

Adsorption removal of cadmium and copper from aqueous solution by areca—A food waste

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Abstract

Areca waste (AW) has been investigated as metal biosorbent for cadmium and copper from aqueous solution for its availability as food waste and also for its cellulosic matrix rich of potential metal binding active sites. The effect of various parameters on adsorption process such as contact time, solution pH, amount of AW and initial concentration of metal ions was studied at room temperature to optimize the conditions for maximum adsorption. Maximum metal sorption was found to occur at pH 5.6. Adsorption process revealed that the initial uptake was rapid and equilibrium was established about in 1 h for cadmium and copper. The equilibrium sorption data for single metal systems at pH 5.6 were described by the Langmuir, Freundlich and D–R isotherm models. The adsorption isotherm studies clearly indicated that the adsorptive behaviour of metal ions on AW not only the Langmuir assumptions but also the Freundlich and the D–R assumptions. The highest value of Langmuir maximum uptake, (*b*), was found for cadmium (1.12 mg/g) and copper (2.84 mg/g). Similar Freundlich empirical constants, *K*, were obtained for cadmium (1.086) and copper (1.119). Ion-exchange and surface adsorption might be involved in the adsorption process of cadmium and copper. Desorption studies revealed that cadmium and copper can be easily removed from AW by altering the pH values of the solution using HNO₃, indicating that AW are a promising adsorbent for wastewater treatment.

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1. Introduction

The removal of toxic metals from wastewater is a matter of great interest in the field of water pollution, which is a serious cause of water degradation. Numerous metals such as chromium, mercury, lead, copper, cadmium, manganese, etc. are known to be significantly toxic.

These facts have motivated many physicochemical methods for heavy metal removal from aqueous solution, including adsorption, chemical precipitation, solvent extraction, reverse osmosis, ion-exchange, chemical oxidation and reduction, filtration and electrochemical treatment. Among the various water-treatment techniques described, adsorption is generally preferred for the removal of heavy metal ions due to its high

efficiency, easy handling, availability of different adsorbents and cost effectiveness. Recently, there is growing interest in using low cost, non-conventional alternative materials which used to be considered as waste [1–16]. Most cases have also confirmed that the use of large quantities of such kind of wastes for the treatment of polluted water is an attractive and promising option with a double benefit for the environment.

Areca nut is known since the pre-Christian era and is still very popular chewing nut in different area of the world. In China, areca is mainly produced in the provinces Hainan, Fujian, Yunnan, Guangxi, Taiwan, etc. They can live outside in southern Florida and other subtropical and tropical regions. Areca catechu produces the well-known betel nut of commerce, which is in great demand in eastern countries for chewing. The AW was collected after chewing the betel nut.

In this research, a new kind biosorbent AW, which is considered as a kind of food waste has been investigated as metal biosorbent for cadmium and copper from aqueous solution. The

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objective of this study is to investigate the adsorption capacity of AW and its characteristics for the removal of cadmium and copper.

2. Materials and methods

2.1. Sample pre-treatment

AW was prepared as follows: AW was collected and washed three times with deionized water (each time 200 mL for 60 min) and then immersed in 0.2 M NaOH aqueous solution for a period of 12 h. Thereafter, it was washed three times with deionized water (each time 200 mL for 60 min) to remove color and excess of NaOH. It was then immersed in 0.2 M H₂SO₄ for a period of 12 h to remove traces of alkalinity and other impurities. The acid treated AW was thoroughly washed with deionized water (each time 200 mL for 60 min) to remove sulphuric acid and other coloring materials till the wash water was colorless. After this, the treated AW adsorbent was dried at 378 K for 10 h and then allowed to cool in the desiccator for use as an adsorbent.

2.2. Characterization

The properties of the prepared AW as characterized by the standard methods are given in Table 1.

2.3. Apparatus and instrumentation

- A PerkinElmer 700 atomic absorption spectrophotometer (AAS, School of Natural Resources) was used to analyze dissolved Cd and Cu. A calibration curve was established. Standard aqueous solutions of cadmium and copper were prepared to read the residual concentrations of metals.
- pH were determined according to a Multiline 330i pHmeter which was standardized using buffer solutions of different pH values (4.01, 7.00, 10.00).
- The suspensions in all studies were filtered through 0.45- μ m Nucleopore polycarbonate membrane filters. All experimental treatments in this study were prepared in triplicate and were conducted in acid-washed (2% HNO₃) polycarbonate labware.

Table 1
Characteristics of AW

Characteristics	Values
Color	Light brown
Ash (%)	10–12
BET surface area (m ² /g)	80
Porosity (%)	30
Mineral ^a	Present
Alkaloids ^a	Present
Phenolic functional group ^a	Present
Carboxylic functional group	Present
Fiber ^a	Present

^a Derived from [17].

2.4. Adsorbate solution

Synthetic stock solution of heavy metals was prepared by dissolution of cadmium nitrate and cupric nitrate in deionized water. All chemicals used were of AR grade, and water for all solutions preparation had been treated by purification system beforehand. The stock solution was further diluted with deionized water to desired concentration for obtaining the test solutions.

2.5. Batch adsorption experiment

Batch experiments were carried out at room temperature (293 \pm 2 K) in beakers by agitating a different mass of areca waste (0.200, 0.400, 0.600, 0.800, 1.000 and 1.200 g), with 100 mL of metal solution at 200 rpm until equilibrium reached.

To evaluate the effect of time and the heavy metal initial concentrations, we first prepared various solutions with initial Cd²⁺ and Cu²⁺ concentrations ranging from 4 to 12 mg/L (4 mg/L interval, 100 mL), and then added 1.000 g AW to each solution. These samples were then mounted on a shaker and shaken continuously for 120 min at room temperature. At predetermined time intervals, samples were collected utilizing a 0.45- μ m Nucleopore polycarbonate membrane filters.

When the initial pH of metal solutions was adjusted to the desired value using 0.1 M NaOH and 0.1 M HNO₃ and then 1.000 g AW was added to each solution. No efforts were made to maintain the solution pH while metal ions were being sorbed. Measurement of pH at the beginning and at the end of process was performed. The reaction time was kept at a room temperature and at a constant agitation rate of 200 rpm on a shaker for 120 min.

After agitation, the solid was removed by filtration through a 0.45- μ m Nucleopore polycarbonate membrane filter. The final metal concentration in the filtrates as well as in the initial solution was determined by AAS. The sorbed metal concentrations were obtained from the difference initial and final metal concentrations in solution.

The % heavy metal removal was calculated using the following equation:

$$\% \text{ metal ion removal} = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial concentration of test solution (mg/L) and C_e is the final equilibrium concentration of test solution (mg/L).

The cadmium and copper adsorption capacities of the AW were calculated in the following equation:

$$q = \frac{(C_0 - C)V}{m} \quad (2)$$

where q , adsorption capacity per unit mass of AW (mg/g); C_0 , initial concentration of metal ions in the aqueous solution (mg/L); C , equilibrium concentration of metal ions aqueous solution (mg/L); m , mass of AW (g); V , volume of sample (L).

Each experiment was carried out in triplicate and the average results are presented in this study.

2.6. Desorption experiments

In order to investigate the desorption capacity of Cd^{2+} and Cu^{2+} from AW. 0.2 g the exhausted AW in 2.4 was dried at 60°C and dispersed into 100 mL deionized water. The pH values of the solution were adjusted, from 1.5 to 5.5 using HNO_3 solution. After the solutions reach equilibrium, the Cd^{2+} and Cu^{2+} concentrations were measured and the desorption results were then obtained.

2.7. Adsorption isotherms

2.7.1. Langmuir isotherm

Langmuir's isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The Langmuir treatment is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface, which is represented as follows:

$$q_e = \frac{abC_e}{1 + bC_e} \quad (\text{non-linear form}) \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{ab} \frac{1}{C_e} + \frac{1}{b} \quad (\text{linear form}) \quad (4)$$

where q_e , the amount of metal per unit of AW at equilibrium (mg/g); a , a constant related to the affinity of the binding sites (L/mg); b , the maximum amount of metal ion per unit of AW (mg/g); C_e , the residual metal concentration in solution at equilibrium (mg/L).

2.7.2. Freundlich isotherm

The Freundlich equation has been widely used for isothermal adsorption. This is a special case for heterogeneous surface energies in which the energy term, a , in the Langmuir equation varies as a function of surface coverage, q_e , strictly due to variations in heat of adsorption. The Freundlich isotherm is represented by Eqs. (5) and (6).

$$q_e = KC_e^{1/n} \quad (\text{non-linear form}) \quad (5)$$

$$\lg q_e = \lg K + \frac{1}{n} \lg C_e \quad (\text{linear form}) \quad (6)$$

where q_e , the amount of adsorbed per unit weight (mg/g); K , Freundlich constants related to adsorption capacity; C_e , the equilibrium concentration (mg/L); n , Freundlich constants related to adsorption intensity.

2.7.3. Dubinin–Radushkevich (D–R) isotherm

Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. D–R isotherm is commonly used to describe the sorption isotherms of single solute systems. The D–R isotherm, apart from being analogue of Langmuir isotherm, is more general than Langmuir isotherm as it rejects the homogeneous surface or constant

adsorption potential [18]. The D–R isotherm is expressed as

$$\ln q_e = \ln V'_m - K'\varepsilon^2 \quad (7)$$

where q_e , the heavy metal amount (mg/g) that is removed per unit AW; V'_m , D–R adsorption capacity (mg/g); K' , constant related with adsorption energy ($\text{mol}^2 \text{kJ}^2$); ε , the Polanyi potential. According to Eq. (7), the Polanyi potential (ε) can be given as

$$\varepsilon = RT' \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

where R is the gas constant ($\text{kJ K}^{-1} \text{mol}^{-1}$) and T' is the temperature (K).

3. Results and discussion

3.1. Effect of time and initial concentration of metal ions

The effect of time and initial concentration of metal ions on the percentage removal by AW is shown in Fig. 1. It can be seen from the figure that the percentage removal decreases with the increase in initial heavy metal concentration not only cadmium but copper. The removal of Cd^{2+} and Cu^{2+} increases with time and attains saturation in about 60–120 min. Basically, the removal of sorbate is rapid but it gradually decreases with time until it reaches equilibrium. The plots represent the percentage removal of cadmium and copper versus the contact time for the initial metal concentrations. The plots reveal that maximum percent metal removal was attained after about 1 h of agitating time. The rate of percent removal becomes almost insignificant due to a quick exhaustion of the adsorption sites. The rate of percent metal removal is higher in the beginning due to a larger surface area of the AW being available for the adsorption of the metals. After the adsorbed material forms a 1 molecule (actually ion) thick layer, the capacity of the adsorbent gets exhausted and then the uptake rate is controlled by the rate at which the sorbate is transported from the exterior to the interior sites of the adsorbent particles. For subsequent experiment, the contact time was thus maintained for 120 min to ensure that equilibrium could be achieved.

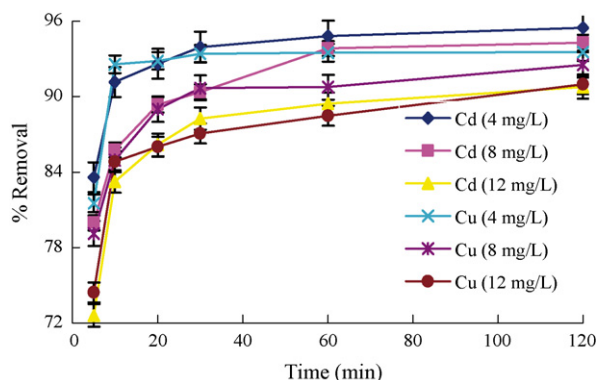


Fig. 1. Effect of the initial concentration on removal of cadmium and copper (amount of AW = 10).

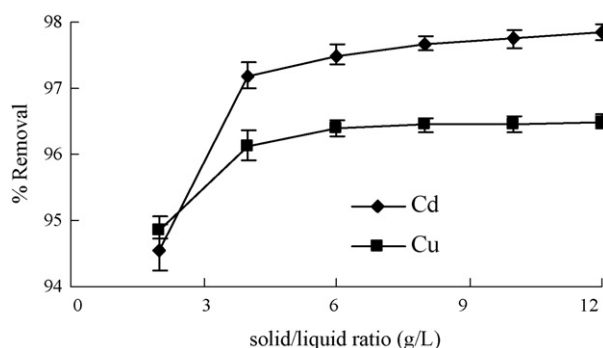


Fig. 2. Effect of amount of AW (pH 5.6, agitation time is 120 min, metal concentration 8 mg/L).

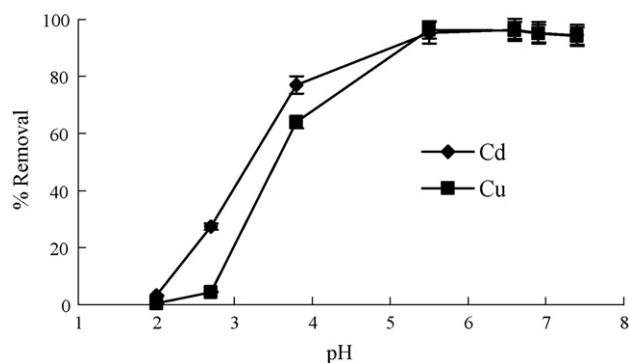


Fig. 3. The effect of pH on metal removal through AW adsorption (amount of AW = 10 g/L, agitation time is 120 min, metal concentration 8 mg/L).

3.2. Effect of amount of AW

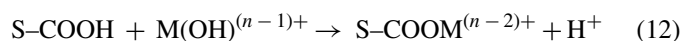
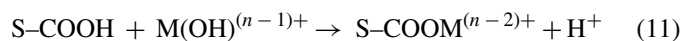
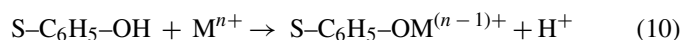
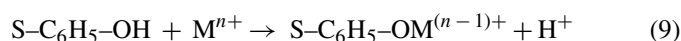
To study the effect of amount of AW on the retention of cadmium and copper, six different values were taken by varying the amount of AW while keeping the volume of the metal solution constant (100 mL) as shown in Fig. 2. It can be observed that the amount of metal ions removed increased with the solid/liquid ratio increasing firstly, due to more active sites or bigger surface area [19–21]. Then a little increase was observed when the solid/liquid ratio reached 8 g/L. This possibly caused by the saturation of the active sites. So the determination of the weight of adsorbent is important when employing AW for cadmium and copper removal. For all subsequent experiments 10 g/L AW was used for adsorption of metal ions.

3.3. Effect of pH

pH is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions [22–25]. Fig. 3 shows the effect of pH on heavy metals removal efficiency.

These studies were conducted at a constant initial concentration of 8 mg/L, adsorbent dose 1 g/100 mL solution and agitation period of 120 min for all heavy metal ions at varying the pH on AW. As can be seen from Fig. 3, metal removal increases with increasing solution pH. In pH < 2.7, there is a little adsorption. The percent adsorption increases in the pH range of 2–5.6, showing the maximum adsorption at pH 5.6, then the percent adsorption decreases in pH range of 5.6–7.4. The greatest increase in the rate of adsorption of metal ions on AW was observed for pH changes from 2 to 3.8 for Cd²⁺ and Cu²⁺. The maximum removal of Cd²⁺ and Cu²⁺ at pH 6.6 was found to be nearly 96.3 and 96.14%, respectively.

Decrease in removal of metal ions at lower pH is apparently due to the higher concentration of H⁺ ions present in the reaction mixture, which compete with the metal ions for the adsorption sites of AW. Decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes. The possible sites on AW for specific adsorption includes H⁺ ions in –C₆H₅–OH and –COOH functional groups in which H⁺ ions can be exchanged for cations in solution. These interactions can be presented as follows:



where S denotes the modified surface.

However, the sites responsible for the adsorption process are not exclusively due to the –C₆H₅–OH and –COOH functional groups. Other sites on the AW can also contribute to the adsorption process. In acidic condition, the electromeric effect of the amide group in AW leads to surface protonation and possesses not positive charge on the surface. These H⁺ ions from the surface are also exchanged with positively charged sorbate species with subsequent coordination of a metal ion.

3.4. Adsorption isotherms studies

A plot of 1/q_e versus 1/C_e gives a straight line of slope 1/ab and intercept 1/b shown in Fig. 4. The sorption data were analyzed according to the linear form of the equation. Results are shown in Table 2. The equilibrium adsorption of cadmium and copper on AW was found to follow the Langmuir model. The experimental data were well correlated (R²_{Cd} = 0.9805; R²_{Cu} = 0.9999) to the Langmuir equation. The adsorption of cadmium and copper could be described by Eqs.

Table 2
Langmuir, Freundlich and D–R isotherm parameters

Metals	Langmuir isotherm constants			Freundlich isotherm constants			D–R isotherm constants		
	a	b	R ²	K	1/n	R ²	K'	V' _m	R ²
Cd ²⁺	3.73	1.12	0.9805	1.086	0.589	0.9929	0.0334	0.978	0.9332
Cu ²⁺	0.59	2.84	0.9999	1.119	0.879	0.9800	0.0632	1.108	0.9671

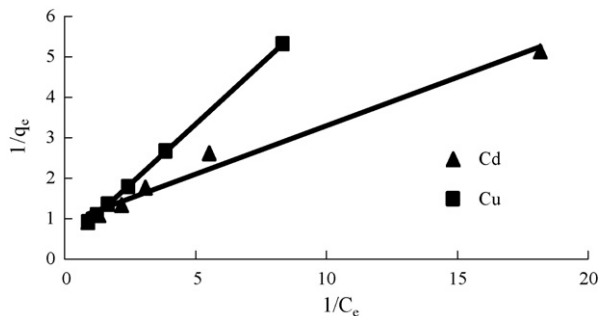


Fig. 4. Langmuir isotherm for the adsorption of cadmium and copper on AW.

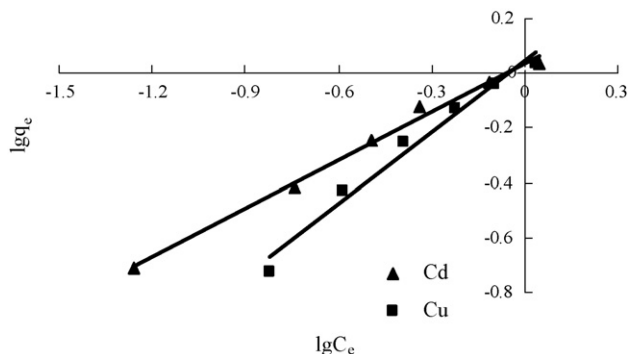


Fig. 5. Freundlich isotherm for the adsorption of cadmium and copper on AW.

(13) and (14), respectively.

$$q_e = \frac{1.118C_e}{0.2681 + C_e} \tag{13}$$

$$q_e = \frac{2.837C_e}{1.6916 + C_e} \tag{14}$$

The linear plot of $\lg q_e$ versus $\lg C_e$ shows that the adsorption also obeys Freundlich isotherm (Fig. 5). The constants K and n are presented in Table 2. The parameter K is related to the distribution coefficient, and consequently to the degree of Cd or Cu affinity and mobility to the AW. Cu has a higher AW affinity than Cd ($K_{Cu} > K_{Cd}$).

A plot of $\ln q_e$ against ε^2 is given in Fig. 6. As it is seen in Fig. 6, the D–R plot yields a straight line. In the D–R isotherm, adsorption capacities (V'_m), adsorption energy constants (K') are

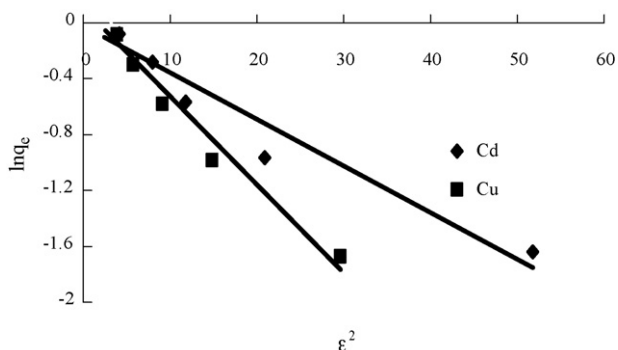


Fig. 6. D–R isotherm for the adsorption of cadmium and copper on AW.

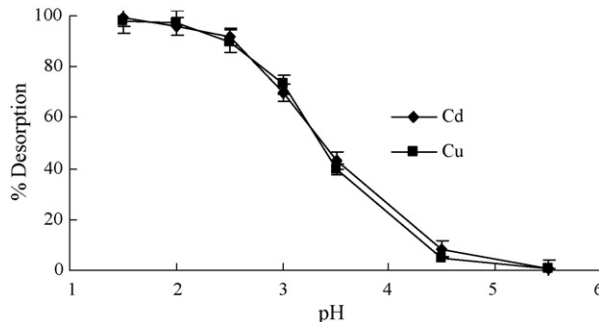


Fig. 7. Desorption of Cd^{2+} and Cu^{2+} from AW by adjusting the pH values of the solution using HNO_3 solution.

calculated for cadmium and copper removal. All of the isotherm model parameters for the adsorption of cadmium and copper are provided in Table 2. As seen from Table 2 in Langmuir isotherm calculated adsorption capacities for cadmium and copper are 1.12 and 2.84 mg/g, respectively. In Freundlich isotherm adsorption intensities are found to be 1.698 and 1.138 for cadmium and copper metals.

3.5. Desorption experiments

A desorption study is also important because it is useful in the recycling of the adsorbent and recovery of heavy metals. Fig. 7 shows the Cd^{2+} and Cu^{2+} desorption curves with regard to various solutions of pH values. It is apparent that the Cd^{2+} and Cu^{2+} desorption percentage increases when the pH value of the solution is reduced using HNO_3 . The desorption percentage of cadmium and copper are almost zero at pH 5.5, increasing gradually and eventually reaches almost 100% at pH 1.5. The results show that the cadmium and copper adsorbed by AW can easily be desorbed, thus the AW can be employed repeatedly in heavy metal adsorption.

4. Summary and conclusions

- Aw showed 97.75% and 96.46% adsorptive removal of Cd^{2+} and Cu^{2+} , respectively under optimized conditions of dosage 1 g/100 mL for aqueous solutions containing 8 mg/L metal ions in 120 min.
- pH has been found to be a most effective variable, controlling the adsorption of metal ions on AW surface. Cd^{2+} and Cu^{2+} can be easily desorbed from AW by adjusting the solution pH values, thus AW exhibits promising application potentials as an adsorbent in wastewater treatment.
- The empirical values are evaluated according to the Langmuir, Freundlich and D–R isotherms that are generally used to describe the adsorption processes. It is stated that all of isotherm models fit very well.
- Cd^{2+} and Cu^{2+} can be easily desorbed from AW by adjusting the solution pH values, thus AW exhibits promising application potentials as an adsorbent in wastewater treatment.
- From the results obtained, other mechanism, i.e. surface adsorption in addition to ion-exchange might be involved in the case of the sorption of the cadmium and copper ions

while ion-exchange is the most important mechanism for cadmium and copper.

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