

# Retention Profile of Zn<sup>2+</sup> and Ni<sup>2+</sup> Ions from Wastewater onto Coffee Husk: Kinetics and Thermodynamic Study

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## Abstract

In this work, Coffee husk (CH) was used as a solid phase extractor (SPE) for removal and/or minimization of  $Zn^{2+}$  and  $Ni^{2+}$  ions in aqueous media. XRD, FESEM and FTIR analysis of the SPE were performed for surface morphology and function groups characterisation. Batch mode adsorption studies were performed by varying the operational parameters such as adsorbent dose, solution pH, initial analyte concentration and contact time. The equilibrium data of both analytes was found a better fit with the Langmuir and Freundlich isotherm models. The  $q_m$  of Langmuir for  $Zn^{2+}$  and  $Ni^{2+}$  ions were 12.987 and 11.11 mg/g, respectively. The adsorption capacities of the CH adsorbent towards Zn<sup>2+</sup> and Ni<sup>2+</sup> resulted of 12.53 and 10.33 mg/g, respectively. In addition, the kinetic data of Zn<sup>2+</sup> and Ni<sup>2+</sup> ions uptake revealed that the present system fitted well with pseudo-second-order kinetic model ( $R^2 > 0.99$ ). Thermodynamic studies showed that the retention step was exothermic, and spontaneous in nature. The results indicated that the coffee husk provides an effective and economical approach in highly reducing or almost eradication of both metals Zn<sup>2+</sup> and Ni<sup>2+</sup> from the aqueous solution.

#### **Keywords**

Coffee Husk Adsorbent,  $\mathrm{Zn}^{2+}$  and  $\mathrm{Ni}^{2+}$  Ions, Kinetic and Isotherm Models, Polluted Water

# **1. Introduction**

Pollution of the aquatic environment by heavy metal ions is progressing and becoming a major challenge due to its silent toxicity and pathological impact to human's general health [1]. The main sources of water contamination are when it contains high quantities of Zn and Ni from industrial activities e.g. zinc base casting, electroplating, storage battery industry, and silver refineries have been reported [1] [2]. In drinking water, the permissible level of zinc set by World Health Organization (WHO) does not exceed 0.01 mg/L [2] [3] [4] whereas the maximum allowable level of nickel must be lower than 10  $\mu$ g/L [5]. Exceeding the permissible level of zinc becomes toxic to the human body and may cause nausea, diarrhea, growth deficiency, and lethargy [6] [7]. Nickel concentration in water greater than the legislative standard level set by the US Environmental Protection Agency (USA-EPA) [5] leads to a variety of abnormalities e.g. dermatitis, dizziness, rapid respiration, and headache [8]. Nickel is also known to have carcinogenic characteristics [8] [9].

In aquatic environment, released metal ions accumulate in the living tissues through food chains. Thus, minimization of their concentrations to acceptable tolerable levels into the aquatic environment is of prime importance [10] [11]. Physical, oxidation and/or reduction [10], ion exchange [11], electrochemical treatment, reverse osmosis [12], evaporation, biological methodologies [13] and adsorption [14] [15] have been reported for lessening and/or removal of trace toxic metal ions in water. In recent years, there are more great attention given to the biomaterials (byproducts, the wastes of industrial processes and agricultural waste materials e.g. priceless agricultural waste) [9] [15] [16] [17] [18] [19].

Recently, many articles have studied the utilization of solid waste with two fold approaches: i) reduction of solid waste generation and ii) use as a low cost solid phase extractor (SPE) for removal of phenols, heavy metal ions [19], and other pollutants in industrial wastewater samples and liquids e.g. Calotropis procera [9], grass, leaf, rice husk [17], sugarcane bags, orange peel [20], hazelnut shells [21], cotton seed hulls, waste tea leaves [22], Pb(II) removal by coffee husk [23], grapes stalks [24], sugar beet pulp [25], sunflower stalks [26], and peanut hulls [27].

Based on the International Coffee Organization (ICO), the estimated number of coffee consumed was 151.3 million of 60 kg bags of coffee/year in 2015/2016 [28] [29]. Hence, this article focuses on the: i) characterization and utilization of the coffee husk CH solid waste as an efficient, inexpensive and sustainable SPE, ii) studying the retention characteristics of  $Zn^{2+}$  and  $Ni^{2+}$  from aqueous solution onto the CH, and finally iii) designating the kinetics, isotherm models, and thermodynamic behavior of  $Zn^{2+}$  and  $Ni^{2+}$  uptake by the used SPE.

### 2. Materials and Methodology

#### 2.1. Reagents and Chemicals

 $Zn(CH_3CO_2)_2 \cdot 2H_2O$  and  $Ni(CH_3CO_2)_2$  were purchased from BDH chemicals (Poole, England) and utilized. Stock solutions (1000 mg/L) of  $Zn^{2+}$  and  $Ni^{2+}$  ions were prepared individually in deionized water from their acetate salts. More diluted solutions of  $Zn^{2+}$  and  $Ni^{2+}$  ions were prepared in deionized water.

#### 2.2. Apparatuses

A Perkin Elmer Inductively Coupled Plasma—Optical Emission Spectroscopy (ICP-OES) model 7000 DV was used for analysis of trace metal concentrations. A JEOL-JSM-6380 model Field Emission Scanning Electron Microscopy (FESEM) and Philips PW1398 model X-ray powder diffractometer (XRD,) with a Cu-K radiation source were used for studying the surface morphology and degree of crystallinity of the coffee husk, respectively. Recording the characterization spectra of the SPE was performed by the usage of A Shimadzu FTIR spectrometer (IRAffinity-1, Japan) equipped with ATR-8200H (PIKE Technologies). The samples were grinded with high speed FOSS Cyclone mill (CT 193 Cyclotec<sup>™</sup>). A digital pH meter (Mettler Toledo MP220) and micropipette (Transferpette 0.5 - 5 mL) were used for pH measurements and preparation of more diluted solutions, respectively.

#### 2.3. Preparation of Adsorbent

In the solid phase extractor (SPE) the coffee husk (CH) was washed initially with tap water until the washing solutions were found clear and colourless. The SPE finally washed with distilled water, dried at room temperature for 10 days due to the thickness of the CH, then ground and sieved to obtain a fraction of the particle size (<180  $\mu$ m). The CH dried powder was stored in a plastic bag for it to be used.

#### 2.4. Batch Adsorption Process

Batch mode of separation was critically applied to study the uptake of  $Zn^{2+}$  and  $Ni^{2+}$  from the test aqueous solutions by the proposed CH. The different adsorption parameters were performed at various metal concentrations (50 - 400 mg/L) at a shaking time of 120 min for  $Zn^{2+}$  and  $Ni^{2+}$  at 300 rpm in a 25 mL aqueous solution at pH 6 ± 0.1, and 25 °C ± 0.1 °C. After establishment of the equilibrium, SPE was separated out by filtration through Whatman No. 2 filter paper. Zn and Ni in the aqueous phase was analysed by ICP-OES. Following these procedures, the influence of adsorbent dose (0.3 - 2.0 ± 0.01 g) was also studied. The collected samples were analysed in triplicate (average ± standard deviation 5%) for metal ion concentrations. The adsorbate analyte retained ( $q_e$ ) and the extraction percentage (%E) on the SPE was evaluated as reported [23] [30]. The analytical parameters e.g. pH, shaking time, adsorbent dose, temperature and analyte concentrations were studied following these procedures. Linear isotherm parameters and the kinetic modelling were accomplished using Windows Microsoft Excel 2013.

## 3. Results and Discussion

#### **3.1. Surface Characterization**

SEM micrographs for the unloaded coffee husk and loaded  $Zn^{2+}$ , and  $Ni^{2+}$  ions are presented in Figures 1(a)-(c). It shows the substantial extent of crevasses



Figure 1. SEM images of (a) unloaded (b) Ni<sup>2+</sup>-loaded and (c) Zn<sup>2+</sup>-loaded *CH* adsorbent.

and bumps, due to the heterogeneous, rough, and spiked nature of the CH [6] [29]. The XRD patterns from 20° to 80° ( $2\theta$ /1min/cm) with a step size of 0.05° is shown in **Figure 2**. It presented that the CH is an amorphous phase in nature of cellulosic material [31].

FTIR spectra of coffee husk before and after adsorption of  $Zn^{2+}$  and  $Ni^{2+}$  ions are demonstrated in **Figure 3**. The observed peaks in the range 3526.07 - 3000 cm<sup>-1</sup> suggested the existence of the hydroxyl and amide -NH groups whereas the peaks at 2917.9 and 1720 cm<sup>-1</sup> are assigned to C-H of alkyl and C=O groups, respectively. The peaks at 1639.7, 1233.8, 1023.4 cm<sup>-1</sup> were also attributed to -C=C- of the aromatic ring, peak (C-O), (OH) of the carboxy groups and alcohols



Figure 2. XRD diagram of CH.



4000 3745 3490 3235 2980 2725 2470 2215 1960 1705 1450 1195 940 685 430 Wave number cm<sup>-1</sup>

Figure 3. Spectra of FTIR for unloaded, Zn<sup>2+</sup>-loaded, and Ni<sup>2+</sup>-loaded CH adsorbent.

groups, respectively. On metal uptake by the used sorbent, these peaks began to decay (**Figure 3**) suggesting electrostatic interaction and/or binding between the available active centres on surface adsorbent and the analyte [32] [33] [34] [35].

#### **3.2. Analytical Parameters**

#### 3.2.1. pH and Adsorbent Dose Effect

The influence of extraction media pH on the analyte (400 mg/L) uptake by the coffee husk was performed in a range of pH (2.0 to 9.0  $\pm$  0.10). The adsorption (% removal) achieved maximum at a pH of 7.0 and 6.0 for the Zn<sup>2+</sup> and Ni<sup>2+</sup> ions respectively, while the minimum uptake was achieved at lower pH **Figure 4(a)**. The decrease in % removal at lower pH perhaps due to the fact that the surface



**Figure 4.** Influence of different (a) pH (b) mass dose (c) residence times (d) metal ion concentrations on the adsorption of  $Zn^{2+}$  and  $Ni^{2+}$  at 25°C onto CH.

of the SPE is associated with hydroxonium ions  $(H_3O^+)$  at low pH which hindered the analyte uptake by the adsorbent surfaces [36] [37] [38] [39] [40]. At higher pH, above 6 and 7 the percentage removal decreases because the surface of the SPE became more negatively charged possibly due to the hydroxide ions absorbed on the surface.

The influence of SPE varying dose  $(0.3 - 2.0 \pm 0.05 \text{ g})$  on analyte retention was also investigated at 400 mg/L initial concentrations of Zn<sup>2+</sup> and Ni<sup>2+</sup> with a controlled 90 min shaking time as demonstrated in **Figure 4(b)**. At 2.0 g, the percentage removal reached 93.09% and 90.75% for Zn<sup>2+</sup> and Ni<sup>2+</sup>, respectively. The amount of percentage removal of  $(Zn^{2+}, Ni^{2+})$  and the SPE dose were directly proportion due to the increase of the available active sites of the SPE.

#### 3.2.2. Influence of Residence Time and Analyte Concentration

The residence time has an impact on analyte uptake by the SPE. The data are demonstrated in **Figure 4(c)**. The metal removal rate was rapid in the initial stage, the uptake was fast, and a slight increase was noticed on increasing time. Within 30 min the equilibrium time achieved maximum capacity of 9.18 mg/g and 12.13 mg/g for  $Zn^{2+}$  and  $Ni^{2+}$ , respectively. Nickel(II) is d<sup>8</sup> while Zinc(II) is d<sup>10</sup>, thus ability of nickel to form complexes with the available active sites is high compared to zinc and account for the observed trend of data. The increased uptake was attributed to the active binding sites on the surface of the SPE. The slow metal removal in the later stage was likely due to the saturation

of the active sites [41].

The influence of metal ions concentration on the removal efficiency is illustrated in **Figure 4(d)**.  $Zn^{2+}$  and Ni<sup>2+</sup> adsorbed by CH increased from 1.96 mg/g to 12.44 mg/g and from 2.55 mg/g to 10.83 mg/g with increasing the concentration from 50 mg/L to 400 mg/L, respectively. The adsorption increase as initial metal ions concentration increases eventually until on further change. The increase in the analytes concentration leads to increasing the equilibrium capacity of the adsorption because of the decrease obstruction to mass transfer between aqueous and solid phase [6] [42].

## 3.3. Kinetic Characteristics

Zn<sup>2+</sup> and Ni<sup>2+</sup> ions uptake from the aqueous solution onto the CH were subjected to kinetic models to understand the dynamic of the retention process. The pseudo-first-order and pseudo-second-order kinetic models were applied in this study. The linearized form of pseudo-first-order model is expressed by the following equation [43]:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{1}$$

The values of  $q_e$  and  $q_t$  represent the analyte (mg/g) adsorbed capacity at equilibrium and at time t (min), respectively.  $k_1$  is the overall rate constant (1/min) of pseudo-first-order. The plot of  $\log(q_e - q_t)$  vs. (t) shown in **Figure 5(a)** was used for determining the values of  $k_1$  and  $q_e$  as reported in literature [44] [45] [46]. The results were also studied by pseudo-second-order kinetic model [47]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(2)

where  $k_2$  represents the rate constant (g/mg min) of pseudo-second-order rate model [48]. A plot of  $(t/q_t)$  vs. t gave a straight-line **Figure 5(b)** with an intercept of  $1/k_2q_e^2$  and slope of  $1/q_e$ . **Table 1** shows the values of the adsorption for both kinetic processes of Zn<sup>2+</sup> and Ni<sup>2+</sup>. The pseudo-first-order model did not provide a good fit, according to the results the correlation coefficient ( $R^2 \le 0.8$ ) and  $(q_{e,cal})$  values were below expectations. The pseudo-second-order data



**Figure 5.** Kinetic adsorption parameters of the (a) Pseudo-first-order model and (b) Pseudo-second-order model of  $Zn^{2+}$  and  $Ni^{2+}$  (400 ppm) onto CH (0.5 g) at 25°C.

Pseudo first order				Pseudo second order			
Metal ions	$q_{e,exp}\mathrm{mg/g}$	$q_{e,cal}\mathrm{mg/g}$	$k_1$ 1/min	$R^2$	$q_{e,cal}\mathrm{mg/g}$	k₂ g/mg·min	$R^2$
Ni(II)	12.13	2.254	0.036	0.813	12.53	0.056	0.999
Zn(II)	9.18	4.305	0.080	0.743	10.33	0.023	0.999

Table 1. The parameters of kinetic models for  $Ni^{2+}$  and  $Zn^{2+}$  adsorption onto the used biomass.

agreement for ( $R^2 > 0.99$ ) and the theoretical ( $q_{e,cal}$ ) values agreed with the actual ( $q_{e,exp}$ ) values for both Zn<sup>2+</sup> (9.18 mg/g, 10.33 mg/g) and Ni<sup>2+</sup> (12.13 mg/g, 12.53 mg/g). This indicated that the sorption of Zn<sup>2+</sup> and Ni<sup>2+</sup> fitted well by pseudo-second-order kinetic model. In the previous study the same indication was found using coffee husk as effective SPE for eliminating Pb (II) in water purification [23]. Moreover, the rate limiting stage of the adsorption involved valence forces through electrostatic attraction between analyte with the solid phase extractor.

#### 3.4. Adsorption Isotherm

The equilibrium adsorption isotherm is fundamental in describing the retention of a substance from the aqueous media to a solid phase. Describing the regression correlation coefficient variations ( $R^2$ ) of Ni<sup>2+</sup> and Zn<sup>2+</sup> adsorbed onto the CH by using the Langmuir and Freundlich isotherm models [49] [50] [51] [52]. The Langmuir model expresses that the uptake of metal ions is monolayer sorption on a homogenous surface [53]. Moreover, Freundlich model presumed a multilayer sorption on a heterogeneous surface on the SPE active sites with different energy [54]. The Langmuir isotherm and its linearized forms are expressed in Equations ((3)-(4)) [51]:

$$q_e = \frac{\left(q_m k_L C_e\right)}{1 + k_L C_e} \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \left(\frac{1}{q_m}\right) C_e \tag{4}$$

where  $K_L$  = Langmuir equilibrium constant (L/mg) related to the free energy of analyte uptake,  $q_m$  = Langmuir maximum adsorption capacities (mg/g), and  $C_e$  is the instantaneous concentration (mg/L) [49]. The Freundlich isotherm model and its linearized forms are presented in Equations ((5)-(6)) [55]:

$$q_e = k_F C \mathrm{e}^{1/n} \tag{5}$$

$$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log K_F \tag{6}$$

The  $K_F$  ((mg/g(L/mg))<sup>1/n</sup> and 1/n are related to the adsorption constant capacity, and the heterogeneity factor related to the intensity of the adsorption, respectively [27]. The range of 1/n is between 0 and 1 which means the adsorption favorable at the studied conditions, but if 1/n value is above one that indicates cooperative adsorption [48].

Langmuir and Freundlich isotherm parameters were determined from the plots of  $C_e/q_e$  vs.  $C_e$  and  $\log q_e$  vs.  $\log C_e$  Figure 6(a) & Figure 6(b), respectively. The calculated data of Langmuir and Freundlich isotherm model were summarized in Table 2. The Langmuir maximum adsorption capacities  $(q_m)$  for  $Zn^{2+}$ and Ni<sup>2+</sup> ions were 12.987 mg/g and 11.11 mg/g, respectively, which is close to the experimental values. Furthermore, the determination of correlation coefficients ( $R^2 > 0.99$ ) for both isotherm models was fitted well with the experimental data [52]. In the presented study the 1/n value for Ni<sup>2+</sup> and Zn<sup>2+</sup> is near to zero that indicated the surface of the SPE was more heterogonous. Based on these data and the available functional groups (C=O, OH groups) on the surface of CH as indicated from the IR data and SEM, it can be concluded that, a dual mode of separation involving "surface adsorption" and an added component for absorption of analyte is most likely proceeded. These indicated that, the sorbent occurred as homogeneous monolayer and heterogeneous multilayer coverage, therefore the nature adsorption process is favorable of Ni<sup>2+</sup> and Zn<sup>2+</sup> ions on CH [27].

#### 3.5. Thermodynamic Characteristics

To calculate the essential energy involved during analyte uptake and the nature of the adsorption the thermodynamic parameters were applied.

The *activation energy* ( $E_a$ , J/mol), the Arrhenius equation for analyte uptake can be expressed as follow [27]:



**Figure 6.** (a) Langmuir and (b) Freundlich sorption isotherms linear regression analysis of  $Zn^{2+}$  and  $Ni^{2+}$  adsorption onto CH.

Table 2. Langmuir and	Freundlich ac	lsorption isot	herm mod	lels for	the adso	orption	of Ni <sup>2+</sup>
	and Zn <sup>2+</sup>	ions onto the	biosrpent	t.			

Isotherm	Ni <sup>2+</sup>			Zn <sup>2+</sup>			
Langmuir	$q_m  \mathrm{mg/g}$	K <sub>L</sub> l/mg	$R^2$	$q_m  \mathrm{mg/g}$	$K_L l/mg$	$R^2$	
	12.936	0.113	0.998	11.111	0.101	0.997	
Freundlih	1/ <i>n</i>	$K_F((\mathrm{mg/g}(\mathrm{L/mg}))^{1/n}$	$R^2$	1/ <i>n</i>	$K_F((\mathrm{mg/g(L/mg)})^{1/n}$	$R^2$	
	0.234	1.611	0.987	0.204	1.230	0.993	

$$\ln K_2 = \ln A - \frac{E_a}{RT} \tag{7}$$

where  $k_2$  = the rate constant of pseudo-second-order model for adsorption (g/mg·min), A = the temperature-independent Arrhenius factor (g/mg·min), T = the solution temperature (K), and R = the gas constant (8.314 J/mol·K). The plot of  $\ln k_2$  vs. 1/*T* is shown in **Figure 7**. The calculated values of Ea for Ni<sup>2+</sup> (0.693 kJ/mol) and Zn<sup>2+</sup> (3.158 kJ/mol) were lower than 8 kJ/mol. This finding showed the adsorption of Ni<sup>2+</sup> and Zn<sup>2+</sup> were physisorption processes [55].

Vant Hoff equation [56] was used to calculate the thermodynamic enthalpy  $(\Delta H^0)$  and entropy  $(\Delta S^0)$  as follows:

$$\ln K_D = \left(\frac{\Delta S^0}{R}\right) - \left(\frac{\Delta H^0}{RT}\right) \tag{8}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \tag{9}$$

where  $K_D$  is the Langmuir equilibrium constant of the adsorption. The plots of  $\ln K_D$  vs. 1/*T* were linear (Figure 8) with good correlation coefficients ( $R^2$ ). The



Figure 7. Activation energy for the adsorption of Zn<sup>2+</sup> and Ni<sup>2+</sup> onto *CH*.





positive value of  $\Delta S^0$  was 53.457 J/mol K for Zn<sup>2+</sup> and 53.189 J/mol K for Ni<sup>2+</sup>, indicating increase of the randomness at the solid/solution interface [27]. The negative values of  $\Delta H^0$  for Zn<sup>2+</sup> (-5.468 kJ/mol) and Ni<sup>2+</sup> (-0.669 kJ/mol) signified that the adsorption was exothermic in nature and it was physisorption due to the low  $\Delta H^0$  value between (1 - 93 kJ/mol).  $\Delta G^0$  values confirmed that the adsorption steps were spontaneous in nature at 298, 318, 328 K due to the negative values (-23.735, -17.079, -17.612 kJ/mol) for Zn<sup>2+</sup> and (-15.924, -16.987, -17.519 kJ/mol) for Ni<sup>2+</sup> [48].

The experimental data revealed that adsorption process for  $Zn^{2+}$  and  $Ni^{2+}$  adsorbates onto CH SPE was found to be a predominantly electrostatic interaction between the SPE and adsorbate. Moreover, thermodynamic studies exposed that the retention step is also random, exothermic, physisorption and spontaneous in nature [47] [61]. The adsorption capacity of CH in this study was compared with those found in previous studies using different biosorbents, as shown in **Table 3**. Thus, coffee husk has moderately higher adsorption capacity for  $Zn^{2+}$  and  $Ni^{2+}$  in aqueous solution; therefore, it is preferable and more attractive than other biosorbents. The regeneration of the SPE with recovery of the metal ion using selective eluting agent, is economically inefficient as it is costly [19].

### 4. Conclusion

Coffee husk has great potentials in being used as an efficient, cost-effective, and green SPE for  $Zn^{2+}$  and  $Ni^{2+}$  removal from environmental water samples. An excellent adsorption capacity of  $Zn^{2+}$  (12.13 mg/g) and  $Ni^{2+}$  (9.18 mg/g) was achieved at 0.5 g mass dose, 30 min time, 25 °C temperature, and pH 7. Analyte uptake is satisfactorily described by pseudo-second-order kinetic model. As a

Table 3. Maximum adsorption capacities of  $Zn^{2+}$  and  $Ni^{2+}$  by the used biomass and other biosorbents.

Metal ion	Biosorption	$q_{ m max}$ (mg/g)	References
Ni <sup>2+</sup>	Coffee husk	12.98	This study
	Dicerocaryum eriocarpum	0.125	[57]
	Coconut dregs residue	5.86	[58]
	<i>Moringa</i> pods	6.0753	[47]
	Pigeon peas hulls	23.63	[59]
	Citrus limetta peels	27.78	[60]
	Sophora japonica	30.30	[61]
$Zn^{2+}$	Coffee husk	11.11	This study
	Dicerocaryum eriocarpum	0.01	[57]
	Cassava	5.965	[62]
	cabbage	8.970	[63]
	Jatropha curcas L.	14.852	[64]
	Sophora japonica	25.71	[60]

result, the Langmuir and Freundlich adsorption isotherms ( $R^2 > 0.99$ ) fitted well for analytes uptake. The sorbent process was exothermic and spontaneous in nature depending on the value of  $\Delta H^0$  and  $\Delta G^0$ . Therefore, CH SPE offers an optimal green alternative approach for the removal of Zn<sup>2+</sup> and Ni<sup>2+</sup> ions from environmental effluents before their discharge into the environment. The significant results suggest a rationale techno-economic sense for an organization to a prudent environmental management program to assess the environmental impacts of global coffee industries are of great importance.

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