

## Adsorption of Heavy Metals by Chopped Human Hair: An Equilibrium and Kinetic Study

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In this work, heavy metal adsorption by hair particles as adsorbents was studied and analyzed. The kinetic and isothermal studies were performed by optimizing the initial concentration and the pH. The adsorption isotherms of the majority of the metals are more suited to either the Langmuir or Freundlich models. The uptake capacity of hair material to absorb metals was found to be in the order of  $Pb^{2+} > Cu^{2+} > Zn^{2+}$ . According to the adsorption data, metal ions adhere to hair particles as confirmed through a pseudo-second-order process. The kinetic study demonstrated that metal adsorption on hair particles involves both intraparticle diffusion and surface adsorption. According to the column studies, hair particles are more effective adsorbent for removing the heavy metals from aqueous solutions.

**Keywords:** Heavy metals, Adsorbents, Hair, Langmuir model, Freundlich model.

### INTRODUCTION

In particular, the excessive release of heavy metals and pesticides from a wide variety of effluents has become one of the most pressing ecological challenges currently [1,2]. It is believed that heavy metals, a group of persistent harmful substances, are the root of cancer. Due to their excessive release into water sources, these metals have a seriously detrimental impact on living organisms, environmental receptors and human health [3]. Heavy metals can have negative impacts on the environment and later on living systems due to their non-degradable nature once they are secreted into the atmosphere by the action of bacteria [4].

There has been a surge in recent research towards the safe and affordable technologies for removing heavy metals from contaminated streams. Many workers have investigated low-cost agricultural waste byproducts such sugarcane bagasse [5,6], rice husk [7-9], sawdust [10,11], coconut husk [12], oil palm shell [13], neem bark [14], etc. Comparing sorbent materials requires taking cost into account, individual sorbent costs vary depending on the degree of processing required and local availability, although pricing data is rarely provided. If an adsorbent needs little processing, is abundant in nature or a byproduct or waste products from another process, it is often regarded as a affordable option.

When a person has a haircut, there is typically a significant amount of waste that needs to be thrown away afterward. Tan *et al.* [15] reported that human hairs as an efficient adsorbent for heavy metals removal from water. Human hair has also been reported for its potential to effectively remove oil from wastewater [16]. Keratin, a fibrous protein, makes up the majority of hair, along with low contents of lipids and water. Keratin is composed of 18 amino acids and the mostly contains sulfur containing amino acids. Thus, the presence of carboxyl, amido, and disulfide groups in human hair suggests that human hair could be an effective biosorbent of a number of pollutants, including heavy metals, despite the fact that it has not extensively been studied for this application.

### EXPERIMENTAL

**Adsorbent:** Only gents hair was employed as an adsorbent in this investigation and obtained from the local saloon. The hair samples were first cleaned with a non-polar detergent before submerged for 20 min in the deionized water. After being submerged and mixed in acetone to remove external contamination, the hair samples were then washed again with deionized water. The hair samples were cut into little pieces after being air dried and finally stored in airtight containers. For use in adsorption analysis, the dry sample material was then sieved

with a #30 mesh (0.6 mm). NaOH and 0.1 N HNO<sub>3</sub> solutions were used to change the pH of the sample [17].

By applying the NH<sub>4</sub>OAc exchange method, the cation exchange capacity (CEC) of the hair sample was found to be 72.1-1.12 meq/100 g [18]. The analytical-grade salt solutions for Pb(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were procured from Sigma-Aldrich, USA. The metal solutions were prepared in 1000 mg/L batches. For additional dilutions in the adsorption tests, the stock solutions were retained.

**Adsorption studies:** Various solutions of different metal ion concentrations (*i.e.* ranging from 2 to 20 mg/L) were prepared from the stock solution (2.0 g). The HCl/NaOH was used to alter the pH of the metal ion solution to the desired level (pH 3.0, 4.5 or 7.0). As blank, the solution without the adsorbent was also prepared. At 211 °C, the reaction mixture was allowed to react in a shaker bath for 15-20 min. At the necessary time intervals, 5 mm of sample solution was collected and filtered using a 0.45 μm syringe filter. With the help of a coupled plasma atomic emission spectroscopy analyzer, the metal ions in the filtrates were identified.

In the adsorption isotherm studies, hair samples were exposed to solutions with varying metal ion concentrations between 10 and 500 mg/L. Once equilibrium had been reached, samples were collected, filtered and then subjected to analysis. The mass balance relationship was used to determine the quantity of heavy metal adsorbed on the hair samples. The experimental tests were carried out three times and the mean value was calculated. The effects of various cations on adsorption have also been studied experimentally under real experimental conditions.

According to the procedure described earlier [19], humic acid purification was used to extract the dissolved organic matter (DOM). The amount of DOM employed in the study was 0, 10, 50 or 100 mg/L in relation to the amount of total organic carbon.

The column studies were conducted using a glass column with a comparable plunger, which consist of 0.15 m long and 0.025 m in diameter and procured from Ace Glass, Inc. The bed's length was set at 0.05 m and 5.0 g of hair as adsorbent were used to fill the column. After column packing, helium gas was utilized to release any trapped air in the sorbent pores. To keep the column operating optimally, more than 100 mL of deionized water were used. Deionized water was used to regulate the temperature and pressure of the column throughout more than a hundred pore volumes. By using a gravimetric analysis, the porosity and bulk density were found to be 515 g/L and 0.70, respectively.

Ion chromatography was used to determine the concentration after the HPLC pump and column were connected by a three-way valve that was kept in line to connect the flow of solutions with and without heavy metals. With a flow rate of 30.0 mL/min, the heavy metal solution consisting of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> was pumped through the column at a concentration of 10 mg/L. The ICP-AES was used to determine the metal concentration in the samples that were collected for analysis at the column end at various time intervals. After finishing the adsorption test, the column was washed with 0.1 M CaCl<sub>2</sub> solution and the samples were then collected and analyzed.

## RESULTS AND DISCUSSION

**Adsorption isotherms:** The heavy metal adsorption on the basis of equilibrium concentration  $q_e$  (mg/g), could be compared with equilibrium concentration,  $C_e$  (mg/L), like in a form of linearized form of the Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{K_L S_m} + \frac{C_e}{S_m} \quad (1)$$

Or the Freundlich isotherm model:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

where  $K_f$  is the Freundlich constant of adsorption capacity,  $1/n$  represents adsorption intensity and  $S_m$  and  $K_L$  are Langmuir constants that show maximal adsorption and energy constant of heat adsorption. The values of  $S_m$  and  $K_L$  from the Langmuir equation were calculated by applying the least linear square approach (1). Similar to this, the intercept in the (linear) plot of  $\log q_e$  versus  $\log C_e$  relates to  $1/n$  and  $\log K_f$ , respectively (Fig. 1). Table-1 displays the equilibrium adsorption of the metal ions (Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>) according to Langmuir/Freundlich adsorption and R<sup>2</sup> values. Although the formation of two types of bilayers on the hair adsorbent surface is indicated by the formation of both isotherms showing the equilibrium concentration of heavy metals [20], the adsorption pattern follows the order Cu<sup>2+</sup> > Pb<sup>2+</sup> > Zn<sup>2+</sup>, which could be explained by the different electronegativity of the observed metals. More electronegative atoms get more adsorbed followed by less electronegative, as can be seen in the cases of the metals of reference Pb<sup>2+</sup> (2.33), Cu<sup>2+</sup> (1.9) and Zn<sup>2+</sup> (1.65), respectively, as it can be mentioned that the adsorption of metals on the hair surfaces can be attributed on the basis of ion-exchange. The ionic radius is a factor that affects the adsorption of metals in addition to electronegativity. When compared to ionic atoms with lesser radii, the metal with a greater ionic radius is more readily absorbed [21]. The same pattern was observed for the reference metals Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>, which have ionic radii of 1.33, 0.87 and 0.88, respectively. However, in addition to electronegativity and ionic radii, many other parameters, including the physical and chemical properties of the metals and the adsorbent, can also affect the metal adsorption on the surface of the adsorbent.

**Contact time effect:** Adsorption of Pb<sup>2+</sup> ions decreases with increasing initial concentration and then remains constant once equilibrium has been reached (Fig. 2). The time required to reach equilibrium ranged between 30 min and 360 min, whereas the time required to equilibrate was found to be concentration independent. It was found that at the initial stage adsorption rate was rapid, with an approximate 90% equilibrium being reached in 25 min. The results demonstrated that Pb<sup>2+</sup> adsorption predominantly takes place at the surface of the hair sample, after which it slows down due to the metal diffusion into the hair. Similar findings were also found for Cu<sup>2+</sup> and Zn<sup>2+</sup>.

**Effect of pH:** The results (Table-2) demonstrated that Pb<sup>2+</sup> adsorption on hair samples is affected by pH. The results show that similar to the adsorption of heavy metals on different biosorbents, Pb<sup>2+</sup> adsorption on hair samples is pH-dependent

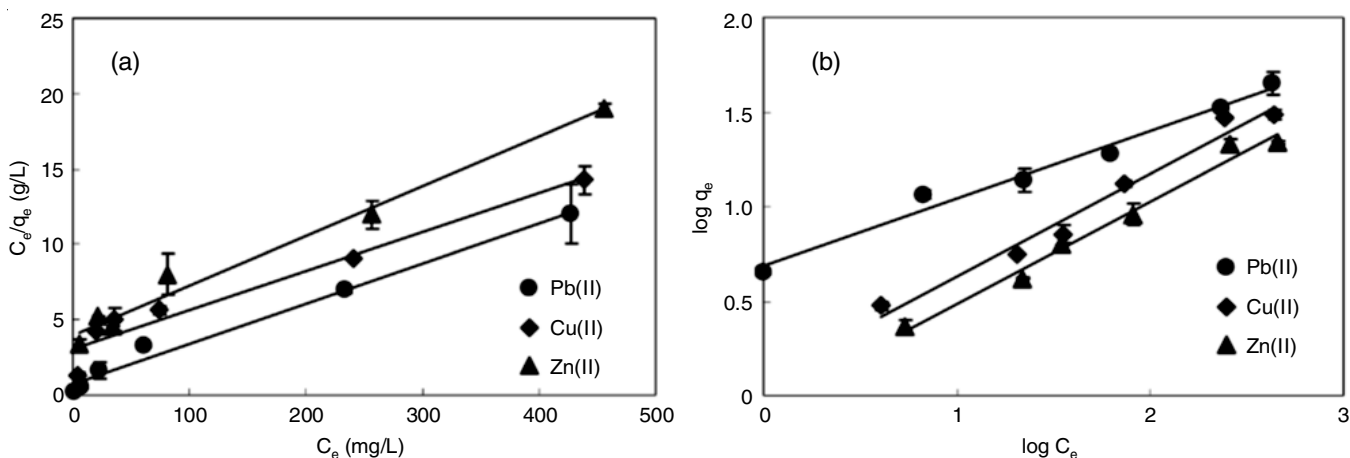


Fig. 1. The plot of Langmuir (a) and Freundlich (b) adsorption isotherm of heavy metals on hair

System	Metal type	q <sub>e,exp</sub>	Langmuir constant			Freundlich constant		
			S <sub>m</sub> (L/mg)	K <sub>L</sub> (mg/g)	R <sub>L</sub> <sup>2</sup>	K <sub>f</sub> (mg <sup>1-n</sup> ·L <sup>n</sup> /g)	1/n	R <sub>F</sub> <sup>2</sup>
Metal ion in single	Pb(II)	25.00	29.37	0.0136	0.997	2.65	0.379	0.979
	Cu(II)	21.40	29.80	0.0072	0.985	1.17	0.489	0.971
	Zn(II)	18.74	25.60	0.0069	0.998	1.10	0.510	0.989
Metal ion in mixture	Pb(II)	23.4	34.10	0.0051	0.983	0.94	0.523	0.987
	Cu(II)	19.00	27.20	0.0058	0.997	0.79	0.523	0.987
	Zn(II)	17.00	27.10	0.0041	0.989	0.40	0.612	0.974

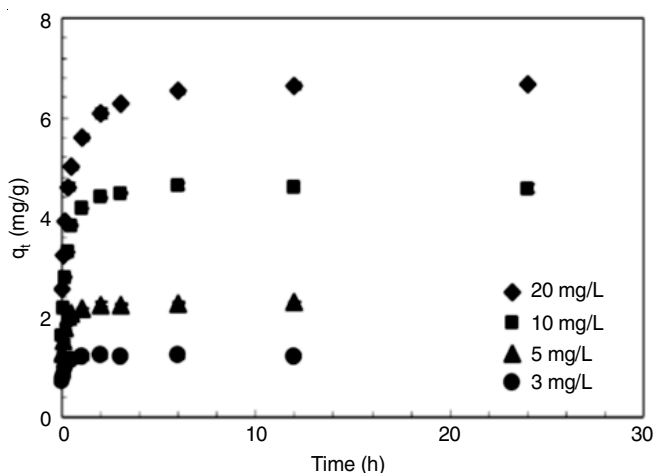


Fig. 2. Pb(II) adsorption rate on hair sample

due to ion exchange reactions with hydrogen ions. Additionally, a significant quantity of anionic ligands in the form of COO- or -OH may cause the metal ions on the surface of hair particles to complex. Complex formation between the metal ions and the donating groups on the adsorbent occurs at lower pH levels.

**Kinetic studies:** The kinetic studies, which are related about the adsorption rate process provides an important knowledge for process design. The kinetic studies of adsorption data are produced with the help of many kinetic studies, viz. pseudo-first-order and pseudo-second-order models [22]. The expression for first-order kinetic is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

where at time t (min) and equilibrium time, q<sub>t</sub> and q<sub>e</sub> adsorbate quantities. Table-2 displays the results of calculating the value of k<sub>1</sub> at different adsorbate concentrations and pH values. A pseudo-second-order model [23] for the kinetics of adsorption is expressed as:

Parameters		First-order kinetics			Pseudo-Second-order kinetic				Intraparticle diffusion parameter
Conc. (mg/L)	pH	q <sub>e,exp</sub> (mg/g)	K <sub>1</sub> (1/h)	R <sup>2</sup>	q <sub>e,cal</sub> (g/mg·hr)	k <sub>2</sub> (mg/g·h)	h (mg/g·h)	R <sup>2</sup>	k <sub>id</sub> (mg/g·h <sup>1/2</sup> )
3	4.5	1.214	5.37	0.973	1.22	3.310	4.926	0.999	0.0217
	5	2.307	0.58	0.767	2.31	0.752	4.013	0.999	0.0434
10	3.0	1.636	0.46	0.765	1.65	0.137	0.373	0.999	0.0991
	4.5	4.679	1.08	0.899	4.68	0.150	3.285	0.999	0.0302
20	7.0	4.942	1.96	0.950	4.95	0.399	9.776	1.000	0.0596
	4.5	7.756	0.05	0.692	7.61	0.015	0.869	0.997	0.1913

[21]. With a decrease in pH, the adsorption of Pb<sup>2+</sup> removal reduces. Heavy metals are believed to adsorb on the hair samples

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where  $k_2$  (g/mg h) gives second-order rate constant, as determined by plotting  $t/q_t$  vs.  $t$ . The rate constant (second order) is used for the calculation of initial adsorption rate by an equation as:

$$h = k_2 q_e^2 \quad (5)$$

Table-2 listed the calculated primary adsorption rates as well as the rate constants for second-order reactions. It is clear that the pseudo-second order reaction rate constant ( $k_2$ ), decreases as the initial concentration increases and the initial adsorption rate ( $h$ ), which is a function of initial concentration, decreases even more as initial concentrations of  $Pb^{2+}$  and other metal ions increase as shown in Fig. 3. The estimated  $q_e$  value and the measured experimental values agree and from the  $R_2$  values, the pseudo-second order reaction can be confirmed over the entire adsorption process.

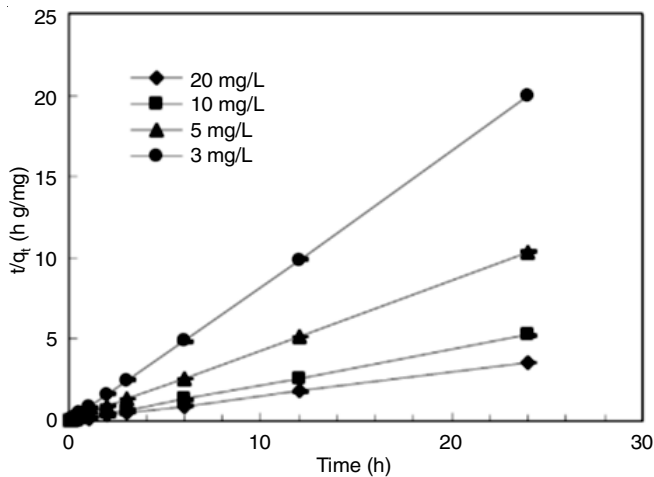


Fig. 3. The plots for Pb(II) adsorption on different adsorbate concentrations following second-order rate constant

The transfer of solute is primarily characterized in the process of solid-liquid adsorption by exterior mass transfer (boundary layer diffusion) and by intraparticle diffusion [24]. The following equation provides the identification of the adsorption mechanism for the rate constant of intraparticle diffusion.

$$q_t = k_{id} t^{0.5} \quad (6)$$

Fig. 4 shows the relationship between  $q_t$  and  $t_{0.5}$  at various adsorption phases. Boundary layer diffusion shows intraparticle type diffusion in both its initially curved portion and subsequent linear segment. After looking at the plot, one area shows surface adsorption and the other region demonstrates the intraparticle diffusion on the hair particles. The slope of the second-linear portion of the plot ( $k_{id}$ ) indicates the intraparticle diffusion coefficient and the average coefficient values are shown in Table-2. However, the intercept shown on the plot indicates the influence of the boundary layer and the larger intercept indicates a greater contribution from surface adsorption. The findings also demonstrate a considerable tendency for surface adsorption at higher starting concentrations.

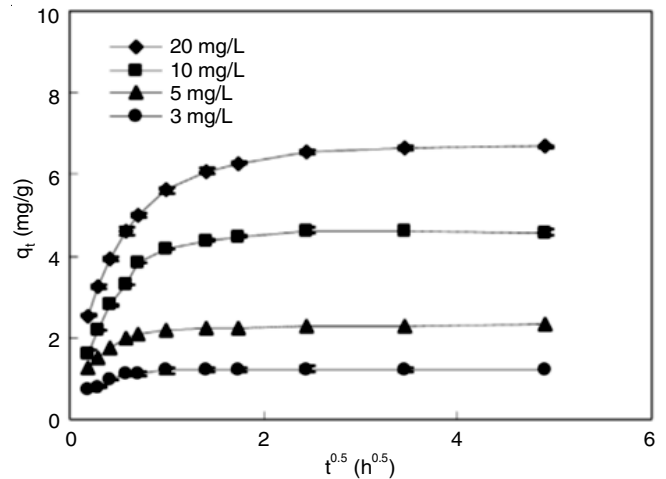


Fig. 4. The plots for Pb(II) adsorption on sawdust at different adsorbate concentrations following intraparticle diffusion

**Column studies:** By plotting the concentration ratio ( $C_i/C_o$ ) versus pore volumes, breakthrough curves (BTCs) were used to analyze the metal adsorption results on a hair sample as an adsorbent (time). The observed BTC of a conservative (Br-) tracer is shown in Fig. 5. The hair samples were found to be usually homogeneous and the BTCs of metals showed substantial extent of retardation, as indicated by the concentration ratio  $C_i/C_o$  equal to 0.5 obtained at a pore volume of 1.0. (Fig. 6).  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  break through volumes have been observed at roughly 800, 500 and 150 pores, respectively.

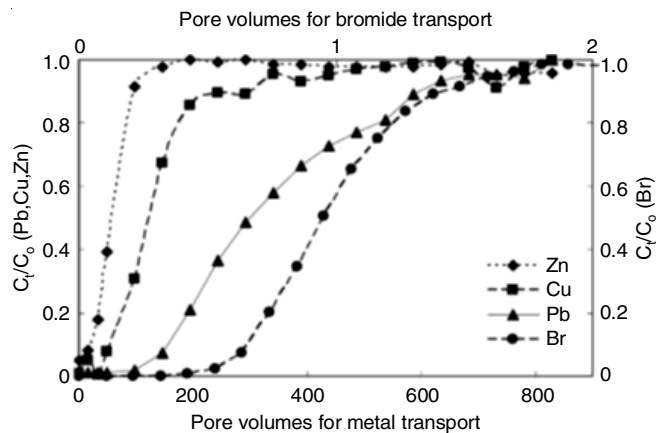


Fig. 5. Heavy metals from hair packed column (metal concentration of feed solution = 10 mg/L) showing breakthrough curves

Lead(II) ions was found to be the most sorbed metal, according to the findings of the batch studies, followed by the less sorbed metals like  $Cu^{2+}$  and  $Zn^{2+}$  ions and the slopes of  $Zn^{2+}$  and  $Cu^{2+}$  curves are less steep than  $Pb^{2+}$ . The region above the BTC curve is numerically integrated to determine the amount of  $Pb^{2+}$  that has been absorbed in the column. The determined values for the sorbent mass's ( $q_e$ ) adsorption capacity were 1.35 for  $Zn^{2+}$ , 7.73 for  $Pb^{2+}$  and 3.26 mg/g for  $Cu^{2+}$ , respectively. These values are lower than those from batch equilibrium experiments. These variations may be brought on by the diffusion's limited adsorption rate [25]. The three elution curves of the concerned heavy metals are shown in Fig. 6 for the elution of

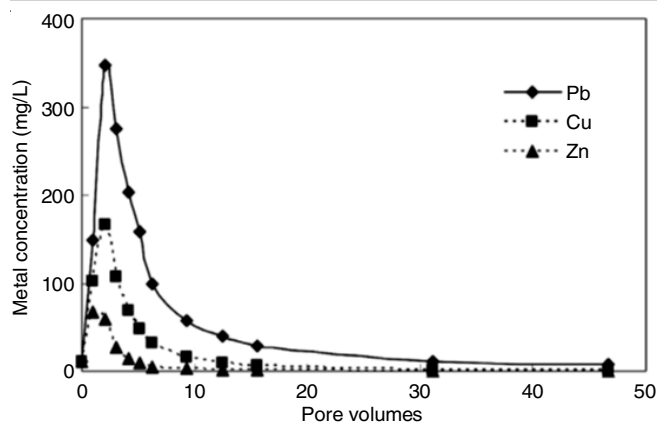


Fig. 6. Heavy metals from a hair-packed column flushed with 0.1 M CaCl<sub>2</sub> solution showing breakthrough curves

heavy metals adsorbed inside the column using 0.1 M CaCl<sub>2</sub> solution. The elution curves initially climb before progressively falling. In the adsorption process, heavy metals are eluted in the following order: Pb<sup>2+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup>. Using an elution curve, the metals eluted were estimated to be 10.6, 37.8 and 6.8 mg for Cu<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup>, respectively.

### Conclusion

In particular for lead, zinc and copper, chopped human hair samples have been found to be highly beneficial as adsorbents due to their greater and more efficient heavy metal sorption. The concentration of adsorbate and the pH have been found directly proportional to the adsorption tendency. At equilibrium conditions, the heavy metal adsorption on the hair samples reasonably complies with the Langmuir and Freundlich models. As the successful adsorption of divalent ions (Pb<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) on the adsorbent materials has shown, the adsorption ability of metals varies from the metal system to metal system. The Pb<sup>2+</sup> elimination was also high at first but slowed down toward the end of the process. The kinetics of the adsorption process in this investigation are consistent with a pseudo-second-order model. The results of the column experiment show an increased metal adsorption onto hair particles because of their high adsorption capacity. Workers found that hair particles could effectively absorb heavy metal solutions without adversely affecting the surrounding ecosystem.

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### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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