.489           | 23.9%                                            |                                                 |
| Exiguobacterium sp.             | Single component                    | Pb(II)                 | 19.5         |                 |                                                  | Park and Chon (2016)                            |
|                                 |                                     | Cd(II)                 | 11.2         |                 |                                                  |                                                 |
|                                 |                                     | Zn(II)                 | 2.55         |                 |                                                  |                                                 |
|                                 | Ternary component (C$_3$ ratio 1:1:1) | Pb(II) (Cd/Pb/Zn)     | 8.08         | 0.414           | 66.5%                                            |                                                 |
|                                 |                                     | Cd(II) (Cd/Pb/Zn)     | 3.15         | 0.281           | 25.9%                                            |                                                 |
|                                 |                                     | Zn(II) (Cd/Pb/Zn)     | 0.915        | 0.359           | 7.6%                                             |                                                 |

(Continued)
### Table 5. (Continued)

| Adsorbent | Solution component | Metal ions | $q_e$ (mg/g) | $q_{e,x}/q_{e,y}$ | $\left( \frac{q_{e,x}}{q_{e,y} + q_{e,z}} \right) \times 100\%$ | Reference |
|-----------|--------------------|------------|--------------|-------------------|------------------------------------------------|-----------|
| Cabbage waste | Single component | Pb(II) | 60.57 | | | Hossain et al. (2014) |
| | | Cu(II) | 10.32 | | | |
| | | Zn(II) | 8.97 | | | |
| | | Cd(II) | 20.57 | | | |
| | Ternary component (Cu ratio 1:1:1) | Pb(II) (Cd/Pb/Cu) | 40.963 | 0.6763 | 66.1% | | |
| | | Cd(II) (Cd/Pb/Cu) | 12.264 | 0.5962 | 19.8% | | |
| | | Cu(II) (Cd/Pb/Cu) | 8.785 | 0.8513 | 14.1% | | |
| | | Pb(II) (Cd/Pb/Zn) | 50.22 | 0.8291 | 84.21% | | |
| | | Cd(II) (Cd/Pb/Zn) | 7.587 | 0.3689 | 12.72% | | |
| | | Zn(II) (Cd/Pb/Zn) | 1.828 | 0.2038 | 3.06% | | |
| | | Pb(II) (Cu/Pb/Zn) | 22.80 | 0.3765 | 61.0% | | |
| | | Cu(II) (Cu/Pb/Zn) | 8.194 | 0.7940 | 21.9% | | |
| | | Zn(II) (Cu/Pb/Zn) | 6.380 | 0.7113 | 17.1% | | |
| Heterogeneous cultures comprising of dried anaerobic bacteria, yeast (fungi), and protozoa | Single component | Pb(II) | 54.92 | | | Sulaymon, Ebrahim, and M-Ridha (2014) |
| | | Cr(III) | 34.78 | | | |
| | | Cd(II) | 29.99 | | | |
| | Ternary component (Cu ratio 1:1:1) | Pb(II) (Pb/Cr/Cd) | 15.68 | 0.2855 | 46.5% | | |
| | | Cr(III) (Pb/Cr/Cd) | 13.86 | 0.3985 | 41.1% | | |
| | | Cd(II) (Pb/Cr/Cd) | 4.18 | 0.1394 | 12.4% | | |
| Xanthate-modified magnetic chitosan | Single component | Pb(II) | 76.9 | | | Zhu, Hu, and Wang (2012) |
| | | Cu(II) | 34.5 | | | |
| | | Zn(II) | 20.8 | | | |
| | Ternary component (Cu ratio 1:1:1) | Pb(II) (Pb/Cu/Zn) | 28.6 | 0.372 | 46.3% | | |
| | | Cu(II) (Pb/Cu/Zn) | 26.3 | 0.762 | 42.5% | | |
| | | Zn(II) (Pb/Cu/Zn) | 6.93 | 0.333 | 11.2% | | |

(Continued)
| Adsorbent               | Solution component | Metal ions                | $q_e$ (mg/g) | $q_{e,1}$/$q_{e,2}$ | $\left(\frac{q_{e,1}}{q_{e,1}+q_{e,2}}\right) \times 100\%$ | Reference                                    |
|------------------------|--------------------|--------------------------|--------------|----------------------|-------------------------------------------------|---------------------------------------------|
| Valonia tannin resin   | Single component   | Pb(II)                   | 98.55        |                      |                                                 | Şengil and Özacar (2009)                   |
|                        |                    | Cu(II)                   | 24.5         |                      |                                                 |                                             |
|                        |                    | Zn(II)                   | 16.5         |                      |                                                 |                                             |
|                        | Ternary component  | Pb(Pb/Cu/Zn)             | 70           | 0.7103               | 78.2%                                           |                                             |
|                        | C$_r$ ratio 20:5:4 | Cu(Pb/Cu/Zn)             | 19           | 0.7755               | 21.2%                                           |                                             |
|                        |                    | Zn(Pb/Cu/Zn)             | 0.5          | 0.0303               | 0.6%                                            |                                             |
| Eichornia crassipes    | Single component   | Pb(II)                   | 26.32        |                      |                                                 | Mahamadi and Nharingo (2010)               |
|                        |                    | Cd(II)                   | 12.59        |                      |                                                 |                                             |
|                        |                    | Zn(II)                   | 12.55        |                      |                                                 |                                             |
|                        | Ternary component  | Pb(Pb/Zn/Cd)             | 14.31        | 0.5437               | 68.1%                                           |                                             |
|                        | C$_r$ ratio 1:1:1   | Zn(Pb/Zn/Cd)             | 3.66         | 0.2916               | 17.4%                                           |                                             |
|                        |                    | Cd(Pb/Zn/Cd)             | 3.04         | 0.2415               | 14.5%                                           |                                             |
adsorption capacities (mostly in mg/g but occasionally in mmol/g) or percentages, comparison of adsorption capacities, sorption thermodynamics, and suitability of kinetic and equilibrium models in describing the sorption data, among many others. Table 8 shows some of the major conclusions made for selected biosorbents when Pb was one of the metals in solution. As an example, Hossain et al. (2014) reported that when Cu, Pb, Zn and Cd were removed from multi-metal solution using cabbage waste, the Competitive Langmuir equation indicated that the biosorbent was more selective towards Pb than to other three metals, and Pb strongly inhibited the adsorption of the other metal ions. In a related study, Martín-Lara et al. (2016) applied the Extended Sips isotherm and showed that the biosorption capacity of Pb was consistently greater than that of Cu for both single and binary solution using pine cone shell biosorbent. Preferential adsorption of Pb was also observed by Şengil and Özacar (2009) for the Pb/Cu/Zn system suing Valonia tannin resin. According to Wang et al. (2017), three biosorbents: calcium alginate, algal biomass, algal/glutaraldehyde-crosslinked polyethyleneimine (PEI) showed a greater affinity for Pb regardless of the molar ratio of competitor ions. More recently, Maity and Ray (2018) applied the Competitive Langmuir equation and reported that for the same operating condition, a chitosan-based nanocomposite showed higher adsorption of Pb(II) than Cd(II).

However, in some cases authors failed to adequately interpret their data, leading to inaccurate conclusions. For example, Ofomaja et al. (2010b) on studying the biosorptive removal of Cu(II) and
| Adsorbent              | Solution component | Metal ions | \(q_m\) (mg/g) | \(\Delta q_m\)/\(q_m\) | % (\(\Delta q_m\)) | Reference                  |
|-----------------------|--------------------|------------|----------------|------------------------|-------------------|-----------------------------|
| Mentha piperita carbon| Single component   | Pb(II)     | 53.19          |                        |                   | Ahmad and Haseeb (2017)     |
|                       | Quaternary component | Pb(II) (Pb/Cu/Ni/Cd) | 50.50          | 0.949                  | -6.00%           |                              |
| Cabbage waste         | Single component   | Pb(II)     | 60.568         | 0.249                  | -75.1%           | Hossain et al. (2014)       |
|                       | Quaternary component | Pb(II) (Cd/Cu/Zn/Pb) | 15.085         | 0.234                  | -76.6%           |                              |
|                       |                     | Cu(II)     | 2.415          |                        | +13.4%           |                              |
|                       |                     | Zn(II)     | 10.170         | 1.134                  | +13.4%           |                              |
|                       |                     | Cd(II)     | 8.697          | 0.423                  | -57.7%           |                              |
| Perlite               | Single component   | Pb(II)     | 26.9           | 2.81                   | -15.2%           | Vijayaraghavan and Raja (2014) |
|                       | Quaternary component | Pb(II) (Pb/Cd/Cu/Ni) | 22.8           | 0.848                  | -15.2%           |                              |
|                       |                     | Cd(II)     | 3.80           | 0.671                  | -32.9%           |                              |
|                       |                     | Cu(II)     | 1.64           | 0.490                  | -51.0%           |                              |
|                       |                     | Ni(II)     | 1.34           | 0.477                  | -52.3%           |                              |
| Coco-peat biomass     | Single component   | Pb(II)     | 100.3          |                        |                   | Vijayaraghavan et al. (2016) |
|                       | Quaternary component | Pb(II) (Pb/Cd/Cu/Ni) | 84.2           | 0.840                  | -16.1%           |                              |
|                       |                     | Cd(II)     | 8.81           | 0.518                  | -48.2%           |                              |
|                       |                     | Cu(II)     | 16.5           | 0.680                  | -32.1%           |                              |
|                       |                     | Ni(II)     | 5.67           | 0.535                  | -46.5%           |                              |
| Biosorbent                        | Metal ions         | Multi-metal adsorption model | Major findings/conclusions                                                                 | Reference          |
|----------------------------------|--------------------|------------------------------|-------------------------------------------------------------------------------------------|--------------------|
| Cabbage waste                    | Cu(II) Pb(II) Zn(II) Cd(II) | Competitive Langmuir Model (\( q_e = \frac{q_m i}{b_i C_{eq} i + \sum_{j=1}^{n} b_j C_{eq} j} \)) | Biosorbent more selective towards Pb(II) than to other 3 metals. Pb(II) strongly inhibited adsorption of other metal ions. | Hossain et al. (2014) |
| Soybean hull                     | Cd(II) Pb(II)      | Competitive Langmuir Equation | There was competition, interaction or displacement effect between Cd(II) and Pb(II) ions. | Módenes et al. (2015) |
| Pine cone shell                  | Cu(II) Pb(II)      | Extended Sips isotherm model (\( q_e = \frac{q_m i}{b_i C_{eq} i + \sum_{j=1}^{n} b_j C_{eq} j} \)) | Biosorption capacity of Pb(II) was consistently greater than biosorption capacity of Cu(II) for both single component and binary sorption systems. | Martín-Lara et al. (2016) |
| Valonia tannin resin             | Pb(II) Cu(II) Zn(II) | Competitive effect deduced from plot of \( q_e Vs t \) | Biosorption capacities of metal ions lowered by 18–80% of those for single metal systems. Pb(II) ions preferentially adsorbed compared to Cu(II) and Zn(II). | Şengil and Özçakar (2009) |
| Calcium alginate, algal biomass, algal/glutaraldehyde-crosslinked polyethyleneimine (PEI) | Pb(II) Cu(II) | Competitive Langmuir Equation | The three sorbents showed a greater affinity for Pb(II) compared to Cu(II) regardless of the molar ratio of competitor ions. | Wang et al. (2017) |
| Calcium alginate, algal biomass, algal/glutaraldehyde-crosslinked polyethyleneimine (PEI) | Pb(II) Cu(II) | Langmuir-type model (\( q_{max} = \frac{q_m}{\left(1 + \frac{K_d}{C_{eq}}\right)} \)) | Pb/Cu system \( q_{max} \) was close to 97% of the total metal uptake due to Pb(II). | Hammaini et al. (2002) |
| Calcium alginate, algal biomass, algal/glutaraldehyde-crosslinked polyethyleneimine (PEI) | Pb(II) Cu(II) | Langmuir-type model (\( q_{max} = \frac{q_m}{\left(1 + \frac{K_d}{C_{eq}}\right)} \)) | Pb/Cd system \( q_{max} \) was close to 88% of the total metal uptake due to Pb(II). | Hammaini et al. (2002) |
| Calcium alginate, algal biomass, algal/glutaraldehyde-crosslinked polyethyleneimine (PEI) | Pb(II) Cu(II) | Langmuir-type model (\( q_{max} = \frac{q_m}{\left(1 + \frac{K_d}{C_{eq}}\right)} \)) | Pb/Zn system \( q_{max} \) was close to 99% of the total metal uptake due to Pb(II). | Hammaini et al. (2002) |

(Continued)
| Biosorbent | Metal ions | Multi-metal adsorption model | Major findings/conclusions | Reference |
|------------|------------|------------------------------|----------------------------|------------|
| *Arthrospira (Spirulina) platensis* and *Chlorella vulgaris* | Pb(II) Zn(II) Ni(II) | Competitive Langmuir model | Whereas Pb(II) significantly reduced the adsorption capacities of the Ni(II) and Zn(II), the effect of Ni(II) and Zn(II) on Pb(II) was almost negligible. | Rodrigues et al. (2012) |
| *Myriophyllum spicatum* | Pb(II) Cu(II) Zn(II) | Competitive Langmuir model | The biosorbent had no preference for Cu(II) and Pb(II) in spite of their differences in physicochemical properties. Effect of Cu(II) and Zn(II) on Pb(II) adsorption were similar. Explained in terms of similarity in molecular mass (63.57 and 65.38 g/mol), ionic radius (73 and 74 pm), and electronegativity (1.90 and 1.65 Pauling). | Yan et al. (2010) |
| Green macroalgae, *Caulerpa lentillifera* | Pb(II) Cu(II) Cd(II) | Partial competitive binary isotherm model | Adsorption capacity was always reduced in the presence of a secondary metal ion. Adsorption preference followed the order: Pb(II)>Cu(II)>Cd(II) Presence of Pb(II) more significantly decreased the sorption of Cu(II) and Cd(II) than vice versa. | Apiratikul and Povasant (2006) |
| *Eichhornia crassipes* | Pb(II) Cd(II) Zn(II) | Competitive Langmuir isotherm model | Combined action of the metal ions found to be antagonistic Metal sorption followed order: Pb(II)>>Cd(II)>>Zn(II) Competitive model not applicable to Zn/Cd system | Mahamadi and Nharingo (2010) |
| Marine bacterium *Pseudoeleocytes* sp. SC1E709-6 | Pb(II) Cd(II) Zn(II) | Competitive Langmuir isotherm model Partial competitive Langmuir | Lead highly dominated sorption of the other metal ions and adsorption capacity followed the order: Pb(II)>>Cd(II)>>Zn(II) No competition existed between Pb and the other two metal ions (Cd and Zn); Competitive adsorption confirmed for the Cd/Zn system | Jiang et al. (2017) |
| Chitosan based nano-composite | Pb(II) Cd(II) | Competitive Langmuir isotherm model | For the same operating conditions, the composite showed higher adsorption of Pb(II) than Cd(II). Similarly, decrease in adsorption of Cd(II) in the presence of Pb(II) was more than decrease in Pb(II) adsorption in the presence of Cd(II). | Maity and Ray (2018) |
| Industrial chili seeds (*Capsicum annuum*) waste | Cd(II) Pb(II) | Competitive Langmuir isotherm model | The affinity of Pb(II) for *C. annuum* was more than 5 times higher than that of Cd(II). | Medellín-Castillo et al. (2017) |
| Biosorbent                          | Metal ions          | Multi-metal adsorption model                      | Major findings/conclusions                                                                 | Reference                      |
|-----------------------------------|---------------------|---------------------------------------------------|---------------------------------------------------------------------------------------------|-------------------------------|
| Xanthate-modified magnetic chitosan | Pb(II) Cu(II) Zn(II) | Original Langmuir isotherm equation               | Combined action of the metals found to be antagonistic Metal sorption followed order: Pb(II)>Cu(II)>Zn(II) | Zhu et al. (2012)            |
| Alginate-immobilized Trichoderma  | Pb(II) Cu(II) Cd(II) Zn(II) | Not mentioned                                   | Pb(II) removed more efficiently in multi-metal system Adsorption order followed: Pb(II)>Cu(II)>Cd(II)>Zn | Chew and Ting (2016)            |
| Exiguobacterium sp.               | Pb(II) Cd(II) Zn(II) | Not mentioned                                   | Adsorption order followed: Pb(II)>Cd(II)>Zn(II)                                               | Park and Chan (2016)          |
Pb(II) from aqueous solution by Mansonia wood sawdust reported values of $q_{\text{mix}}^{\text{Cu}} / q_{o}^{\text{Cu}}$ and $q_{\text{mix}}^{\text{Pb}} / q_{o}^{\text{Pb}}$ of 0.8676 and 0.8356, respectively, but went on to write that $q_{\text{mix}}^{\text{Pb}} / q_{o}^{\text{Pb}} > q_{\text{mix}}^{\text{Cu}} / q_{o}^{\text{Cu}}$, which suggested that copper biosorption onto Mansonia sawdust was more affected by the simultaneous presence of a competing metal ion than for lead ions. However, the results actually show that it is the Pb(II) ions that would be more affected by the presence of copper, since it has a lower $q_{\text{mix}}^{\text{Pb}} / q_{o}^{\text{Pb}}$ value. Furthermore, the authors noted that the amount of copper ions biosorbed reduced from 26.8 to 19.2 mg/g when lead ion concentration was increased from 0 to 60 mg/dm$^3$. Again, this is not correct according to results presented in the paper which show that in fact the adsorption capacity of 26.8 mg/g was obtained using an initial concentration of 140 mg/dm$^3$ Cu(II) and 0 mg/dm$^3$ Pb(II). When the Pb(II) concentration was increased from 0 to 60 mg/dm$^3$, the results show that the adsorption capacity for Cu(II) actually increased from 26.8 to 39.1 mg/g at 140 mg/dm$^3$. Therefore, the results would then suggest that adsorption of Cu(II) ions was actually enhanced in the presence of Pb(II). Results published in a separate paper by Yan et al. (2010) also emphasize the need for authors to thoroughly analyse their biosorption results. The authors reported that the biosorbent had no preference for Cu(II) and Pb(II) in spite of the differences in physicochemical properties of the metal ions. However, an analysis of results reported by the authors shows that the equilibrium sorption capacities were $\approx 0.15$ and $0.17 \text{ mmol/g}$ for Pb(II) and Cu(II), respectively. Although these quantities seem to be comparable (in mmol/g), the difference is significant when converted to mg/g, i.e., 31.1 and 11.1 mg/g for Pb(II) and Cu(II), respectively. This would actually lead to different conclusions, i.e., that the biosorbent had preferential sorption for Pb(II).

Overall, therefore, these findings are significant in that despite the differences in biosorbents, experimental conditions, and models used to analyse the data, all biosorption systems analysed showed that Pb was preferentially removed from solution compared to the other metals. Such a general conclusion is an important contribution to the knowledge base on biosorption technology and has great potential to influence the design of the industrial process.

2.5. Application of response surface methodology

Further insights into biosorbent preference for metal sorption can be obtained by analysing findings from statistical methods such as Surface Response Methodology (SRM), which seeks to statistically explore the relationships between several explanatory variables and one or more response variables. It is evident from Table 9 that most of the reported findings confirm the dominance of Pb over other metal ions during in biosorption studies. However, a few authors showed that some biosorbents preferentially adsorbed other metals in the presence of Pb. Rao and Khatoon (2017) reported that for single-metal sorption using aluminate treated Casuarina equisetifolia leaves, adsorption capacities followed the order: Cu(II) (44.0 mg/g) > Ni(II) (39.0 mg/g) > Pb(II) (28.0 mg/g). It was also shown that adsorption capacities for single-metal sorption using Trichoderma viride decreased in the order of Cu(II) (0.360 mg/g) > Cd(II) (0.139 mg/g) > Pb(II) (0.103 mg/g) (Singh et al., 2010). Elsewhere, it was also reported that adsorption capacities for single-metal sorption followed the trend Cu(II) (204.1 mg/g) > Pb(II) (188.7) > Hg(II) (181.8 mg/g) (Alipanahpour Dil, Ghaedi, Ghezelbash, Asfaram, & Purkait, 2017).

2.6. Current and future perspectives

It was observed that a lot of data has been generated on multi-metal systems over the years. In particular, there exist published material on multi-metal systems with Pb(II) co-existing with other heavy metals, to allow reasonable conclusions on the influence of metal on sorption dynamics to be made. However, an exhaustive discussion of these systems can be hindered by limited data available for more complex systems, especially the quaternary system. More insights into the behaviour of the multi-metal systems would be realized if experiments on a given biosorbent are carried out under a combination of conditions indicated in Table 2, and also covering single, binary, ternary and quaternary sorption. This would allow more comprehensive and objective data analysis, e.g., how the total adsorption capacities would compare across different systems.
Table 9. Major conclusions from selected studies applying Response Surface Methodology

| Adsorbent                     | Metal ions          | Surface Response Methodology | Summary of conclusions                                                                 | Reference                      |
|-------------------------------|---------------------|------------------------------|----------------------------------------------------------------------------------------|--------------------------------|
| Aspergillus niger             | Pb(II)              | Central composite design (CCD)| Adsorption capacities for the removal of metal ions followed the order: Pb(II) (4.7 mg/g) > Cd (2.2 mg/g) > Ni (1.6 mg/g). | Amini and Younesi (2009)       |
|                               | Cd(II)              |                              |                                                                                        |                                 |
|                               | Ni(II)              |                              |                                                                                        |                                 |
| Immobilized spent Tricholoma  | Pb(II)              | Central composite design     | Preference of biosorbent for the three metals in ternary sorption was in the order of Pb(II) > Cu(II) > Cd(II). Lead ions could still be effectively removed from aqueous solution in the presence of both cadmium and copper ($q_{\text{max}} = 370.4$ mg/g), while removal of the cadmium and copper ions would be suppressed by lead ($q_{\text{max}} = 221.1$ and $91.7$ mg/g, respectively). | Cao, Liu, Cheng, Jing, and Xu (2010) |
| labayense                     | Cu(II)              | followed by mixture design   |                                                                                        |                                 |
|                               | Cd(II)              |                              |                                                                                        |                                 |
| Aluminate treated Casuarina   | Cu(II)              | Central composite design (CCD)| Single metal adsorption capacities followed the order: Cu(II) (44.0 mg/g) > Ni(II) (39.0 mg/g) > Pb(II) (28.0 mg/g). However, for multi-metal systems, the order was: Pb(II) (21.7 mg/g) > Cu(II) (13.0 mg/g) > Ni(II) (7.8 mg/g). | Rao and Khatoon (2017)          |
| equisetifolia leaves          | Pb(II)              |                              |                                                                                        |                                 |
|                               | Ni(II)              |                              |                                                                                        |                                 |
| Enterobacter sp. J1           | Pb(II)              | Combinative experimental     | Preference of metal sorption of Enterobacter sp. J1 in single metal systems decreased in the order of Pb(II) > Cu(II) > Cd(II). | Lu, Kao, Shi, and Chang (2008)  |
|                               | Cu(II)              | design and response surface  |                                                                                        |                                 |
|                               | Cd(II)              | methodology                  |                                                                                        |                                 |
| Trichoderma viride            | Cu(II)              | Box-Behnken design           | Biosorbent preference for metal sorption decreased in the order of Cu(II) (0.360 mg/g) > Cd(II) (0.139 mg/g) > Pb(II) (0.103 mg/g). | Singh et al. (2010)            |
|                               | Cd(II)              |                              |                                                                                        |                                 |
|                               | Pb(II)              |                              |                                                                                        |                                 |

(Continued)
| Adsorbent | Metal ions | Surface Response Methodology | Summary of conclusions | Reference |
|-----------|------------|-----------------------------|------------------------|-----------|
| Live yeast Yarrowia lipolytica 70,562 | Cu(II) Pb(II) Hg(II) | Central composite design (CCD) | Biosorbent preference for metal sorption decreased in the order of Cu(II) (204.1 mg/g)>Pb(II) (188.7 mg/g)>Hg(II) (181.8 mg/g). | Alipanahpour Dil et al. (2017) |
| Pretreated sporopollenin | Pb(II) Cu(II) | Box-Behnken design | Order of maximum biosorption capacity was Pb(II) (6.10 mg/g)>Cu(II) (4.84 mg/g). | Şener, Reddy, and Kayan (2014) |
| Magnetic Prussian blue nano-sorbent | Pb(II) Ni(II) Cu(II) Co(II) | Central Composite Rotatable Design Adsorption capacities followed the order: Pb(II) (778 mg/g)>Ni(II) (155 mg/g)>Cu(II) (138 mg/g)>Co(II) (111 mg/g). | Uoginte, Lujiunie and Mazieka (2019) |
| Grape stalks wastes | Pb(II) Cu(II) Cd(II) Ni(II) | Homogeneous Surface Diffusion Model (HSDM) | Values of the Langmuir affinity constant, b, followed the order: Pb (54.5 ± 0.2) Cu (15.2 ± 0.3) Cd (9.4 ± 0.1) > Ni (8.1 ± 0.2) for sorption in ternary mixtures. | Escudero-Oñate, Poch and Villaescusa (2017) |
| Activated Carbon | Pb(II) Cd(II) Ni(II) | Central composite design (CCD) | Adsorption capacity sequence toward the metal ions followed the order: Pb(II) (9.44 mg/g)> Cd(II) (9.37 mg/g)>Ni(II) (4.52 mg/g). | Kavand, Soleimani, Kaghazchi and Asasian (2016) |
It can be noted that in more recent times, green engineered nanoscale zero-valent metals (NZVMs) have emerged as novel adsorbent materials offering unique advantages (Al-Qahtani, 2017; Fazlzadeh et al., 2017; Lu et al., 2016; Malacas et al., 2019). However, very limited research has been published on the application of the NZVMs in multi-metal systems. Mahmoud, Abdou, Mohamed, and Osman (2016) showed that engineered Staphylococcus aureus immobilized on magnetic Fe₃O₄-phthalate nanoparticles showed high selectivity for Pb(II) compared to Ni(II) and Cu(II) ions. In related studies, non-competitive and competitive trials revealed that nanoscale zero-valent iron (NZVI) functionalized Posidonia oceanica marine biomass had a higher affinity for Cu(II) and Pb(II) compared to Cd(II). Given the potential for commercialization shown by NZVI-based biosorbents, it is projected that an increasing number of papers will be published in testing application of these systems for more complex multi-metal sorption. Some authors have already published such research, exemplified by Ojima et al. (2019) who investigated recovery of metals from complex systems including rare earth metal ions such as Ce³⁺, Dy³⁺, Gd³⁺, La³⁺, Nd³⁺, Pr³⁺, and Yb³⁺.

3. Conclusion

Unravelling the behaviour of Pb(II) is important in understanding sorption dynamics given its widely reported dominance in multi-metal systems. In this study, probes based on ratios of adsorption capacities revealed the tendency of Pb(II) ions to outcompete co-existing metal ions. It was shown that despite the differences in biosorbents and experimental conditions used, the ratio: \( q'_{m,Pb}/q'_{m,Cu} \) was consistently less than unity, whereas \( (q'_{m,Pb} + q'_{m,Cu}) > (q'_{m,Pb} + q'_{m,Cu}) \), thus confirming that adsorption was depressed due to co-existence of the metal ions in solution. An in-depth analysis using the Pb-Cu system showed that the ratios \( q'_{m,Pb}/q'_{m,Cu} \) and \( q'_{m,Pb}/q'_{m,Cu} \) were consistently greater than unity, thereby confirming the superiority of Pb(II) as a sorbate across a wide range of biosorbents. Furthermore, Pb(II) contributed to more than 70% and 77% of the total adsorption capacity for the binary and ternary systems reviewed, and it was shown that the % change in adsorption capacity \((\Delta q_i)\) was negative for all systems studied. For most biosorbents, Pb(II) is effectively removed from solution even in the presence of other heavy metals. However, the removal of Cu(II), Cd(II), Zn(II), Ni(II) and Cr(III) would be significantly suppressed in the presence of Pb(II). Such general conclusions are important in the designing and optimization of sorption processes utilizing the biosorption technology.

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