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Investigation of simultaneous adsorption properties of Cd, Cu, Pb and Zn by pristine rice husks using ICP-AES and LA-ICP-MS analysis

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ABSTRACT

Rice husks are an agricultural waste product that has unique metal adsorption capabilities to remediate heavy metal contaminated sites. It is insoluble in water, has strong chemical stability and mechanical strength with a high silica content (~20%), and possesses a high surface area with granular structure for adsorption that is rich with cation exchanging silanol (—Si—OH) functionalities. The purpose of this study is to determine the adsorption capabilities of pristine rice husks (PRH) for practical field applications. Sorption experiments were performed to evaluate simultaneous Cd, Cu, Pb, and Zn sorption by rice husk at varying pH, concentration, reaction temperature, and maximum adsorption capability using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Optimum adsorbent mass of 1.0 g of husk was determined by using increasing amounts of PRH (0.1–2.0 g) with 10 ppm concentration of Cd, Cu, Pb, and Zn at environmentally relevant pH 6.92. The resulting percent Cd, Cu, Pb and Zn removal efficiency (%R) order by 1. 0 g of PRH was highest for Pb and lowest for Zn under competitive equilibration conditions. Isotherm model plots of Cd, Pb, and Zn adsorption follows better with the Freundlich model than Langmuir model. Copper and Zn adsorption is endothermic while Cd and Pb adsorption process is exothermic. Spatial elemental distribution plots obtained by LA-ICP-MS on the PRH visually demonstrate metals are adsorbed on the silica rich areas of the rice husk. The ability to successfully sequester Cd, Cu, Fe, Pb and Zn in contaminated soils and acid mine water was demonstrated. Due to its abundance as an agricultural waste and its low cost it is clear that untreated raw rice husk has a great potential as a sustainable metal sequestering medium for metal contaminated acid mine water and soils.

1. Introduction

The growth of human civilization follows closely with the history of rice cultivation. With the successful domestication of rice (*Oryza sativa* L.), it has become a major staple food in many countries specially in Asia, and it is cultivated in arable lands of all inhabited continents [1]. An estimated total of 748 million tons of rice is produced annually worldwide and China alone produces ~207 million tons per annum [2]. In Asia alone, 770 million tons of rice husk or hull (RH) - the outer most tissue of the rice seed- is available annually as an agricultural waste product [3]. Consequently, rice husk is a low-cost yet abundant waste bio solid with many untapped uses. Rice husk typically contains 32.24% cellulose, 21.34% hemicellulose and 21.44% lignin by weight and rest is mineral ash (15.05%), water and other minor constituents [4–5]. The mineral ash is predominantly silica (SiO_2 ~ 96.34%) [5]. Rice husk is abundant in rice producing areas, and has posed problems for proper disposal partly due to its high mineral ash content [5].

Rice husk is insoluble in water, has high chemical stability and mechanical strength with a high silica content (~20%), yet its bulk density ($0.73\ g/cm^3$) is surprisingly low [5]. Rice husk's high surface area ($272.5\ m^2/g$) [5] and granular structure facilitate effective adsorption sites for both inorganic cations [6] and dyes [5]. Omnipresent silanol (—SiOH), —Si—O—Si (siloxane), along with carboxylic (—COOH), and OH and >C═O, functional groups present in the rice husk biomatrix are potential metal binding and exchanging sites [7–9]. Several studies have demonstrated that ion exchange and complexation reactions occur between the functional sites on the rice husk and metal cations [8,10,11]. One pathway is the silicon dioxide (SiO_2) sites can that be readily hydrolyzed to form —SiOH (silanol) groups on the surface of the rice husk resulting in weekly acidic silica surface with a $pK_a = 6–8$ [12]. These silanol functional groups [x(—SiOH)] undergo cation/proton ion exchange reactions with metal ions (M^{n+}) as follows [8,12]:

$$x(-SiOH) + M^{n+} \leftrightarrows [(SiO-)M]_x^{n-x} + xH^+ \tag{1}$$

Furthermore, phenolic (—OH), carboxylic (COOH), NH_2 and carbonyl (>C═O) sites in lignin, cellulose and hemi-cellulose as well as siloxane (—Si—O—Si—) in silica moieties of the rice husk could form complexes with metal cations via coordination [9,11].

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Rice husk has unique metal adsorption capabilities to remediate heavy metal contaminated sites [5,7,13] and sorption capability of metals by lignocellulose rich rice husk was reviewed by Chuah et al. [5] and Ngah and Hanafiah [6]. The removal of inorganic As species in water and wastewater by rice hull bio char and other biosorbents was reviewed by Ungureanu et al. [14]. Tarley and Arruda [11] demonstrated the ability to remove Al(III), Pb(II) as well as Cd(II), Cu(II), and Zn(II) from waste effluent solutions using milled (<355 μm size) rice husk powder. The adsorption of Cd(II), Ni(II) and Zn(II) at pH 6.0 by mesoporous (diameter between 200 and 5000 nm) rice husk ash (RHA) was achieved by Srivastava et al. [8]. Krishnani et al. [7] reported absorption of eight critical metals by 1.5% alkali treated rice husk and demonstrated the rice husk's capacity to sorb these elements as well its ability to reduce more toxic Cr(VI) species to less toxic Cr(III). In another study chemically (i.e. using 0.1 M HNO_3 and 1 M K_2CO_3) and thermally activated rice husks (ARH) at 473 K were used for successful sequestration of Cu(II), Cd(II), Pb(II), and Zn(II) from aqueous solutions. Chemical and thermal treatments have increased the sorption surface area as well as microporous cavities in the ARH and able to desorbed metals sorbed onto SRH using 0.1 M HCl solution [15]. The removal of Cd(II) from aqueous solutions by rice husk was demonstrated by Kumar et al. [16]. Kinetic and thermodynamic investigation of Cd adsorption by rice husk revealed its pseudo second order adsorption kinetics and spontaneous exothermic nature of the sorption of Cd from aqueous solutions [16]. Recently application of rice husk-derived bio char to remove As(III) and As(V) [17], and sequestration of Sb by untreated basmati rice husks was demonstrated [10].

The purpose of this study is to determine the adsorption capabilities of pristine rice husk (PRH) for mitigation of contaminated environmental media as an appropriate and low-cost technology. Experiments were performed to evaluate simultaneous Cd, Cu, Pb, and Zn sorption by rice husk at varying pH, concentration, reaction temperature, and maximum adsorption capability using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Based on these experiments, simultaneous adsorption of Cd, Cu, Pb and Zn by virgin rice husks at environmentally relevant pH was evaluated, and their adsorption isotherms properties and thermodynamic parameters were investigated. The visual identification of adsorption sites on the rice husk surface was probed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Finally, raw rice husks were applied for sequestration metals from acid mine water and contaminated soils.

2. Experimental methods

2.1. Rice husk

An organic rice husk sample was purchased from a brewer supplier (Brewer filter grade, More Flavor Brewing Company, Concord, CA). This unground pristine rice husks (PRH) were used for all metal adsorption experiments except for the initial pH optimization experiments. For metal sorption vs. pH experiments ground rice husks with particle size > 0.125 μm were used.

2.2. Metal adsorption experiments

Unground rice husk samples were weighed to ~0.1 or 1.0 g depending on the type of experiment. Ten milliliter of 10 μg/mL Cd, Cu, Pb and Zn rice husk sample solutions were placed in 15 mL polyproperlyene test tubes and mixed using a vortex mixer for a minute before ~16 h. agitation at 170 rpm on a platform shaker (Innova 2000, New Brunswick Scientific, USA). Samples were allowed to settle after agitation for 1 h or centrifuged at 3000 rpm for 10 min (Sorvall Legend XI, Thermo Scientific, Waltham, MA, USA). Finally, the supernatant was filtered using 0.45 μm Teflon (PTFE) syringe filter with polypropylene syringe assembly (Environmental Express, Charleston, SC) and stored in a refrigerator at 4 °C for ICP-AES analysis.

2.3. Preparation of Cd, Cu, Pb and Zn solutions for ICP-AES analysis

A blank solution containing 2% (v/v) nitric acid and a series of Cd, Cu, Pb, and Zn multielement standards (0.1, 0.5. 1.0. 5.0 and 10.0 μg/mL) in 2% (v/v) nitric acid was prepared using serial dilution of 1000 μg/mL elemental standards (Spex CertiPrep, Metuchen, NJ) for the calibration of the ICP-AES (Perkin Elmer Optima 2000 DV, Shelton, CT). ICP-AES emission wavelengths 226.502, 324.752, 220.353, and 213.857 nm were used for determination of Cd, Cu, Pb, and Zn, respectively. Linear calibration functions (correlation coefficient - r^2 of ≥0.9990) were established for the determination of residual Cd, Cu, Pb, and Zn concentrations after metal-rice husk equilibration.

2.3.1. Preparation of As, Cd, Cu, Pb and Zn solutions for ICP-MS analysis

A 250 mL of 20 ng/mL ^{74}Ge, ^{103}Rh, and ^{209}Bi internal standard solution was prepared for ^{112}Cd, ^{64}Cu, ^{208}Pb, ^{66}Zn, and ^{75}As determination of contaminated environmental samples by ICP-MS (Elan 6000a, Perkin Elmer Instruments, Shelton, CT). A suite of multielement standards containing 0 (Blank), 0.1, 1.0 10 and 100 ng/mL As, Cd, Cu, Pb, and Zn was prepared by diluting of 1000 μg/mL respective elemental standards (Spex CertiPrep, Metuchen, NJ). Linear calibration functions were obtained (r^2 of ≥0.9950).

2.4. Adsorption of metals with different rice husk amounts

Unground PRH weights ranging from 0.1 g to 2.0 g of were used for the determination of the optimum metals sorption mass of the adsorbent. Four replicates (n = 4) were prepared with 0.1, 0.4, 0.6, 1, 1.5,

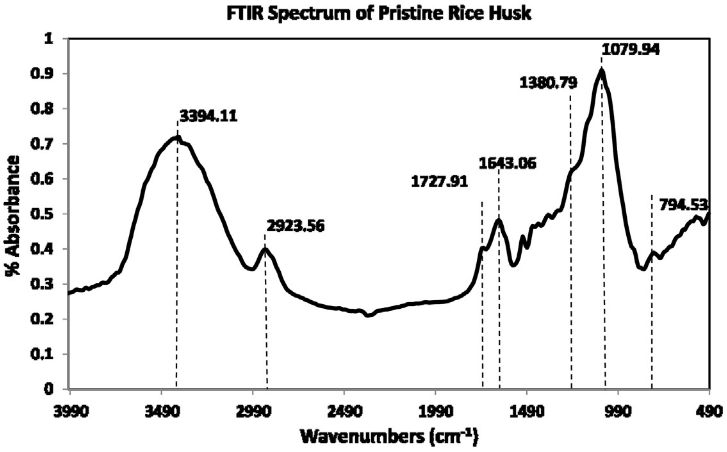


Fig. 1. FTIR spectrum of pristine rice husk.

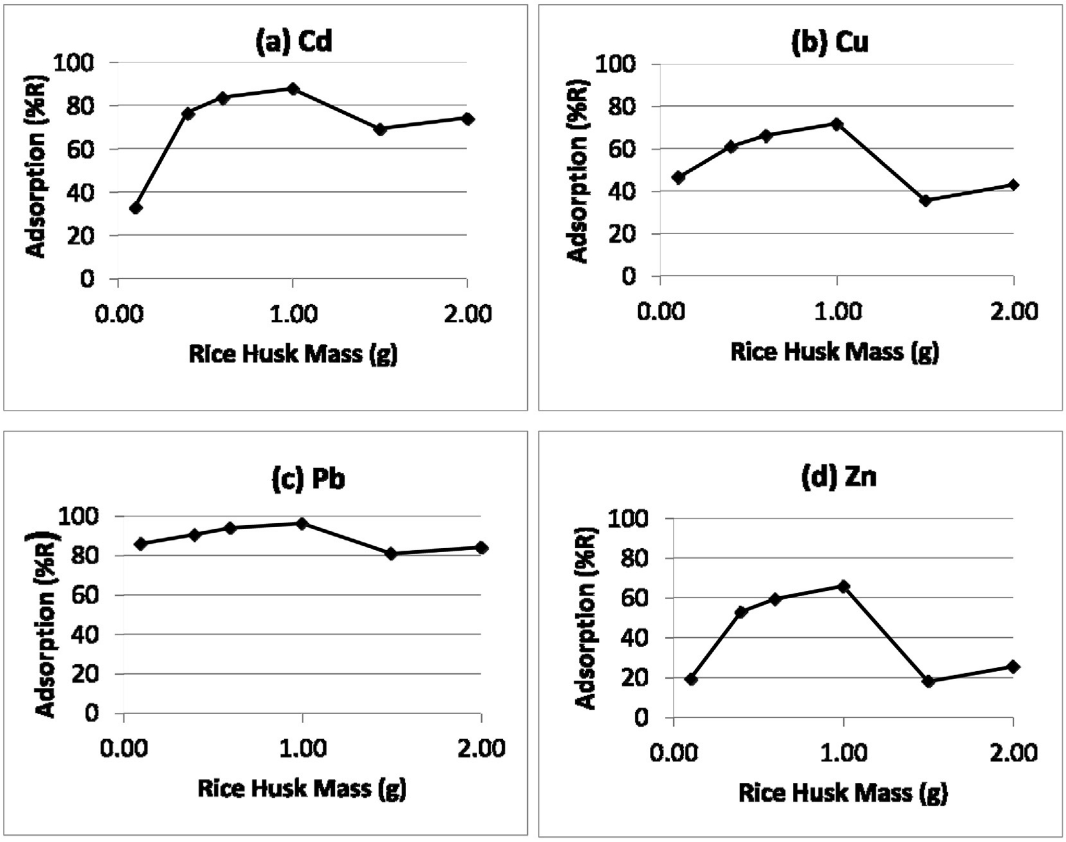


Fig. 2. a–d: percent simultaneous adsorption of (a) Cd, (b) Cu, (c) Pb and (d) Zn by various masses of pristine rice husk.

2.0 g amounts of rice husk per each adsorption experiment. Four replicate solutions were equilibrated with a 10 μg/mL Cd, Cu, Pb, Zn solution at pH 6.94 with rice husk masses of 0.1 g to 1.0 g. For 1.5 and 2.0 g rice husk experiments 20 mL of 10 μg/mL, Cd, Cu, Pb, and Zn solution was used. All samples were vortex mixed for ~1 min, agitated at 170 rpm for ~16 h by platform shaker at room temperature (RT), and filtered using 0.45 μm syringe filter for elemental concentration determination of the filtrate.

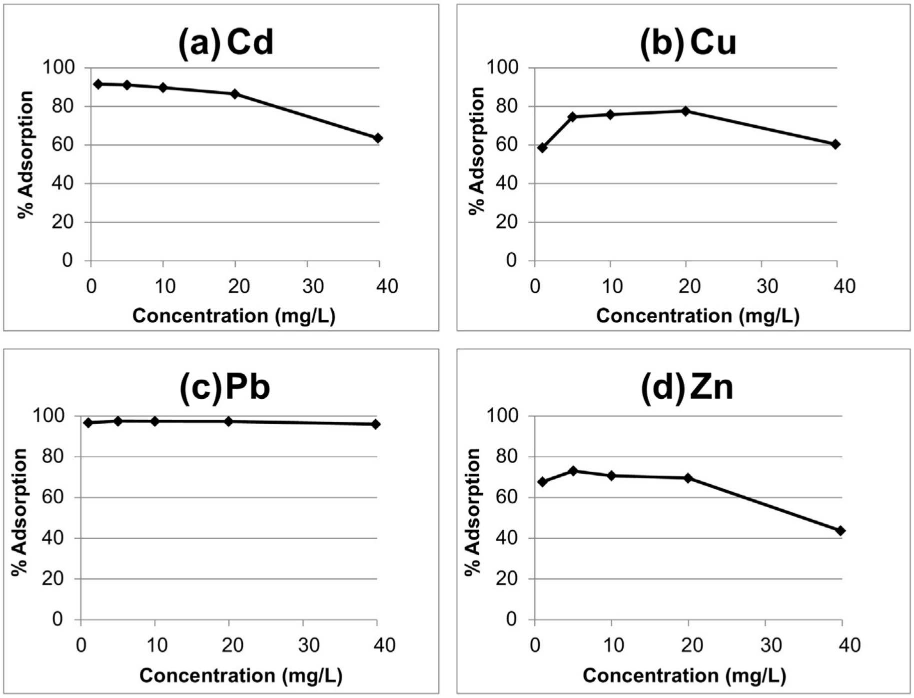


Fig. 3. a–d: percent simultaneous adsorption of (a) Cd, (b) Cu, (c) Pb and (d) Zn at various adsorbate concentrations by 1.0 g pristine rice husk.

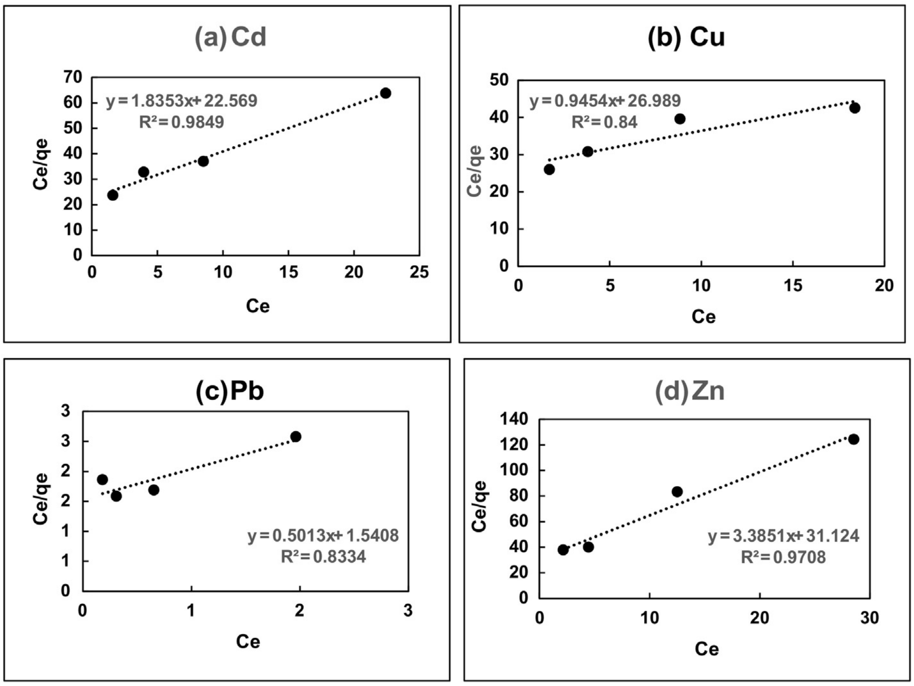


Fig. 4. a–d: Langmuir isotherm plots of (a) Cd, (b) Cu, (c) Pb and (d) Zn.

2.4.1. Metal adsorption efficiency of rice husk at various metal concentrations

Replicate samples ($n = 4$) were prepared to determine the adsorption efficiency of rice husk with varying concentrations of trace metal solutions. Untreated unground rice husks (~1.0 g) were mixed with 10 mL of 5, 10, 20, and 40 μg/mL Cd, Cu, Pb, and Zn solution at pH ~ 6.8–7.0. Samples were vortexed for ~1 min and agitated for ~16 h on platform shaker. Samples were then centrifuged at 3000 rpm for 10 min and filtered using Teflon syringes with 0.45 μm filters. All samples were diluted appropriately, and analyzed by ICP-AES. The percent removal (%R) of test cations by PRH was calculated using following relationship:

$$\%R = [(C_o - C_e)/C_o] \times 100 \qquad (2)$$

where, C_o is the initial or original cation concentration of metal ions (mg/L) added, C_e is the equilibrium concentration of metal ions (mg/L).

2.4.2. Metal adsorption at various temperatures

One gram of rice husk was equilibrated with 10 mL of 10 μg/mL Cd, Cu, Pb, Zn solution ($n = 4$) at three different temperatures: room temperature (RT = 23 °C), 41.2 °C, and 60 °C (pH was set to 6.91, 6.97, and 6.91, respectively to each temperature). In each experiment samples were vortex mixed for ~1 min, and placed into a reciprocal shaking temperature controlled water bath except RT experiment which was carried on a platform shaker. All experiments were agitated for ~16 h at 165 rpm. Samples were then centrifuged for 10 min at 3000 rpm and filtered using 0.45 μm filters before ICP-AES analysis.

2.5. FTIR spectroscopy of rice husks

Rice husks were dried in an oven at 60 °C (Fisher Scientific Isotemp 6901) for complete drying and ground to powder form. Spectroscopic grade KBr (Thermo Spectra-Tech, Shelton, CT) blank pellet and rice husk pellets (3 mg ground rice husk and 97 mg KBr) were prepared for analysis. Potassium bromide (KBr) powder and rice husks (PRH) were ground and mixed with a quartz mortar and pestle, then placed in a screw press for ~6 min to form a clear pellet. After taking a background KBr spectrum, the sample spectra are taken at 16 cm^{-1} resolution using 100 scans and a gain multiple of 1 using MIDAC 2000 M series FTIR spectrometer (MIDAC Corp. Irvine, CA). Recorded FTIR spectra were downloaded into Excel (Microsoft Corp. Redmond, WA) spreadsheet format for further spectral analysis.

2.6. Investigation of spatial distribution of adsorbed metals on pristine rice husk surface using LA-ICP-MS

Pristine and metal sorbed rice husk samples were mounted on glass slides. The LA-ICP-MS system was calibrated with a pellet made out of NIST (National Institute for Science and Technology, Gaithersburg, MD) Tomato Leaves 1573a standard reference material (SRM). The preparation of solid pressed pellets was discussed for LA-ICP-MS analysis previously [18]. ^{13}C intensity (I_{13C}) was used as an internal standard to normalize ^{63}Cu, ^{111}Cd. ^{208}Pb, and ^{66}Zn signal intensities (I_M). Response factors ($RF = [M_S] / (I_M/I_{13C})$) were obtained using elemental concentrations $[M_S]$ reported in the SRM except for Pb which was not certified. Elemental distribution of the outer surface of rice husk was probed in laser ablation spot center area of ($280 \times 280\ \mu m^2$) using laser ablation system (213 nm, UV laser, Eclipse, ESI, Fremont, CA)

Table 1
Comparison of adsorption isotherm (a) Langmuir and (b) Freundlich models for Cd, Cu, Pb, and Zn and their correlation coefficients, and related isotherm parameters.

1a. Langmuir model

Elements	r^2	q_{max} (mg/g)	K_L (L/mg)	SF
Cd	0.9849	0.545	0.0813	0.552
Cu	0.8400	1.058	0.0350	0.741
Pb	0.8334	1.995	0.3254	0.235
Zn	0.9708	0.295	0.1088	0.479

1b. Freundlich model

Elements	r^2	1/n	n	K_F
Cd	0.9858	0.6403	1.56	0.0515
Cu	0.9978	0.7822	1.28	0.0429
Pb	0.9730	0.8464	1.18	0.4768
Zn	0.9513	0.5042	1.98	0.0435

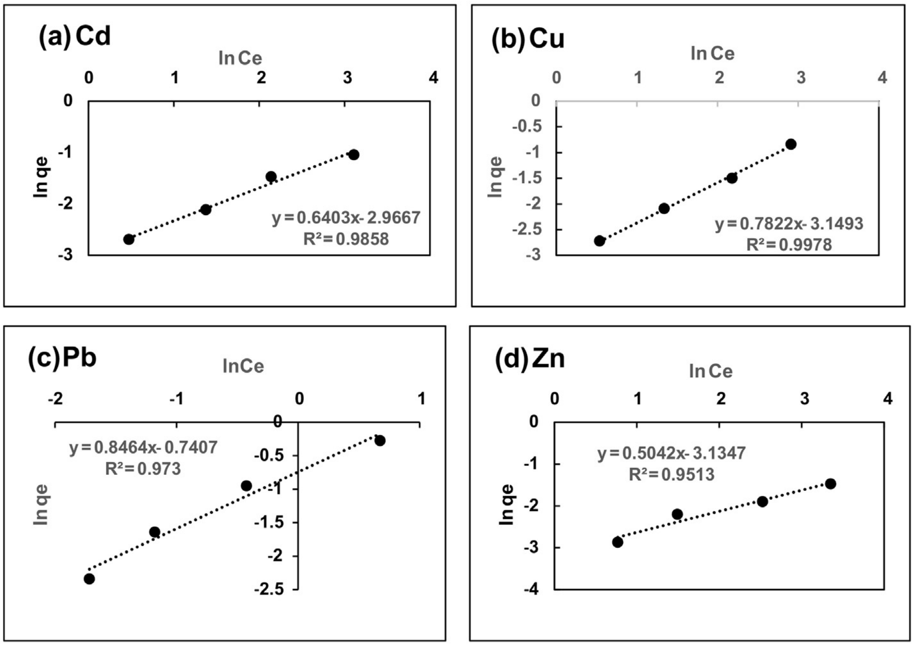


Fig. 5. a–d: Freundlich isotherm plots for (a) Cd, (b) Cu, (c) Pb and (d) Zn.

coupled to ICP-MS (Elan 6000a, Perkin Elmer Instruments, Shelton, CT) using spot ablation approach. ESI low volume laser chamber was used for all laser ablation experiments. The spot size, frequency of laser shots, and laser energy, dwell time between spots, and average fluence, are as follow: 50 μm, 10 Hz, 1 s, 12 J/cm^2, respectively. Surface elemental distribution of both pristine rice husk (PRH) and metal treated rice husk were probed using above instrument conditions. The raw intensity (cps) vs time data were transferred to Excel spreadsheet (Microsoft Corp., Redmond, WA) and subsequent data analysis and surface plots were made using OriginPro 2016 software (OriginPro, Northampton, MA).

2.7. Sequestration of trace metals in contaminated acid mine water and soils using PRH

Acid mine drainage water (AMD: Mine shaft effluent from the mine shaft brook – MSB5) from the defunct Davis Mine, Rowe, MA and contaminated soils from Jingwang village, Xikuangshan mine (XKS) area, Hunan, China [19] were used for this study. Pretreatment metal concentrations of MSB5 water and soil leachate were determined by ICP-AES. Pristine rice husks (c.a. 5.0 g) and 20 mL of AMD water (MSB 5; n = 3) added, pH was adjusted to 6–7 and vortexed, shook in 50 mL polyproperlyene test tubes in batch mode, and

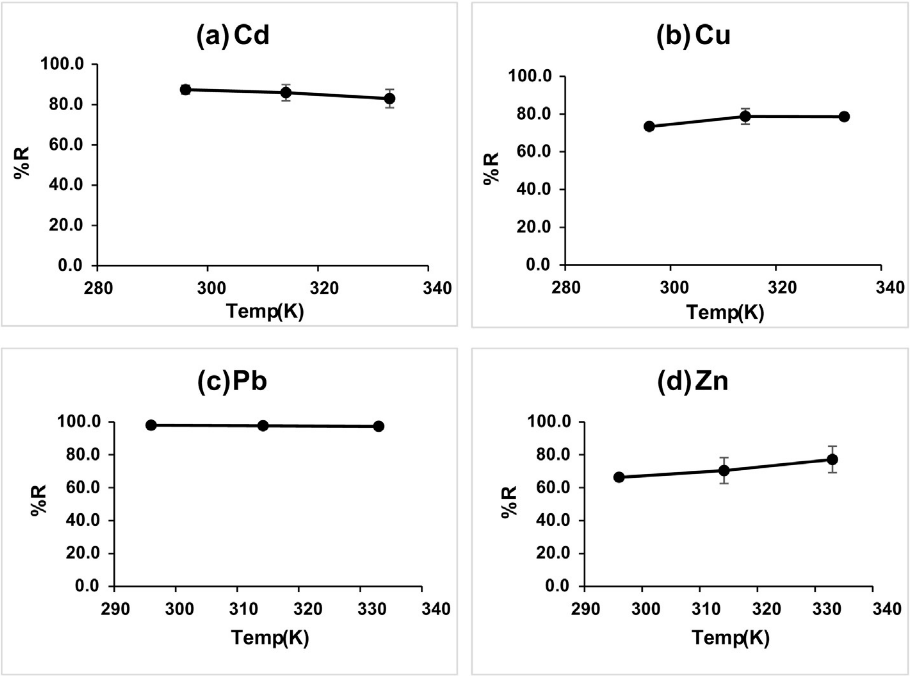


Fig. 6. a–d: percent recovery of (a) Cd, (b) Cu, (c) Pb, and (d) Zn against different temperatures 296 K, 314.2 K, and 333 K.

Table 2
Thermodynamic parameters related to simultaneous adsorption of Cu, Cd, Pb, and Zn by pristine rice husk at 296 K.

Element	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol·K)	$\Delta G°$ (kJ/mol)	K_c
Cd	−7.85	−10.50	−4.76	6.92
Cu	6.38	30.40	−2.51	2.77
Pb	−6.12	11.57	−9.54	48.24
Zn	11.96	45.81	−1.67	1.97

allowed to sequester metals at room temperature. Dried, powdered Jingwang soil samples were mixed with 20 mL distilled water allowed to leach for 16 h. to simulate environmentally relevant leaching conditions. The leached cations (in water extracts) from contaminated soils in XKS was used for metal sequestration experiments with PRH. Similarly, blank batch experiments (n = 3) were carried out using 20 mL distilled deionized water and ~5.0 g PRH to discern any native trace metals leaching from the rice husk. After ~16 h. equilibration, test tubes were centrifuged (5000 rpm for 5 min) the liquid phase was decanted and filtered using 0.45 μm PTFE filter for determination of Cu, Cd, Fe, Pb and Zn concentrations using ICP-AES.

3. Results and discussion

3.1. FTIR spectroscopy of PRH and metal exchange and metal binding functionalities

FTIR spectroscopy is commonly used to determine characteristic functional groups for trace metal adsorption onto the rice husk biomatrix. Fig. 1 shows the absorbance peaks for PRH using FTIR from wavenumbers 4000–490 cm^{-1}. FTIR peak analysis of the FTIR spectrum of PRH identifies ~3600 cm^{-1} (stretching of —OH group due to the silanol, —Si—OH group as well as adsorbed water and NH amide stretch), ~2900 cm^{-1} (aliphatic —CH_2 stretching from methyl groups in lignin), ~1720 cm^{-1} (ketonic >C=O), ~1600 cm^{-1} (-due to stretching of >C=O functionality based in aldehyde and ketonic moieties), ~1380 cm^{-1} (—CH_3), ~1080 cm^{-1} and ~790 cm^{-1} (corresponding to —Si—O—Si— stretching and bending of siloxane linkages of the rice husk), as relevant functional groups for trace metal adsorption and these bands are consistent with functional groups determined by previous studies [7–9,11,20]. The silanol, Si—OH band at ~3600 cm^{-1} in silica rich rice husk play a major role in cation exchange, by the mechanism described in the introduction. It is also likely that visible —Si—O—Si— (siloxane), —OH and >C=O functionalities could play a role in ligand binding of metals.

3.2. Simultaneous adsorption of Cd, Cu, Pb, and Zn by pristine risk husk (PRH)

Initial experiments at low pH revealed that the absorption of cations was poor as expected due to the protonation of ion exchange sites on the ground rice husk. As a consequence, a significant adsorption of Cd onto the ground husk didn't occur at pH 0.53 and 2.04 due to unfavorable cation exchange reaction at highly acidic conditions, but the percent sorption rose to 64.5 ± 1.2% and 80.0 ± 3.1% (n = 4) at higher pH of 7.04 and 8.72, respectively. It is evident that at increasing pH the cation exchange reaction presented in the Eq. (1) was favored, and we have chosen environmentally relevant pH ~ 6.9 at ambient temperature for all remaining metal adsorption experiments.

Varying masses (0.1 to 2.0 g) of adsorbent (pristine rice husk – PRH) was equilibrated with 10 mL of 10 mg/L Cd, Cu, Pb and Zn solution (adsorbate) at the room temperature and results are depicted in Fig. 2a–d. It is evident that 1.0 g unground PRH yielded the highest percent adsorption (or % recovery) of trace metals in the order of Pb > Cd > Cu > Zn under competitive equilibration reaction conditions with these model solutions. Lead (96.2%) had the highest adsorption whereas Zn had the lowest (65.8%). The sorption sites of metals by PRH could be saturated beyond 1.0 g of PRH indicating potential saturation of cation exchange sites on the husk matrix with the above metal absorbates amounts (100 μg), and it is consistent with the Khalid et al. [10] observations on removal of Sb using rice husk [10]. Optimal mass of adsorbent has determined to be 1.0 g unground PRH at an adsorbate concentration of 10 mg/L.

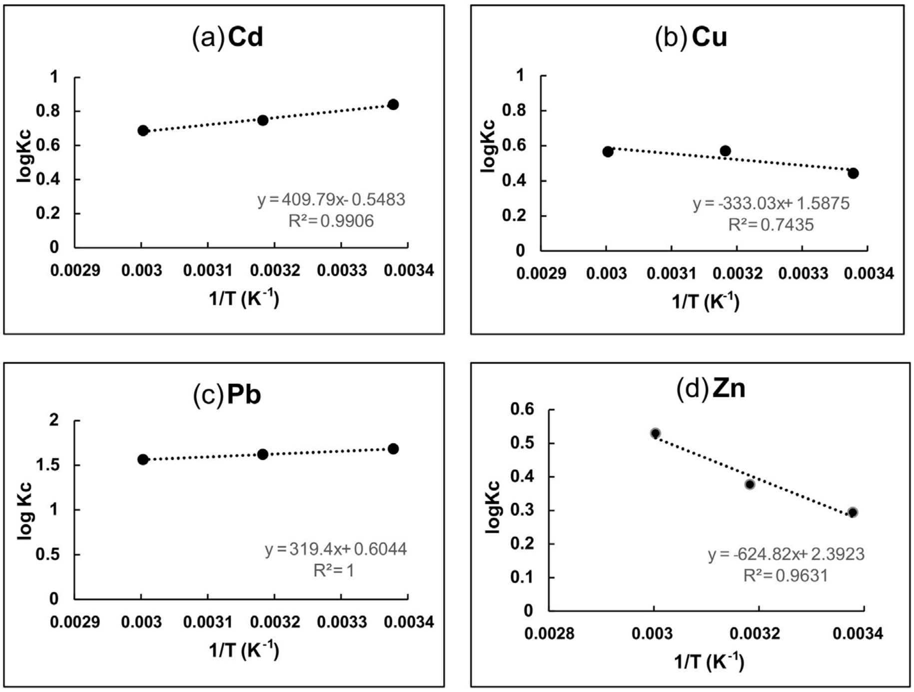


Fig. 7. a–d: Log K_c vs. 1/T Van't Hoff Plots for (a) Cd, (b) Cu, (c) Pb and (d) Zn.

Different concentrations of Cd, Cu, Pb and Zn solutions (1–40 mg/L) at the room temperature was equilibrated with 1.0 g PRH and the percent adsorption results at pH 6.96 are shown in the Fig. 3a–d. The results show that the maximum simultaneous adsorption of metals equilibrated with 10 mg/L mixed Cd, Cu, Pb and Zn solution; and ≥90% Cd and Pb and over 70% Cu and Zn absorbed by ~1.0 g PRH at room temperature but typically the sorption efficiency dropped off past 20 mg/L concentration, which is likely due to saturation of sorption sites.

3.3. Adsorption isotherms and thermodynamic properties Cd, Cu, Pb, and Zn sorption by pristine rice husk (PRH)

3.3.1. Adsorption isotherms

Using Cd, Cu, Pb, and Zn residual concentrations at the equilibrium (C_e μg/mL, at pH 6.91) and their solid phase adsorbate (i.e. PRH) concentration (q_e) were fitted with two adsorption isotherm models, namely Langmuir and Freundlich models, respectively [21–23]. Assuming complete monolayer coverage of adsorbate on the PRH surface, the

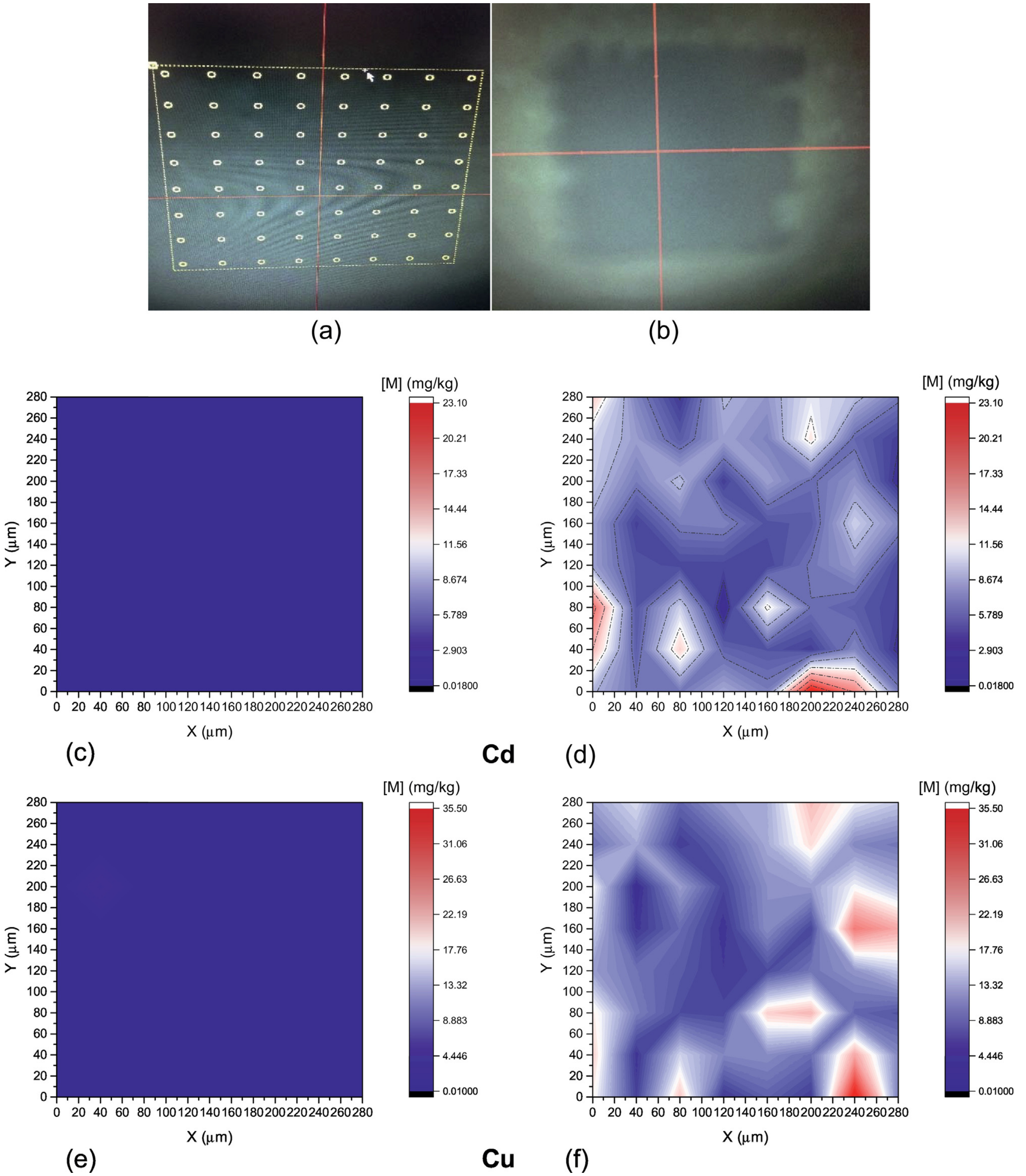


Fig. 8. a–k: panel (a) pre and panel (b) and post laser ablation areas. Elemental distribution images of native and adsorbed (panels c & d) Cu, (panels e & f) Cd, (panels g & h) Zn (mg/kg) and (panels i & j) Pb (as ^{208}Pb/^{13}C), and (panel k) native Si (as ^{29}Si/^{13}C) distribution on rice husk using LA-ICP-MS.

Langmuir model equation as follows:

$$q_e = q_{max} K_L C_e / 1 + K_L C_e \tag{3}$$

where q_e is the metal sorption coefficient.

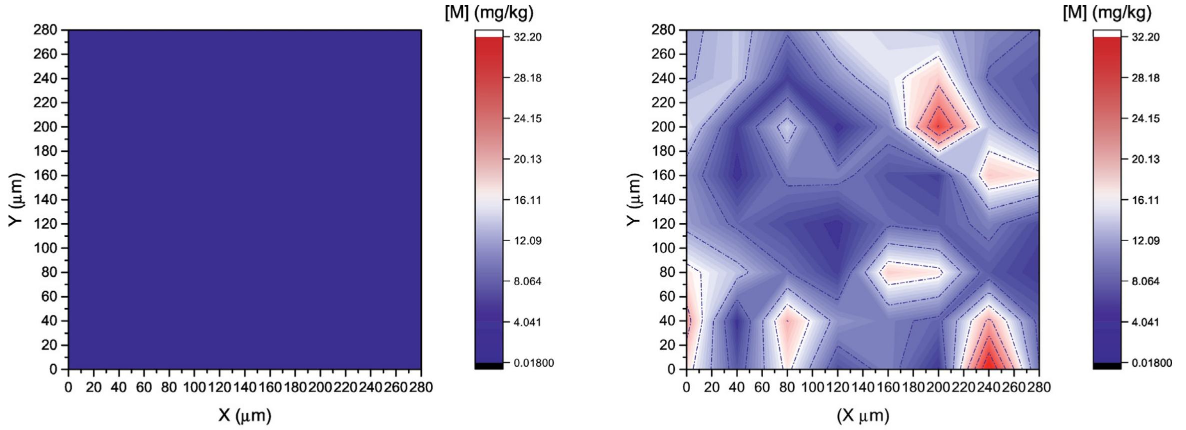
$$q_e = (C_o - C_e)\, V/m \tag{4}$$

V = volume of the metal solution added

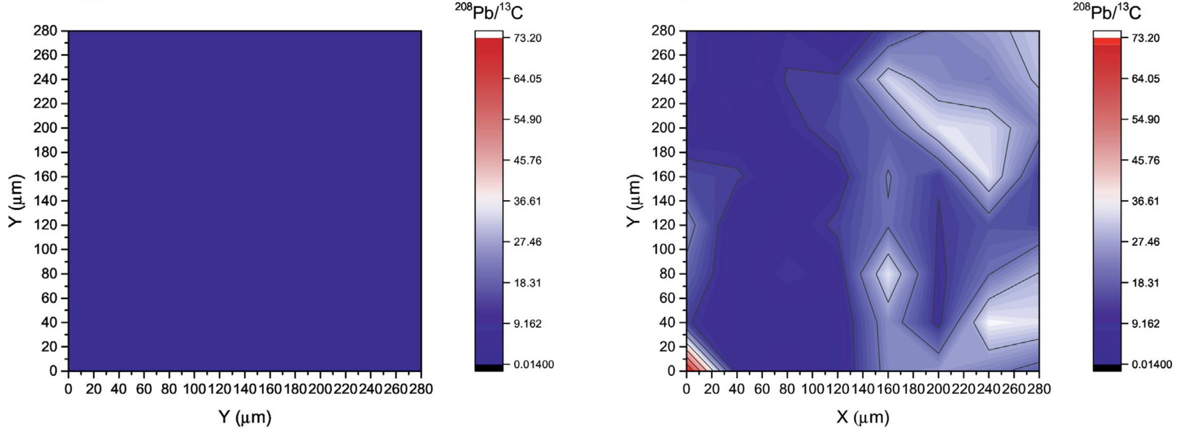
C_o = initial metal ion concentration and C_e = equilibrium metal ion concentration

Table 3
Recovery of Cd, Cu, Fe, Pb and Zn in acid mine water (MSB, Rowe, MA, USA) and contaminated soils (Jingwang, Hunan, China soil water leachate) by pristine rice husk.

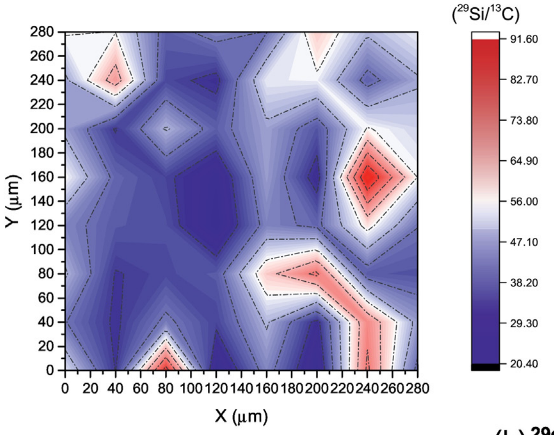
	% recovery by pristine rice husk	
	MSB 5 (pH 6.68); n = 3	Jingwang soil (pH 6.97); n = 3
Element		
Fe	91.6 ± 1.2	97.4 ± 0.2
Zn	90.4 ± 0.8	86.1 ± 4.4
Cu	40.8 ± 4.2	68.5 ± 2.3
Pb	101.2 ± 1.0	91.2 ± 1.8
Cd	100.0 ± 0.0	107.1 ± 0.0



(g) **Zn** (h)



(i) **^{208}Pb/^{13}C** (j)



(k) **^{29}Si/^{13}C**

Fig. 8 (*continued*).

K_L = Langmuir constant

The linearized Langmuir equation is as follows:

$$C_e/q_e = 1/q_{max}\,K_L + C_e/q_m \tag{5}$$

The Langmuir isotherm data regression fits (r^2) are shown in Fig. 4a–d. The resulting Langmuir parameters such as maximum adsorption capacity for solid phase (i.e. PRH), q_m and the energy constant (K_L) were calculated from the intercept and the slope, respectively for the all adsorbate elements are shown in the Table 1a. Cadmium and Zn fits well with the Langmuir model compared to Cu and Pb. The sorption capacity (q_{max}) indicates the maximum monolayer coverage and Pb demonstrated highest q_{max} of 1.995 mg/g while Zn had the lowest maximum sorption capacity of mg/g. This is consistent with the percent recovery (%R) order discussed in the Section 3.2. Langmuir adsorption coefficient (K_L) is lowest for Cu (0.035 L/mg) while highest for Pb (0.325 L/mg). The K_L is generally related to apparent energy of adsorption, thus Pb may be not readily binding to the PRH due to high apparent energy of adsorption while Cu binding is most favorable. This may be likely due to limited access to binding sites with a large ionic radius of Pb^{2+} (119 pm) compared to smaller Cu^{2+} (73 pm) [24]. The competitive adsorption of Cu, Cd, Pb and Zn properties of PRH were further evaluated using Langmuir constant (K_L) and an initial metal ion concertation of 10 mg/L (C_o) to obtain a dimensionless constant referred to as separation factor (S_F) or equilibrium parameter as described by Poots et al. [22].

$$S_F = \frac{1}{1 + K_L C_o} \tag{6}$$

If S_F is $0 < S_F < 1$ the it's a favorable isotherm; $S_F > 1$ (unfavorable isotherm), $S_F = 0$ (irreversible isotherm) and $S_F = 1$ (linear isotherm) [22]. As depicted in the Table 1a, all S_F values are ranged from 0.74 to 0.23 and therefore the sorption of all divalent cations tested in this work are favorable isotherms, and therefore raw rice husks function as an effective biosorbent of these metals.

The same sorption data were used to verify competitive adsorption isotherms of Cu, Cd, Pb, and Zn at pH 6.91 following linearized Freundlich empirical model given below:

$$\ln q_e = 1/n \ \ln C_e + \ \ln K_F \tag{7}$$

A plot of natural logarithm of metal sorption coefficient (q_e) vs. log metal concentrations at the equilibrium (C_{eq}, mg/L) was plotted following Freundlich isotherm equation above [22,23]. The resulting Freundlich isotherm plots for each element (see Fig. 5a–d), their correlation coefficients (r^2), and 1/n and K_F parameters derived from slope and intercept, respectively of those plots are summarized in the Table 1b. By comparing the linearity (r^2 ~ 0.95 or better) of the respective plots in Figs. 4a–d and 5a–d, it appears that Freundlich model obeys well for Cd, Cu, and Pb cations as compared to Langmuir models described earlier while Zn is a better fit with Langmuir model. The highest K_F value was obtained for Pb^{2+} and lowest for Cd^{2+}. The 1/n indicates the intensity of adsorption, and calculated 1/n values for all cations absorbed are below unity (1) demonstrating favorable adsorption on PRH. K_F constant for Pb is the highest (0.48) among the cations examined, and thus pristine rice husks have the greater ability to adsorb Pb than the rest of the cations suite studied.

3.3.2. Thermodynamic properties

The percent recovery of Cd, Cu, Pb, and Zn were investigated at 23 °C, 41.2 °C, and 60 °C temperatures at ~pH 6.9 for 16 h period in temperature controlled water bath (see Figs. 6a-d). The competitive sorption properties of cations with pristine rice husk (PRH) adsorbate varied with the reaction temperature and equilibration reactions. The replicate results (n = 4) shows that Zn had the most significant increase in percent recovery and followed by moderate rise in Cu sorption with slight decrease in percent sorption from 314.2 K to 333 K. This suggests that the adsorption of Zn and Cu by PRH are endothermic processes. On the other hand, percent sorption of Cd decreased and Pb moderately decreased as the temperature increased to 333 K. Thus, Pb and Cd surface adsorption reactions shows exothermicity likely due to the drop in surface chemical activity at elevated temperature [16]. In order to develop insights on physico-chemical properties of competitive adsorption of Cd, Cu, Pb and Zn, thermochemical parameters such as Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) related to adsorption process was calculated and presented in Table 2. Using Gibb's free energy equation ($\Delta G° = \Delta H° - T\Delta S°$), the relationship between the equilibrium constant $K_c(= q_{ad}/q_e)$ of metal adsorption reaction with PRH, and its relationship with the free energy ($\Delta G° = -RT\ln K_c$) the following form of the temperature dependent (T) the Van't Hoff relationship (Eq. (8)) was used to glean on thermochemical parameters, ΔH° and ΔS° (assuming those parameters remain constant during the temperature changes) related to simultaneous adsorption of those elements [16, 21]. The log K_c vs. 1/T (K^{-1}) Van't Hoff plots were linear and correlation coefficients (r^2) values were very close to unity except for copper (Cd: $r^2 = 0.9906$; Cu: $r^2 = 0.\ 7435$; Cd: $r^2 = 1.0000$; Zn: $r^2 = 0.9631$).

$$\log K_c = \Delta S^{\circ}/2.303R - \Delta H^{\circ}/2.303RT \tag{8}$$

Thermochemical parameters determined from Van't Hoff plots for adsorption of Cd, Cu, Pb and Zn by PRH at 296 K are presented in the Table 2. The Cd and Pb sorption reaction by rice husk had negative enthalpies (ΔH°) −7.85 and −6.12 kJ/mol, respectively, and are exothermic. On the other hand, positive enthalpies were observed for Cu (6.38 kJ/mol) and Zn (11.96 kJ/mol) adsorption by pristine rice husk indicates Cu and Zn adsorption reaction processes are endothermic. The entropy change during simultaneous adsorption of tested metals with PRH demonstrates the change in the degree of randomness; it appears that entropy increased during the sorption of Cu, Pb, and Zn while disorder decreased with the sorption of Cd by PRH. Again Pb demonstrates highest equilibrium constant K_c ($= q_{ad}/q_e$) of 48.2 among the cations examined and suggest vary favorable adsorption conditions for lead by PRH. All ΔG° values for metal adsorption reactions with PRH had negative free energy change and varied from −9.54 kJ/mol (Pb) to −1.67 kJ/mol (Zn) confirming these reactions are thermodynamically spontaneously driven and favors metal adsorption by rice husk. Since all ΔG° values for cations tested are below −20 kJ/mol the adsorption mechanism is considered largely as an electrostatic interaction between PRH sorption sites and divalent cations [16,23].

3.4. Spatial distribution of Cd, Cu, Pb, and Zn sorption zones visualized by LA-ICP-MS

The micro-spatial distribution of divalent cation adsorption sites was probed using LA-ICP-MS. The typical surface of pristine rice husk depicting the ablation spot grid and its post ablated area on a rice husk is shown in Fig. 8a and b, respectively. Subsequent Fig. 8c–j show spatial concentration distributions (280 × 280 μm^2 area) of native Cd, Cu, Zn, Pb and Si in a randomly selected rice husk spot against spatial distribution of (280 × 280 μm^2) same elements after equilibration with 10 mg/L Cu, Cd, Pb and Zn solution at pH 6.6–7.0 at RT. All other elemental spatial distribution plots are presented in concentration units (mg/kg) except for Pb and Si (see Fig. 8j–k as presented as $^{208}Pb/^{13}C$ and $^{29}Si/^{13}C$ intensity ratios).

Figures on the left are pristine rice husk with respective native elemental concentrations but scale was adjusted to compare with adsorbed metals on the rice husk on the right. Red zones in all figures indicate zones of elevated metal adsorption sites while blue zones indicate areas of low concentrations of metals adsorbed. Intermediate concentrations are in white. Fig. 8c shows the distribution of native Cd in PRH at low level concentration in blue color while Fig. 8d clearly shows zones (i.e. in red) rich with Cd in particular at the bottom half of the ablated grid area of PRH demonstrating its ability to adsorb cadmium. The comparison of Cu distribution on PRH shows low concentration of native Cu (Fig. 8e) against clearly prominent sorbed zones (in red) of Cu on the right hand side of the ablated rice husk (Fig. 8f). Similarly, from the Zn concentration plots (Fig. 8g vs. h), visibly shows that Zn is adsorbed by tested area of the PRH particularly in the right side of the grid. Fig. 7i shows uniformly distributed native $^{208}Pb/^{13}C$ in the PRH but shows bands of moderately concentrated areas on the right side of the grid (Fig. 8j) as well as a small yet intense spot at the bottom left where $^{208}Pb/^{13}C$ is readily adsorbed by PRH surface after equilibration. Finally, Fig. 7k depicts the Si distribution (as $^{29}Si/^{13}C$ intensity ratio) on the ablated area of pristine rice husk. A closer look at the elevated metal adsorbed zones reveal that some of these sites are anatomically associated with silica rich outcrops of the rice husk tissue [25]. It appears that metals are sequestered on the dome-shaped silica rich (SiO_2) zones on the rice husk structure. To our knowledge, this the first time that the Cu, Cd, Zn and Pb adsorbed sites on the rice husk are visually demonstrated. It is conceivable that these outcrops are rich with silanol (—SiOH) functionalities that facilitate ion exchange reactions with Cu, Cd, Zn and Pb.

3.5. Adsorption of metals from contaminated acid mine water and soils by rice husk

The percent adsorption of metals from acid mine waters (MSB 5, Davis Mine Shaft Brook, Rowe, MA) and contaminated Jingwang soils from XKS mining region in Hunan, China was evaluated using rice husks (PRH). The resulting recoveries Cd, Cu, Fe, Pb and Zn are summarized in the Table 3.

The results of the metal sequestration experiments with the above environmental media demonstrate good ability to adsorb Cu, Cd, Fe, Pb and Zn by PRH. At environmentally relevant pH range of 6.97, rice husk adsorbed Cd, Fe, Pb and Zn in the range of 86–107% from the contaminated Jingwang village, agricultural soil ($n = 3$) from XKS, Hunan, China. Likewise, pH adjusted (from 2.6 ambient pH to 6.68) AMD water from Davis acid mine effluent water ($n = 3$) showed that competitive % adsorption (90.4 ± 0.8–101.2 ± 1.0%) of Cd, Fe, Pb and Zn. However, Cu adsorption by PRH low for both soil (68.5% ± 2.3) and AMD water (40.8% ± 4.2) compared to other elements. Adsorption of metals by PRH were likely via ion-exchange and chelation mechanism with oxygen and nitrogen sites in the lignocellulose husk matrix. It appears that rice husk is a strong contender, among other sustainable remedial approaches to sequester metal contaminants simultaneously under competitive adsorption conditions.

4. Conclusions

Metal adsorption experiments with pristine rice husk indicate significant sorption of Cd, Cu, Pb and Zn under environmentally relevant conditions. The percent adsorption of trace metals in model solutions by PRH in the order of Pb > Cd > Cu > Zn under competitive equilibration conditions. The adsorption of metals is likely facilitated by physisorption followed proton-cation exchange reactions via silanol groups present in the husk surface or ligand binding with oxygen and nitrogen sites. It is also likely ubiquitous siloxane groups (—Si—O—Si—) in silica moieties and oxygen and nitrogen containing functionalities in lignin, cellulose and hemi-cellulose could also be responsible for potential ligand binding for observed adsorption of metals. Surface distribution plots of sorbed metals by PRH determined by LA-ICP-MS shows sorbed metals zones are closely associated with domed shaped silica rich sites on the rice hull surface further supporting the above model. Cadmium, Pb, and Zn adsorption follows slightly better with the Freundlich isotherm than Langmuir isotherm model whereas Cu fits well with Langmuir model. Adsorption of Cd and Pb is exothermic and Cu and Zn is endothermic process. Significant sequestration ability of Cd, Fe, Pb and Zn from contaminated soil (i.e. XKS mine area soils, Hunan, China) extracts by PRH was demonstrated while rice husk also has the ability to adsorbed same elements from acid mine waters (including Fe) efficiently. Our findings with raw rice husk are supported by other metal/metalloid sequestration studies with chemically or physically modified rice husks and other biosorbents [5,7,8,10,11,15,16]. Effective metal sorption ability of untreated unground rice husk indicates potential field applications for remediation of contaminated sites like XKS and acid mine drainage effluents as a low-cost, alternative due to its abundance as an agricultural waste. While many studies have shown improved adsorption capability with modified RH, activated RH, and treated RH [5,8,10,11,15,16], the unique feature of this study was to use pristine or raw rice husk to adsorb metal cations. Thus, the pristine raw husk exhibits strong capabilities of remediation of metal contaminated water and soils.

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