



# Quantifying the influence of surface physico-chemical properties of biosorbents on heavy metal adsorption

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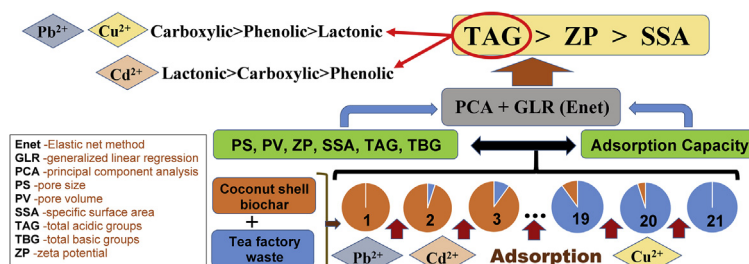
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## HIGHLIGHTS

- The influence of acidic surface functional groups is prominent in metal adsorption.
- SSA alone does not exert a significant influence on metal adsorption.
- Carboxylic groups exert more influence on binding hard acids.
- Lactonic groups are more important in providing binding sites to soft acids.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Heavy metals present in industrial wastewater contribute to human and ecosystem health risk when discharged without proper treatment. Low-cost biosorbents with high metal-binding capacity are increasingly being utilized for the removal of heavy metals. Inherent physico-chemical properties of biosorbents significantly influence their adsorption capacity. Studies quantifying the influence exerted by these properties on adsorption capacity are scarce. This study quantifies the influence and relative importance of selected physico-chemical properties on the adsorption capacity of three divalent heavy metals; Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> using multivariate analysis. Twenty one biosorbent mixtures were created, systematically varying their physico-chemical properties using tea factory waste and coconut shell biochar. Their adsorption capacities were measured using batch sorption studies. The influence of physico-chemical properties on the adsorption capacity is comparable for all three metal cations. Regression models were developed to quantify the influence of physico-chemical parameters on the adsorption capacity based on regression coefficients. All models were found to have high reliability with R<sup>2</sup> values above 0.98. Acidic surface functional groups were found to act as the key property that governs the adsorption capacity of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup>. Carboxylic groups played a major role in the adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup>, while lactonic groups were more important in providing binding sites to Cd<sup>2+</sup>. SSA

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failed to demonstrate a significant impact on the adsorption capacity of these three metals on its own when the biosorbent had a low surface functional group density.

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## 1. Introduction

Heavy metals play a major role in the degradation of water quality and can cause significant human and ecosystem health impacts if discharged without proper treatment (Terry and Stone, 2002; Jaishankar et al., 2014). They are persistent in the environment and can be easily accumulated in the food chain (Wang et al., 2009), while increasing their concentrations through natural processes such as bioaccumulation and biomagnification (Gautam et al., 2014; Anastopoulos et al., 2017). This is particularly significant in the case of industrial wastewater where high concentrations of heavy metals can be present.

Metals in water are found in both particulate and dissolved phases. Though particulate metals can be effectively removed using secondary treatment techniques such as filtration, wetlands and retention basins, these techniques are not effective for the removal of dissolved metals (Yousef et al., 1990; Pontier et al., 2004), which are known to be more hazardous, being readily bioavailable to organisms (Dils and Heathwaite, 1998). In this context, an efficient treatment method is required for the removal of heavy metals in wastewater, before being discharged into the environment. Among the available treatment techniques, adsorption is generally considered to be an effective, relatively inexpensive and eco-friendly treatment technique, but it would depend on the sorbents used (Fu and Wang, 2011). Utilisation of low-cost biosorbents with high metal-binding capacities has been studied widely (Babel and Kurniawan, 2004; Gautam et al., 2014). These include a variety of biomaterials such as microalgae (Pereira et al., 2013), bacteria species (Xu et al., 2017), fungal species (Iqbal and Edyvean, 2005), sawdust (Ofomaja, 2010) and plant materials (Dubey and Shiwani, 2012). Use of different biosorbents from agricultural waste such as walnut shells (Najam and Andrabi, 2016), potato peel (Guechi and Hamdaoui, 2016), rice straw (Amer et al., 2017), sesame (Cheraghi et al., 2015) and tea waste (Wan et al., 2014) in both, original and modified forms, are an important research focus (Hansen et al., 2010). Such studies have commonly emphasized the possibility of overcoming disposal issues associated with the specific agricultural waste materials by utilizing them as biosorbents.

A number of studies have investigated heavy metal removal capacities of different biosorbents (Fu and Wang, 2011; Cherdchoo et al., 2019) and suggested that material surface physico-chemical properties such as specific surface area (SSA), pore size (PS), pore volume (PV), zeta potential (ZP) and surface functional groups play a critical role in the metal adsorption capacity (Anastopoulos et al., 2013; Han et al., 2013; Gupta and Sen, 2017). Treating biosorbents physically and chemically to enhance their adsorption capacity has provided information as to how these treatments modify physico-chemical properties of the material and thus, influence the adsorption capacity (Gundogdu et al., 2013; Anastopoulos et al., 2017). Han et al. (2013) compared heavy metal adsorption of four kinds of biochars, demonstrating that acidic functional groups play a prominent role when the pore structure is similar. Sun et al. (2014) also prepared four different biochars and analysed their metal adsorption capacities along with physico-chemical properties. To our knowledge however, there is no consensus reached on the influence of physico-chemical properties of biosorbents on metal adsorption capacity and the relationship between these

characteristics and the adsorption capacity has not been quantitatively defined.

This significantly limits the design of effective biosorption based treatment systems for heavy metal removal. A quantitative analysis and identification of mathematical relationships would significantly aid in designing biosorption based treatment systems to achieve optimal adsorption by modifying their physico-chemical properties. Furthermore, such mathematical relationships will help in understanding the relative importance of each physico-chemical property in dictating the adsorption capacity, thereby aiding the implementation of treatment methods targeting specific metal species.

As such, the objective of this study was to investigate the above mentioned physico-chemical properties and surface functional groups that are influential in relation to the metal adsorption capacity of selected biosorbents and to quantify their relative importance. The outcomes of this study are expected to make a significant contribution to the design of low-cost and efficient industrial wastewater treatment systems for heavy metal removal using locally available biosorbents.

Three divalent metal ions;  $Pb^{2+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$  which are commonly present in heavy metal-laden industrial wastewater capable of causing significant adverse human and ecosystem health impacts (Jaishankar et al., 2014), were selected for this study. The research study was based in Sri Lanka and the preliminary biosorbent selection was based on common, locally available, low-cost agricultural waste materials. Special consideration was given to the possibility of mitigating any associated disposal problems associated with these waste materials by using as biosorbents.

## 2. Materials and methods

### 2.1. Biosorbent selection and sample preparation

Out of the initially selected five biosorbents, two with distinct physico-chemical properties were chosen using PROMETHEE analysis (Table S1, Supplementary information), which is a multi-criteria decision making technique which ranks objects based on the preference and weighting of variables associated with the object. Accordingly, coconut shell biochar (CSB) generated using slow pyrolysis at 300 °C and tea factory waste (TFW) were identified as suitable biosorbents (Fig. S1, Supplementary information). This selection was based on the significant differences in physico-chemical properties between them as evident from Table S1 in the supplementary information. For example, specific surface area (SSA) of TFW was 1 m<sup>2</sup>/g while it was 200 m<sup>2</sup>/g for CSB. In addition, their capability for removing heavy metals has been proven in past studies (Wan et al., 2014; Inyang et al., 2015). Both biosorbents were reduced to small pieces, washed with deionised water, oven dried for 24 h, ground and sieved to obtain a particle size between 125 µm and 150 µm.

The experimental design for investigating the influence of physico-chemical properties on adsorption capacity required systematic variation of these properties. However, physico-chemical properties are inherent properties of biosorbents and therefore, cannot be altered individually. Hence, systematic variation of physico-chemical properties was achieved by mixing TFW and CSB

in different weight percentages. Sample 1 contained CSB alone while sample 2 had 95% of CSB and 5% of TFW by weight. TFW weight percentage was increased by 5% increments in each of the new samples till sample 21 contained TFW alone. Accordingly, twenty one different mixtures were created (Table S2, Supplementary information) and ANOVA undertaken confirmed that physico-chemical properties of these mixtures vary significantly ( $p < 0.05$ ) except for zeta potential.

## 2.2. Sample characterisation

SSA, PS, PV and ZP were the physico-chemical properties investigated in this study while total acidic groups (TAG) and total basic groups (TBG) were included as surface functional groups. Further, TAG was divided into carboxylic, phenolic and lactonic groups (Basso et al., 2002).

SSA was measured using nitrogen gas adsorption isotherms at 77 K (ASAP 2020 from Micrometrics Instrument Co., USA) using the Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938). PV and PS were measured using the Barrett–Joyner–Halenda (BJH) method via desorption isotherm (Barrett et al., 1951) at the relative pressure of 0.99. ZP was measured using a Malvern Zetasizer Nano ZS (Malvern Instruments, UK) at pH  $5.5 \pm 0.5$  (Mishra et al., 2009). Quantification of surface functional groups (TAG, carboxylic, phenolic, lactonic and TBG) was carried out using the Boehm titration method (Boehm et al., 1964) followed by the standardisation of CO<sub>2</sub> expulsion and end point determination (Goertzen et al., 2010).

## 2.3. Batch sorption studies

Batch experiments were conducted to determine the adsorption capacities of the two selected biosorbents for each metal ion by adding 3.0 g of biosorbent to 1000 mL of solution containing heavy metal ions at pH  $5.5 \pm 0.5$  (adjusted by using 0.1 M NaOH or HNO<sub>3</sub>). Keeping the concentrations of Pb<sup>2+</sup>, Cd<sup>2+</sup> and Cu<sup>2+</sup> at a range of 2–300 mg/L, metal ion solutions were prepared by dissolving the corresponding metal nitrates in deionised water. The chemicals used for the study were of analytical grade or ACS certified compounds from Sigma-Aldrich. Metal nitrates were used because nitrate anions do not hydrolyse metals or form metal-anion complexes (Perić et al., 2004; Ziyath et al., 2011) and hence, do not pose any interference with the metal adsorption processes of biosorbents. The equilibrium time was 24 h and the experiments were conducted using a mechanical shaker at 150 rpm. The amount of adsorbed metals was calculated according to the following equation:

$$q_e = \frac{V(C_e - C_o)}{m} \quad (1)$$

Where;  $q_e$  (mg/g) is the quantity of metal ions adsorbed per unit mass of adsorbent,  $C_o$  (mg/L) is the initial metal ion concentration,  $C_e$  (mg/L) is the equilibrium metal ion concentration in the solution,  $V$  (L) is the volume of solution used and  $m$  (g) is the mass of the adsorbent. Atomic adsorption spectrometer (Thermo Scientific, iCE 3500) was used to determine the heavy metal concentrations. This was done in triplicate and the average value was considered.

## 2.4. Data analysis

Principal component Analysis (PCA) was performed on the data matrix as the first step. PCA is an efficient multivariate data analysis technique commonly employed to reduce the dimensionality of large sets of data and to streamline the representation of the data

field in question. It produces a set of hypothetical, orthogonal variables known as principal components (PCs), of which the first few are capable of representing most of the variation denoted in the original data matrix. Further information on PCA can be found in Supplementary information.

Pearson correlation analysis was performed as the second step to investigate the strength of associations between variables (pairwise). Research literature recommends using a correlation matrix to confirm the correlations which are visually evident in a PCA biplot (Miguntanna et al., 2010). For each significantly correlating pair, correlation coefficient value and  $p$  value were reassessed by running a permutation test for Pearson's product-moment correlation (10000 permutations for each test). A permutation test builds sampling distribution by resampling the observed data which is highly useful in increasing the accuracy of correlation analysis when the number of samples is relatively small (Önder et al., 2003).

As the third step, multicollinearity between the independent variables was investigated aiming to eliminate or to combine these variables for statistical modelling. Results of the correlation matrix (Table 1) coupled with the calculation of variance inflation factors (VIFs) was employed for this purpose. Since the correlation matrix is only focused on pairwise correlations, analysis of VIF was done as factors with VIF values above 10 are indicative of high multicollinearity, which can adversely influence the statistical modelling outcomes (O'Brien, 2007). The selected sets of independent variables were carried over to the next step of data analysis.

The fourth step, generalised linear regression (GLR), is a multivariate technique for analysing correlation between one or more dependent variables (responses) and independent variables (predictors). It models the relationship between the responses and predictors by fitting a linear equation to the observed data. Depending on the algorithm employed, the choice of predictive variables is undertaken using an automatic procedure. Variable selection methods such as stepwise regression and Elastic Net (Enet) are commonly used to select a subset of the original set of variables to build the model. Enet is a 'penalized regression method' or 'shrinkage method' (Wang et al., 2010) that can shrink the coefficients of redundant variables exactly to zero (Zou and Hastie, 2005), thereby employing a selection of variables as an integral feature. It has the ability to overcome limitations of other popular methods such as Ridge regression and Lasso regression (Ter Braak, 2009). Further details of Enet is provided in Supplementary information. R software (Ver. 3.5.1) with RStudio was employed for the data analysis. The specific R packages and commands are provided in the Supplementary information. Fig. S1 in Supplementary information summarises the statistical approach adopted for the data analysis.

## 3. Results and discussion

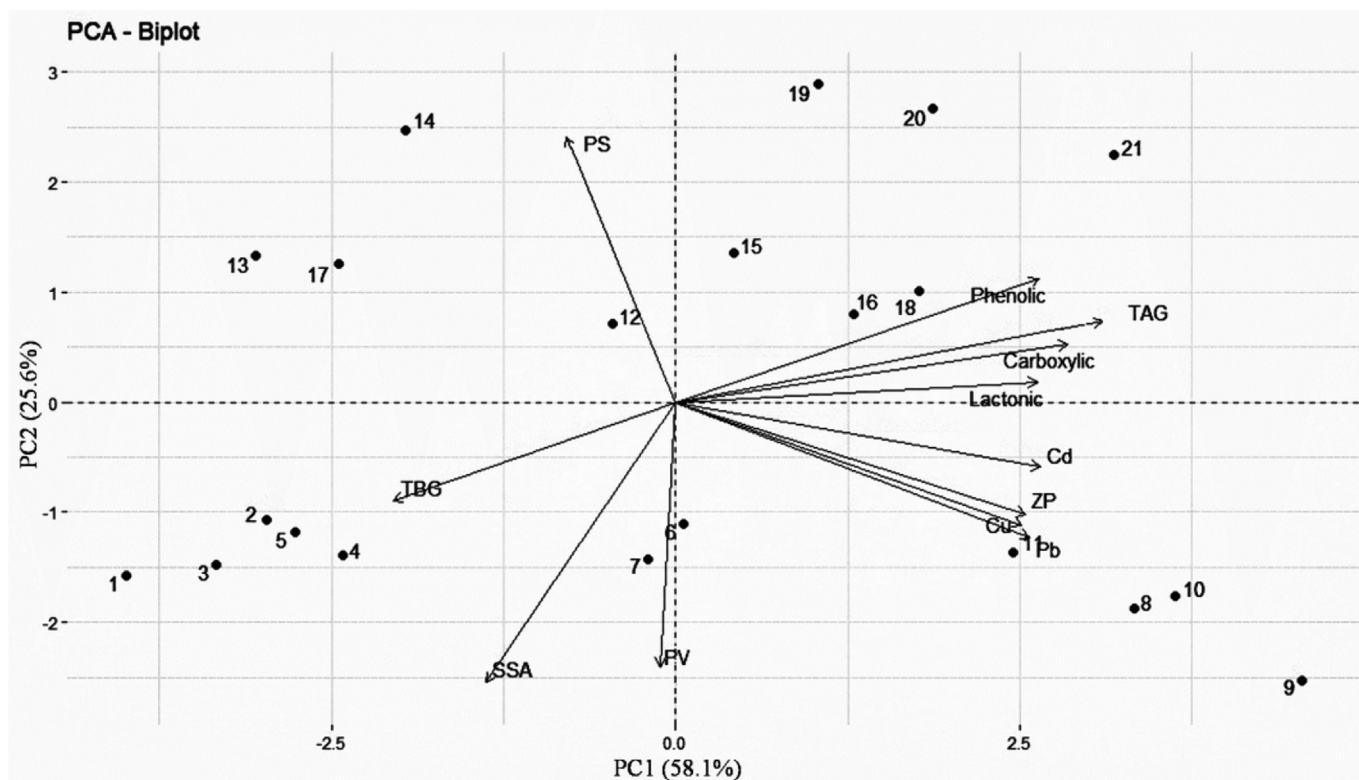
### 3.1. Qualitative relationships between physico-chemical properties of biosorbents and metal adsorption capacity

The raw data matrix consisted of twelve variables and twenty-one objects which were the twenty-one biosorbent mixtures. The variables were the adsorption capacities of the three heavy metals Pb<sup>2+</sup>, Cd<sup>2+</sup> and Cu<sup>2+</sup>, SSA, PS, PV, ZP, carboxylic, phenolic, lactonic, TAG and TBG. PCA was performed on the raw data matrix to assess and visualise relationships between variables in the analysis. The first two PCs accounted for 83.7% of the total variance and the corresponding biplot is given in Fig. 1. In addition, Pearson's product-moment correlation coefficient (PPMCC) values resulting from Pearson correlation analysis of the raw data matrix is presented in Table 1. Further details on PPMCC is provided in the

**Table 1**  
Pearson correlation matrix.

	SSA	PS	PV	ZP	Carboxylic	Phenolic	Lactonic	TAG	Cu	Cd	Pb	TBG
SSA		**	***		*	**		**				**
PS	−0.620		***	*					*	*	*	
PV	0.717	−0.788										
ZP	−0.137	−0.538	0.197		***	*	**	**	***	***	***	*
Carboxylic	−0.579	−0.089	−0.156	0.702		***	***	***	***	***	***	**
Phenolic	−0.673	0.065	−0.326	0.582	0.910		***	***	*	**	*	**
Lactonic	−0.404	−0.254	−0.028	0.624	0.781	0.802		***	**	***	**	**
TAG	−0.606	−0.072	−0.197	0.682	0.978	0.964	0.865		**	***	***	**
Cu	−0.068	−0.493	0.214	0.853	0.743	0.553	0.592	0.688			***	
Cd	−0.224	−0.484	0.025	0.809	0.777	0.672	0.693	0.764	0.775		***	*
Pb	−0.050	−0.548	0.276	0.852	0.750	0.560	0.685	0.711	0.950	0.791		
TBG	0.595	0.028	0.167	−0.452	−0.595	−0.628	−0.686	−0.651	−0.366	−0.512	−0.363	

Note: The lower triangular segment depicts correlation coefficient values while the upper triangular segment represents statistical significance levels;  $p < 0.05$  (\*),  $p < 0.005$  (\*\*),  $p < 0.0005$  (\*\*\*).



**Fig. 1.** PCA biplot consisting of physico-chemical properties and adsorption capacities of biosorbent mixtures (Note: SSA specific surface area, PV pore volume, PS pore size, ZP zeta potential, TAG total acidic group and TBG total basic group).

#### Supplementary information.

According to Table 1, PV has high correlation with PS (PPMCC =  $-0.788$ ,  $p < 0.0005$ ) and SSA (PPMCC =  $0.717$ ,  $p < 0.0005$ ). For this study, PS assessment was done via BJH Desorption method, which calculates PS as a function of PV and BJH Desorption cumulative surface area. While the surface area values obtained from BJH Desorption method is different from SSA values obtained for this study (using BET method) for the same material, they are closely related. This explains the correlations detected regarding PV, PS and SSA. The direction of the relationship between PS and PV for a particular surface mainly depends on its pore distribution (Bose et al., 2003).

The PCA biplot illustrates that the angles between the vectors corresponding to carboxylic, phenolic, lactonic, TAG, Cd, Cu and Pb are acute suggesting a strong correlation between acidic surface

functional groups and metal adsorption capacity. This is confirmed by the significant positive correlation coefficient ( $p < 0.05$ ) as evident in Table 1. According to Wang et al. (2007a), functional groups could participate in adsorption through electrostatic interaction or exchange of electrons to form complexes. Hence, a biosorbent with high total acidic surface functional groups is capable of cation adsorption resulting in high adsorption capacity (Fan et al., 2018). In contrast, TBG has a negative correlation with metal adsorption capacity as indicated by the PCA biplot. This suggests that electrostatic repulsion caused by these basic functional groups weaken the adsorption forces of positively charged metal ions (Jacobasch et al., 1998). Therefore, materials with high TBG could have lower adsorption capacities for positively charged metals.

Vectors related to carboxylic, phenolic, lactonic, TAG and ZP are



at acute angles indicating strong positive correlations among these parameters. This implies that these acidic functional groups can be ionised into negative ions, resulting in negative zeta potential (Wang et al., 2007b). ZP shows a strong correlation with metal adsorption capacity and this observation is confirmed by the correlation matrix (PPMCC values above 0.8 with  $p < 0.0005$ ). This could be attributed to the contribution of ZP to the process of physisorption. During physisorption, dipole interactions are developed when metal cations approach the negative sites of sorbents allowing a relatively weak van der Waals attractive force to develop between the outer sphere of metal cations and the sorbent framework (Inglezakis and Pouloupoulos, 2006). Zeta potential provides an indication of surface negativity, which is favourable for cation adsorption. High ZP value is favourable for attraction between the negatively charged biosorbent surface and cations. The strong attraction draws cations towards the biosorbent surface and increases the dispersion forces between the surface and cations. Jacobasch et al. (1998) noted that van der Waals forces can be assessed by zeta potential measurements. This suggests that physisorption yields a higher contribution to the adsorption process in materials with high zeta potential values.

Amarasinghe and Williams (2007) found that metal adsorption capacity increases with SSA when the SSA of a material is increased by reducing the particle size. This is because, the increase in SSA leads to an increase in the contact area between the biosorbent and metal cations. However, Han et al. (2013) and Agrafioti et al. (2013) reported that materials with high surface functional group densities, i.e. the quantity of the functional groups per unit area, demonstrate high adsorption capacities even when their SSA values are low. Further, Bradl (2004) also noted that the influence of SSA on adsorption capacity should be understood in the context of the density of surface functional groups. Similarly, according to PCA (Fig. 1) and the correlation matrix (Table 1), SSA does not have a significant correlation with the metal adsorption capacity, whereas a strong correlation was observed between metal adsorption capacity and the functional groups. This highlights the influence of surface functional group density on metal adsorption capacity.

The variation of acidic functional groups, TAG, ZP, SSA and the adsorption capacity of metal cations is illustrated in Fig. 2. Quality of representation of each variable on the two PCs was calculated via the squared cosine ( $\cos^2$ ) value (Krzanowski, 1979), which indicates the contribution of a component to the squared distance of the observation to the origin. Further details on the calculation of  $\cos^2$  including the R software code and the individual  $\cos^2$  values are given in Supplementary information.  $\cos^2$  for PC1 was the highest in TAG followed by ZP, while  $\cos^2$  for PC2 was the highest in SSA followed by PS and PV. These values are consistent with the visual observations of the biplot, which confirms that PC1 discriminates the samples based on acidic functional groups since the 11 samples with the highest TAG have positive PC1 scores (Fig. 2a). On the other hand, PC2 demonstrates a clear discrimination based on SSA as samples 1 to 11 with the highest SSA values scored the lowest on PC2 (Fig. 2d).

The clustering seen with the first five samples having lower PC1 and PC2 scores can be explained by  $\cos^2$  values of variables where TAG and SSA have the highest  $\cos^2$  for PC1 and PC2, respectively. Fig. 2a and d indicate that the first five samples have the lowest TAG values (resulting in low PC1 scores) coupled with the highest SSA values (resulting in low PC2 scores). Samples 8, 9, 10 and 11 with high PC1 scores and low PC2 scores are also clustered together. These four samples have a relatively higher capacity for metal adsorption (Fig. 2c), suggesting that samples with high PC1 scores and low PC2 scores would have a relatively higher adsorption capacity.

Analysis of multicollinearity was done as the next step. The

correlation matrix illustrated high correlation between PV and SSA as well as PV and PS. Since PS was also calculated using PV (Section 3.1), PV was excluded to reduce multicollinearity for subsequent statistical modelling. The VIF quantifies the severity of multicollinearity in the least squares regression analysis. When all the independent variables were considered for the calculation of VIFs, R software detected an error caused by 'perfect multicollinearity'. Since the value of TAG is equal to the sum of carboxylic, phenolic and lactonic values, 'Perfect multicollinearity' could be removed either by using TAG to represent carboxylic, phenolic and lactonic (Method 1) or by using them separately (Method 2). Calculation of VIFs was done using both these approaches with the results shown in Table 2. VIFs were below 10 for other variables suggesting that variable selection could be done as per Method 1 or Method 2. Since TAG value can be obtained using a single titration, TAG was retained (Method 1) for the modelling, while the three surface acidic groups were excluded.

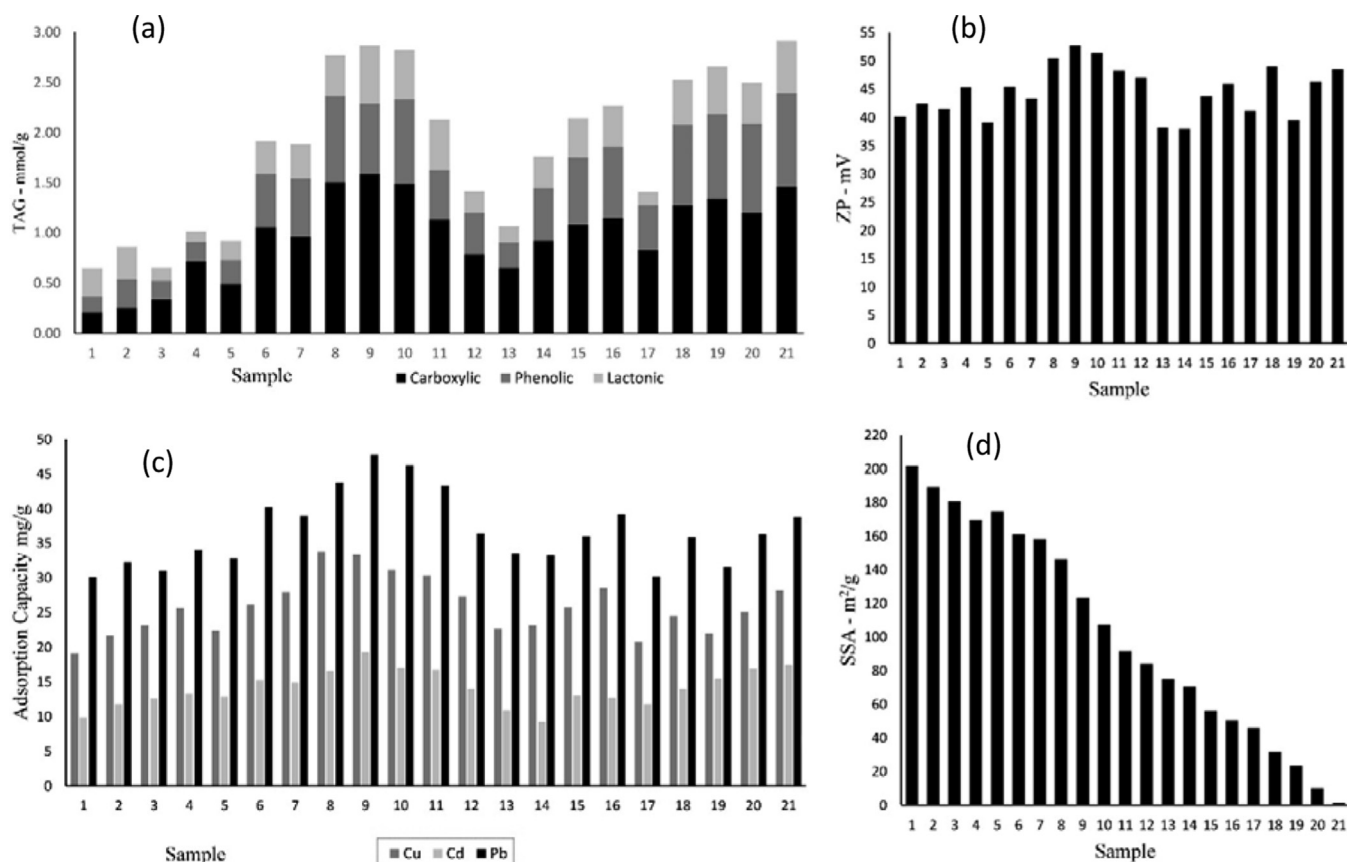
### 3.2. Relative importance of physico-chemical properties on adsorption

Mathematical regression models were developed to define the influence of physico-chemical parameters on the adsorption capacity using generalised linear regression using the Enet method for the three metal ions. Repeated k-fold cross validation ( $k = 10$ , repeated 10 times) was used as the resampling method and Enet algorithm was employed via R software for the regression. The codes used for the analysis are given in the Supplementary Information.

Table 3 provides a summary of the three regression models for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  adsorption. The Enet algorithm selects the optimal model by using Root Mean Squared Error (RMSE) to determine optimal values for two parameters called 'lambda' and 'alpha'. Lambda is a penalization parameter while alpha sets the ratio between L1 and L2 regularizations. Further details of these parameters and the regression method is given in the Supplementary information. RMSE value represents the square root of the variance of residuals and indicates how close the observed measurements are to the predicted values. Relevant RMSE values and regression coefficients for each model are given in Table 3.

Influence of different physico-chemical properties of the materials on adsorption capacity is comparable for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ . In all three cases, the influence of TAG is the highest followed by that of ZP, while the influence of TBG, PS and SSA is much smaller. This suggests that ion exchange and chemisorption are the important mechanisms in metal adsorption by biosorbents, where the acidic functional groups bind with metal cations via coordination and chelation (Lourie and Gjengedal, 2011) with physisorption playing a lesser role. A relatively higher influence of ZP despite the limited variation among samples (Section 2.2 and Fig. 2b) highlights the prominent role of ZP in metal adsorption. Similar results were obtained by Li et al. (2003), for adsorption of  $\text{Cd}^{2+}$  and by Dai (1994), for the adsorption of cationic dyes.

Physisorption of metal ions by sorbent materials depends on the charge densities of the metal ions (Erdem et al., 2004). Cations with high charge densities have a strong cationic field. Therefore, their interaction with an anionic field of sorbents is stronger compared to cations of low charge densities (Eisenman, 1962). Consequently, the physisorption force is stronger for cations with high charge densities. Hence, the relatively higher influence of ZP on  $\text{Cu}^{2+}$  adsorption compared to  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  could be attributed to the higher charge density of  $\text{Cu}^{2+}$ . Considering the adsorption of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ , the five parameters follow the same order of importance while the coefficient of PS was set to zero by the Enet algorithm. The same coefficient is low for  $\text{Cd}^{2+}$  as well, implying that the



**Fig. 2.** Variation of main physico-chemical properties and metal adsorption capacities of samples; (a) Acidic functional groups and TAG, (b) Zeta potential, (c) Adsorption capacity of metal cations, and (d) Specific surface area (SSA surface area, ZP zeta potential, TAG total acidic group).

**Table 2**

Variance inflation factors (VIFs) of the independent variables.

Method 1: TAG was used to represent acidic surface functional groups		Method 2: carboxylic, phenolic and lactonic groups were considered separately	
Variable	VIF	Variable	VIF
SSA	8.683927	SSA	7.074937
PS	7.697411	PS	8.018565
PV	3.525524	PV	3.849023
ZP	3.668455	ZP	3.990223
TAG	4.079687	carboxylic	8.190078
TBG	2.608812	phenolic	9.011234
		lactonic	4.660444
		TBG	3.156745

**Table 3**

Regression coefficients and model parameters.

Dependent variable	TAG	ZP	TBG	PS	SSA	RMSE	R squared
Pb <sup>2+</sup>	98.824	72.609	4.4789	Zero	0.1092	2.7591	0.9906
Cu <sup>2+</sup>	103.127	98.858	7.5709	Zero	0.8308	2.2503	0.9842
Cd <sup>2+</sup>	79.683	34.720	1.4538	0.5371	0.2603	1.2081	0.9831

influence of PS on metal adsorption is low.

This study implies that increasing acidic functional groups and/or ZP of biosorbents will result in enhancing the adsorption capacity of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup>. This knowledge is essential for undertaking modifications to existing biosorbents for enhancing their adsorption capacity. Furthermore, available data in literature as well as future studies on key physico-chemical properties such as

TAG and ZP of biosorbents, can be used to predict their adsorption capacities when designing biosorbent based industrial wastewater treatment systems. Since the influence of different physico-chemical properties of the materials on adsorption capacity is comparable for all three selected metal ions, it is possible that other metal ions would yield similar results. This could serve as a topic for future research.

**Table 4**  
Regression coefficients of acidic functional groups.

Dependent variable	Carboxylic	Phenolic	Lactonic
Pb <sup>2+</sup>	28.3657	16.3951	11.2503
Cu <sup>2+</sup>	23.4117	15.4223	10.2314
Cd <sup>2+</sup>	14.2123	10.2378	19.2528

### 3.3. Individual influence of acidic functional groups on adsorption

As an extension of the final step of the data analysis, these mathematical models were recreated after substituting individual values of carboxylic, phenolic and lactonic for TAG (Method 2 of variable selection) in order to investigate the influence of the acidic functional groups on metal adsorption. As evident in Table 4, carboxylic group has a higher influence on Cu<sup>2+</sup> and Pb<sup>2+</sup> adsorption followed by phenolic and lactonic groups. This is compatible with the observation described by Neris et al. (2019) on the adsorption of metal cations to modified water hyacinth fibres. For Cd<sup>2+</sup>, lactonic group has a higher influence followed by carboxylic and phenolic groups. These observations can be explained by Lewis Hard Soft Acid Base (HSAB) theory (Pearson, 1963). As Cu<sup>2+</sup> and Pb<sup>2+</sup> can be considered hard acids, they generally prefer to bind to hard bases such as carboxylic and phenolic groups.

## 4. Conclusions

This study was conducted to mathematically quantify the influence of surface physico-chemical properties of biosorbents on heavy metal adsorption capacity using Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>. The study outcomes confirmed that:

- Though various physico-chemical properties could influence Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> adsorption, they do not equally contribute or are equally important for adsorption.
- The key physico-chemical property governing the adsorption capacity of biosorbents for all the three metal cations are the acidic surface functional groups. Among these, carboxylic groups play a relatively prominent role in adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> which are hard acids, while lactonic groups are more important in providing binding sites to Cd<sup>2+</sup>, which is a soft acid.
- ZP can be used to assess the physisorption of these three metal cations.
- Though adsorption is a surface phenomenon, SSA alone does not exert a prominent influence on the adsorption of Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>, if materials with different functional group densities and same particle size are used.
- Identifying as to which physico-chemical properties should be manipulated to achieve higher adsorption of these three metal ions would aid in designing treatment methods by modifying locally available biosorbents.

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## CRedit authorship contribution statement

**Chaamila Pathirana:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing - original draft, Writing - review & editing. **Abdul M. Ziyath:**

Conceptualization, Formal analysis, Methodology, Validation, Writing - original draft, Writing - review & editing. **K.B.S.N. Jina-dasa:** Conceptualization, Investigation, Methodology, Project administration, Resources, Supervision, Writing - original draft, Writing - review & editing. **Prasanna Egodawatta:** Formal analysis, Methodology, Supervision, Validation, Writing - original draft, Writing - review & editing. **Sarina Sarina:** Formal analysis, Methodology, Supervision, Validation, Writing - original draft, Writing - review & editing. **Ashantha Goonetilleke:** Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing - original draft, Writing - review & editing.

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These organisations did not participate in the study design; in the collection, analysis and interpretation of data; in the writing of the manuscript; and in the decision to submit the article for publication.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.06.074>.

## References

- Agrafioti, E., Bouras, G., Kalderis, D., Diamadopoulos, E., 2013. Biochar production by sewage sludge pyrolysis. *J. Anal. Appl. Pyrolysis* 101, 72–78. <https://doi.org/10.1016/j.jaap.2013.02.010>.
- Amarasinghe, B., Williams, R., 2007. Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chem. Eng. J.* 132, 299–309.
- Amer, H., El-Gendy, A., El-Haggar, S., 2017. Removal of lead (II) from aqueous solutions using rice straw. *Water Sci. Technol.* 76, 1011–1021.
- Anastopoulos, I., Karamesouti, M., Mitropoulos, A.C., Kyzas, G.Z., 2017. A review for coffee adsorbents. *J. Mol. Liq.* 229, 555–565. <https://doi.org/10.1016/j.molliq.2016.12.096>.
- Anastopoulos, I., Massas, I., Ehalotis, C., 2013. Composting improves biosorption of Pb<sup>2+</sup> and Ni<sup>2+</sup> by renewable lignocellulosic materials. Characteristics and mechanisms involved. *Chem. Eng. J.* 231, 245–254. <https://doi.org/10.1016/j.cej.2013.07.028>.
- Babel, S., Kurniawan, T.A., 2004. Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere* 54, 951–967. <https://doi.org/10.1016/j.chemosphere.2003.10.001>.
- Barrett, E.P., Joyner, L.G., Halenda, P.P., 1951. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* 73, 373–380. <https://doi.org/10.1021/ja01145a126>.
- Basso, M.C., Cerrella, E.G., Cukierman, A.L., 2002. Lignocellulosic materials as potential biosorbents of trace toxic metals from wastewater. *Ind. Eng. Chem. Res.* 41, 3580–3585. <https://doi.org/10.1021/ie020023h>.
- Boehm, H.-P., Diehl, E., Heck, W., Sappok, R., 1964. *Surface Oxides of Carbon*, vol. 3, pp. 669–677. <https://doi.org/10.1002/anie.196406691>.
- Bose, S., Darsell, J., Kintner, M., Hosick, H., Bandyopadhyay, A., 2003. Pore size and pore volume effects on alumina and TCP ceramic scaffolds. *Mater. Sci. Eng. C* 23, 479–486. [https://doi.org/10.1016/S0928-4931\(02\)00129-7](https://doi.org/10.1016/S0928-4931(02)00129-7).
- Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soil constituents. *J. Colloid Interface Sci.* 277, 1–18. <https://doi.org/10.1016/j.jcis.2004.04.005>.
- Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60, 309–319. <https://doi.org/10.1021/ja01269a023>.
- Cheraghi, E., Ameri, E., Moheb, A., 2015. Adsorption of cadmium ions from aqueous solutions using sesame as a low-cost biosorbent: Kinetics and equilibrium studies. *Int. J. Environ. Sci. Technol.* 12, 2579–2592.
- Cherdchoo, W., Nithetham, S., Charoenpanich, J., 2019. Removal of Cr(VI) from synthetic wastewater by adsorption onto coffee ground and mixed waste tea. *Chemosphere* 221, 758–767. <https://doi.org/10.1016/j.chemosphere.2019.01>.

- 100.
- Dai, M., 1994. The effect of zeta potential of activated carbon on the adsorption of dyes from aqueous solution: I. The adsorption of cationic dyes: Methyl green and methyl violet. *J. Colloid Interface Sci.* 164, 223–228. <https://doi.org/10.1006/jcis.1994.1160>.
- Dils, R.M., Heathwaite, A.L., 1998. Development of an iron oxide-impregnated paper strip technique for the determination of bioavailable phosphorus in runoff. *Water Res.* 32, 1429–1436. [https://doi.org/10.1016/S0043-1354\(97\)00346-1](https://doi.org/10.1016/S0043-1354(97)00346-1).
- Dubey, A., Shiwani, S., 2012. Adsorption of lead using a new green material obtained from Portulaca plant. *Int. J. Environ. Sci. Technol.* 9, 15–20. <https://doi.org/10.1007/s13762-011-0012-8>.
- Eisenman, G., 1962. Cation selective glass electrodes and their mode of operation. *Biophys. J.* 2, 259.
- Erdem, E., Karapinar, N., Donat, R., 2004. The removal of heavy metal cations by natural zeolites. *J. Colloid Interface Sci.* 280, 309–314.
- Fan, Q., Sun, J., Chu, L., Cui, L., Quan, G., Yan, J., Hussain, Q., Iqbal, M., 2018. Effects of chemical oxidation on surface oxygen-containing functional groups and adsorption behavior of biochar. *Chemosphere* 207, 33–40. <https://doi.org/10.1016/j.chemosphere.2018.05.044>.
- Fu, F., Wang, Q., 2011. Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manag.* 92, 407–418. <https://doi.org/10.1016/j.jenvman.2010.11.011>.
- Gautam, R.K., Mudhoo, A., Lofrano, G., Chattopadhyaya, M.C., 2014. Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration. *J. Environ. Chem. Eng.* 2, 239–259. <https://doi.org/10.1016/j.jece.2013.12.019>.
- Goertzen, S.L., Thériault, K.D., Oickle, A.M., Tarasuk, A.C., Andreas, H.A., 2010. Standardization of the Boehm titration. Part I. CO<sub>2</sub> expulsion and endpoint determination. *Carbon* 48, 1252–1261. <https://doi.org/10.1016/j.carbon.2009.11.050>.
- Guechi, E.-K., Hamdaoui, O., 2016. Biosorption of methylene blue from aqueous solution by potato (*Solanum tuberosum*) peel: Equilibrium modelling, kinetic, and thermodynamic studies. *Desalination Water Treat.* 57, 10270–10285.
- Gundogdu, A., Duran, C., Senturk, H.B., Soylak, M., Imamoglu, M., Onal, Y., 2013. Physicochemical characteristics of a novel activated carbon produced from tea industry waste. *J. Anal. Appl. Pyrolysis* 104, 249–259. <https://doi.org/10.1016/j.jaap.2013.07.008>.
- Gupta, N., Sen, R., 2017. Kinetic and equilibrium modelling of Cu (II) adsorption from aqueous solution by chemically modified Groundnut husk (*Arachis hypogaea*). *J. Environ. Chem. Eng.* 5, 4274–4281. <https://doi.org/10.1016/j.jece.2017.07.048>.
- Han, Y., Boateng, A., Qi, P., Lima, I., Chang, J., 2013. Heavy Metal and Phenol Adsorptive Properties of Biochars from Pyrolyzed Switchgrass and Woody Biomass in Correlation with Surface Properties.
- Hansen, H.K., Arancibia, F., Gutiérrez, C., 2010. Adsorption of copper onto agriculture waste materials. *J. Hazard Mater.* 180, 442–448. <https://doi.org/10.1016/j.jhazmat.2010.04.050>.
- Inglezakis, V.J., Pouloupoulos, S.G., 2006. 4 - adsorption and ion exchange. In: Inglezakis, V.J., Pouloupoulos, S.G. (Eds.), *Adsorption, Ion Exchange and Catalysis*. Elsevier, Amsterdam, pp. 243–353.
- Inyang, M.I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., Pullammanappallil, P., Ok, Y.S., Cao, X., 2015. A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. *Crit. Rev. Environ. Sci. Technol.* 46, 406–433. <https://doi.org/10.1080/10643389.2015.1096880>.
- Iqbal, M., Edyvean, R.G.J., 2005. Loofa sponge immobilized fungal biosorbent: A robust system for cadmium and other dissolved metal removal from aqueous solution. *Chemosphere* 61, 510–518. <https://doi.org/10.1016/j.chemosphere.2005.02.060>.
- Jacobasch, H.-J., Simon, F., Weidenhammer, P., 1998. Adsorption of ions onto polymer surfaces and its influence on zeta potential and adhesion phenomena. *Colloid Polym. Sci.* 276, 434–442.
- Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., Beeregowda, K.N., 2014. Toxicity, mechanism and health effects of some heavy metals. *Interdiscip. Toxicol.* 7, 60–72. <https://doi.org/10.2478/intox-2014-0009>.
- Krzanowski, W.J., 1979. Between-groups comparison of principal components. *J. Am. Stat. Assoc.* 74, 703–707. <https://doi.org/10.1080/01621459.1979.10481674>.
- Li, Y.-H., Wang, S., Luan, Z., Ding, J., Xu, C., Wu, D., 2003. Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes. *Carbon* 41, 1057–1062. [https://doi.org/10.1016/S0008-6223\(02\)00440-2](https://doi.org/10.1016/S0008-6223(02)00440-2).
- Lourie, E., Gjengedal, E., 2011. Metal sorption by peat and algae treated peat: Kinetics and factors affecting the process. *Chemosphere* 85, 759–764. <https://doi.org/10.1016/j.chemosphere.2011.06.055>.
- Miguntanna, N.S., Egodawatta, P., Kokot, S., Goonetilleke, A., 2010. Determination of a set of surrogate parameters to assess urban stormwater quality. *Sci. Total Environ.* 408, 6251–6259. <https://doi.org/10.1016/j.scitotenv.2010.09.015>.
- Mishra, P.R., Shaal, L.A., Müller, R.H., Keck, C.M., 2009. Production and characterization of Hesperetin nanosuspensions for dermal delivery. *Int. J. Pharm.* 371, 182–189. <https://doi.org/10.1016/j.ijpharm.2008.12.030>.
- Najam, R., Andrabi, S.M.A., 2016. Removal of Cu (II), Zn (II) and Cd (II) ions from aqueous solutions by adsorption on walnut shell-Equilibrium and thermodynamic studies: Treatment of effluents from electroplating industry. *Desalination Water Treat.* 57, 27363–27373.
- Neris, J.B., Luzardo, F.H.M., Santos, P.F., de Almeida, O.N., Velasco, F.G., 2019. Evaluation of single and tri-element adsorption of Pb<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> ions in aqueous solution on modified water hyacinth (*Eichhornia crassipes*) fibers. *J. Environ. Chem. Eng.* 7, 102885.
- O'Brien, R.M., 2007. A caution regarding rules of thumb for variance inflation factors. *Qual. Quantity* 41, 673–690. <https://doi.org/10.1007/s11135-006-9018-6>.
- Ofomaja, A.E., 2010. Intraparticle diffusion process for lead (II) biosorption onto mansonia wood sawdust. *Bioresour. Technol.* 101, 5868–5876.
- Önder, H., Şahin, M., Çankaya, S., Tahtalı, Y., Cebeci, Z., 2003. Use of T-Statistics with Permutation Test: For Small Sample Size. *International Congress on Information Technology in Agriculture. Food and Environment, Izmir-Turkey*, pp. 7–10.
- Pearson, R.G., 1963. Hard and soft acids and bases. *J. Am. Chem. Soc.* 85, 3533–3539.
- Pereira, M., Bartolomé, M.C., Sánchez-Fortún, S., 2013. Bioadsorption and bioaccumulation of chromium trivalent in Cr(III)-tolerant microalgae: A mechanism for chromium resistance. *Chemosphere* 93, 1057–1063. <https://doi.org/10.1016/j.chemosphere.2013.05.078>.
- Perić, J., Trgo, M., Vukojević Medvidović, N., 2004. Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms. *Water Res.* 38, 1893–1899. <https://doi.org/10.1016/j.watres.2003.12.035>.
- Pontier, H., Williams, J.B., May, E., 2004. Progressive changes in water and sediment quality in a wetland system for control of highway runoff. *Sci. Total Environ.* 319, 215–224. [https://doi.org/10.1016/S0048-9697\(03\)00410-8](https://doi.org/10.1016/S0048-9697(03)00410-8).
- Sun, J., Lian, F., Liu, Z., Zhu, L., Song, Z., 2014. Biochars derived from various crop straws: Characterization and Cd(II) removal potential. *Ecotoxicol. Environ. Saf.* 106, 226–231. <https://doi.org/10.1016/j.ecoenv.2014.04.042>.
- Ter Braak, C.J., 2009. Regression by L1 regularization of smart contrasts and sums (ROSCAS) beats PLS and elastic net in latent variable model. *J. Chemom.: J. Chemom. Soc.* 23, 217–228.
- Terry, P.A., Stone, W., 2002. Biosorption of cadmium and copper contaminated water by *Senedesmus* abundans. *Chemosphere* 47, 249–255. [https://doi.org/10.1016/S0045-6535\(01\)00303-4](https://doi.org/10.1016/S0045-6535(01)00303-4).
- Wan, S., Ma, Z., Xue, Y., Ma, M., Xu, S., Qian, L., Zhang, Q., 2014. Sorption of lead(II), cadmium(II), and copper(II) ions from aqueous solutions using tea waste. *Ind. Eng. Chem. Res.* 53, 3629–3635. <https://doi.org/10.1021/ie402510s>.
- Wang, H., Zhou, A., Peng, F., Yu, H., Yang, J., 2007a. Mechanism study on adsorption of acidified multiwalled carbon nanotubes to Pb (II). *J. Colloid Interface Sci.* 316, 277–283.
- Wang, H., Zhou, A., Peng, F., Yu, H., Yang, J., 2007b. Mechanism study on adsorption of acidified multiwalled carbon nanotubes to Pb(II). *J. Colloid Interface Sci.* 316, 277–283. <https://doi.org/10.1016/j.jcis.2007.07.075>.
- Wang, T.H., Li, M.H., Teng, S.P., 2009. Bridging the gap between batch and column experiments: A case study of Cs adsorption on granite. *J. Hazard Mater.* 161, 409–415. <https://doi.org/10.1016/j.jhazmat.2008.03.112>.
- Wang, X., Park, T., Carriere, K.J.C.S., Analysis, D., 2010. Variable selection via combined penalization for high-dimensional data analysis. *54*, 2230–2243.
- Xu, C., He, S., Liu, Y., Zhang, W., Lu, D., 2017. Bioadsorption and biostabilization of cadmium by *Enterobacter cloacae* TU. *Chemosphere* 173, 622–629. <https://doi.org/10.1016/j.chemosphere.2017.01.005>.
- Yousef, Y., Hvitved-Jacobsen, T., Harper, H., Lin, L., 1990. Heavy metal accumulation and transport through detention ponds receiving highway runoff. *Sci. Total Environ.* 93, 433–440.
- Ziyath, A.M., Mahbub, P., Goonetilleke, A., Adebajo, M.O., Kokot, S., Oloyede, A., 2011. Influence of physical and chemical parameters on the treatment of heavy metals in polluted stormwater using zeolite—a review. *J. Water Resour. Prot.* 03, 758–767. <https://doi.org/10.4236/jwarp.2011.310086>.
- Zou, H., Hastie, T., 2005. Regularization and variable selection via the elastic net. *J. R. Stat. Soc. Ser. B* 67, 301–320.