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Activated carbon produced from pigeon peas hulls waste as a low-cost agro-waste adsorbent for Cu(II) and Cd(II) removal

D.K. Venkata Ramana, Kim Min*

Department of Safety Engineering, Dongguk University, 123 Dongdae-ro, Gyeongju 780 714, Gyeongbuk, Republic of Korea, Tel. +82 54 770 2253; Fax: +82 54 770 2280; emails: dkvramana76@gmail.com (D.K. Venkata Ramana), kimmin@dongguk.ac.kr (K. Min)

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ABSTRACT

Pigeon peas hulls (PPH) as an agro-waste by-product and activated carbon produced from PPH (APPH) were used as effective and efficient adsorbents for the removal of Cu(II) and Cd(II) from aqueous solutions. The adsorbents were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, X-ray diffraction and Brunauer, Emmett and Teller surface area measurements. The influence of various parameters, such as the effect of pH, adsorbent dose, contact time, initial metal ion concentration, and temperature, were evaluated. The experiments showed that the removal of metal ions followed a pseudo-second-order kinetic model and equilibrium adsorption studies confirmed that the Langmuir model provided a better-fit, and showed that APPH has greater potential than PPH. The thermodynamic properties, i.e. (ΔG°), (ΔH°), and (ΔS°), showed that the adsorption of Cu(II) and Cd(II) onto PPH and APPH was endothermic, spontaneous, and feasible over the temperature range, 293–313 K.

Keywords: Pigeon peas hulls; Activated carbon; Adsorption; Kinetics; Isotherms

1. Introduction

Heavy metals are a cause of severe environmental- and health-related problems because of their persistency and propensity for bioaccumulation in numerous components of the ecosystem [1]. The major toxic metal ions Ni, As, Pb, V, Cd, Hg and trace metal ions Cu, Co, Fe, Cr, Se, Zn, etc are hazardous to humans and other forms of life. The toxic effects of copper and cadmium have been well documented [2,3]. The permissible concentrations of Cu and Cd in drinking water have been set to 0.05 and 0.01 mg L^{-1} in India, 1.0 and 0.01 mg L^{-1} in the USA, 3.0 and 0.005 mg L^{-1} in the UK, and 1.0 and 0.005 mg L^{-1} in Canada, respectively [4]. Copper has adverse effects on plants, and the exposure of plants to excess Cu generates oxidative stress and reactive oxygen species (ROS), which can cause disturbances in the metabolic pathways and damage to macromolecules. Human exposure to Cu levels above 1.3 mg L^{-1} for short periods of time leads to stomach and intestinal problems, and longer contact leads to kidney and liver damage [5,6]. Cadmium is a non-essential, non-beneficial, and highly toxic element to plants and animals [7]. Cd has outstanding importance among toxic heavy metals because of its mobility in the plant–soil system. Through this path, Cd can enter the nutrition chain and accumulate in

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*Corresponding author.

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the human body, particularly in the kidneys, leading to dysfunction of the kidney [8].

In view of their toxicity and to meet regulatory safe discharge standards, considerable focus and attention have been placed upon the removal of toxic heavy metals from water/waste streams. A variety of physical, chemical, and biological technologies are currently used for the removal of heavy metals from wastewater and aqueous solutions. Conventional methods for the removal of metal ions have been suggested, such as filtration, ion exchange, chemical precipitation, membrane technologies, electrochemical treatment, adsorption on activated carbon, and evaporation [9]. Adsorption is a promising alternative among the above-mentioned techniques because of its high efficiency and low-cost, wide adaptability, and selectivity in removing different types of heavy metals and stable performance in purifying wastewater with low metal concentrations [10]. On the other hand, adsorption on activated carbon (AC) has been studied intensively and it is one of the most widely used and versatile techniques [11]. Solid waste generated as agricultural by-products have been estimated to exceed by 320,000,000,000 kg annually, creating significant disposal problems [12].

Every year, an estimated 11.2 billion metric tons of solid waste are collected worldwide; the global waste market from collection to recycling is estimated to be US$410 billion a year [13]. According to the EPA estimate, Americans create approximately 251 million tons (228 million metric tons) of garbage per year, and recycle and compost over 85 million tons of this material, which is equivalent to 34.1% of recycling rate [14]. On the other hand, the Ministry of Urban Development, in its manual on solid waste management (year 2000), estimated a waste generation of 1,000,000 MT [15].

Currently, the urban areas of Asia produce approximately 760,000 tons of municipal solid waste (MSW) per day, or approximately 2.7 million m^3/d. In 2025, this figure is expected to increase to 1.8 million tons of waste per day, or 5.2 million m^3/d. These estimates are conservative; the real values are probably more than double this amount. Urban areas of Asia now spend approximately US$25 billion on solid waste management per year, and this figure is expected to increase in about US$47 billion in 2025 [16]. This bulk biomass has potential use as a cheap heavy metal remediation material. Accordingly, the use of agricultural waste as a adsorbent may be important in the next few years because they symbolize an unused resource with serious disposal problems, and saves disposal costs while alleviating potential environmental problems. Several studies have examined the preparation and application of effective adsorbents from waste biomaterials for the removal of various toxic heavy metal pollutants from aqueous solutions, such as pigeon peas hulls [17], activated carbon [18], grape stalk waste [19], dried plants [20], maple leaves [21], peanut shell [22], and sunflower hulls [23]. Agricultural by-products are high volume, low value, and underutilized lignocellulosic biomaterials that contain high levels of cellulose, hemicelluloses, and lignin [10]. Being rich in cellulosic and lignin materials, agricultural by-products have a strong tendency to attract and remove heavy metal ions from aqueous solutions. The components of agricultural by-products containing hydroxyl, carbonyl, carboxylic, and ether functional groups bind heavy metals by donating an electron pair and form complexes or exchange hydrogen ions for heavy metal ions in solution [24].

Pigeon pea hulls (*Cajanus cajan*), a member of the legume family, is an agricultural and industrial waste product that is distributed mainly in semiarid and subtropical areas of the world [17]. Pigeon pea products possess antioxidant, anti-inflammatory, and protein kinase inhibitory activities [25]. The distribution of nutrients in the seed coat of pigeon pea is as follows: crude protein—5.6%, ether extractives—0.3%, crude fiber—3.19%, ash—3.5%, and carbohydrate—58.7% [26]. The World demand for virgin-activated carbon is forecast to expand by 9% per annum through 2014 to 1.7 million metric tons [27].

Being a waste product, insoluble in water, chemically stable, high mechanical strength, and high local availability at almost no cost, the use of PPH and its derivatives as adsorbents might also solve their disposal problem. Present study examined and compared the sorption ability of Cu(II) and Cd(II) by two different adsorbents derived from pigeon peas hulls waste. Studies relating to pH, adsorbent dose, contact time, kinetics, isotherms, and thermodynamics on Cu(II) and Cd(II) adsorption were carried out to optimize the adsorbents, and finally desorption tests were conducted.

2. Methods

2.1. Reagents and instruments

Analytical reagent grade $Cu(NO_3)_2$ and $Cd(NO_3)_2$ $4H_2O$ (St. Louis, MO, USA) were used to prepare Cu(II) and Cd(II) stock solutions of 1,000 mg L^{-1}. ACS reagent grade HCl, NaOH, and buffer solutions were used to adjust the pH of the solution. DI water obtained from a Milli-Q system (Millipore) was used, and working standards were prepared by the appropriate dilution of the standards. The Thermo

Scientific Orion Star A111 pH meter was used for the pH measurements. Fourier transform infrared (FT-IR, Thermo-Nicolet FT-IR, Nicolet IR-200, USA) spectroscopy was used to analyze the organic functional groups of the adsorbents. Field-emission scanning electron microscopy (FESEM, LEO SUPRA 55, Carl Zeiss, Oberkochen, Germany; Genesis 2000, EDAX, Mahwah, NJ, USA) and transmission electron microscopy (TEM, JEM 200CX, JEOL, Tokyo, Japan) were performed to examine the morphology of the samples. The structural properties were investigated by X-ray diffraction (XRD; M18XHF-SRA, Mac Science, Yokohama, Japan). The Brunauer, Emmett and, Teller (BET) surface area and pore volume of APPH was estimated by Barret–Joyner–Halenda (BJH) analysis. Inductively coupled plasma (ICP-7510, Shimadzu, Kyoto, Japan) spectroscopy was used to determine the metal ion concentrations.

2.2. Preparation of activated PPH

As a continuation of previous work [17], and to compare the adsorption capacity, activated carbon was prepared from PPH waste. The PPH were soaked with a base and mixed with two parts of concentrated sulfuric acid, stirred with a glass rod to form a homogenous mixture. The mixture swelled quickly in a couple of minutes with the evolution of gas. A few minutes later (8–10 min), a dark colored and capacious substance was formed. The substance was left overnight in a hot air oven until dry. To obtain activated PPH, the dry mass obtained was placed in a quartz tube over which N_2 was flowed at a flow rate of 60 ml min^{-1}. The sample was moved to the center of a furnace with a reduced N_2 flow rate of 30 ml min^{-1}, heated to 625 K at 10 K min^{-1} and held at that temperature for 3 h. This product was cooled to room temperature, washed with diluted H_2SO_4 and then with double distilled water until it was free of sulfate ions, and dried at room temperature. The product obtained is called APPH, it was stored in stoppered bottles for further use.

2.3. Batch experimental program

Batch experiments were conducted to examine the effects of the significant parameters, such as pH, sorbent mass, and contact time, on the adsorptive removal of Cu(II) and Cd(II). For each experimental run, 50 ml of a metal ion solution of a known concentration, pH and a known mass of adsorbent were taken into a 100 ml stoppered conical flask. The mixture was agitated in a temperature-controlled shaker water bath (HB-205SW, Han Baek Scientific Company, Bucheon, Korea) at a constant rate of 180 rpm to reach equilibrium. The samples were withdrawn at the appropriate time intervals. After equilibrium, the solutions were filtered and the metal ion concentrations were determined. Blank solutions of Cu(II) and Cd(II) ions (without the adsorbent) were treated similarly, and the concentrations were recorded.

The amount of metal ion sorbed onto the adsorbents, Q_e, was calculated using the following equation:

$$Q_e = \frac{v}{m}(C_0 - C_e) \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of Cu(II) and Cd(II) ions in solution, respectively, and v and m are the solution volume and mass of the adsorbents, respectively.

3. Results and discussion

3.1. Characterization

3.1.1. FT-IR Spectroscopy studies

The characteristic studies of PPH are reported elsewhere [17]. From Fig. 1(a), the sharp absorption bands at 3,784 and 3,750 cm^{-1} for APPH were assigned to isolated OH groups. The broad peak at 3,176 cm^{-1}was attributed to the stretching vibrations of the carboxylic acid OH groups. The absorption bands at 2,933 and 2,867 cm^{-1}were assigned to the stretching vibrations of aliphatic CH, CH_2, and CH_3 side chain groups of the aromatic nuclei. The absorption peak at 2,320 cm^{-1} on APPH may be due to C–N stretching [28]. The absorbance peak at 1,689 cm^{-1}was assigned to the –C=O stretching of carboxylic acids and at 1,560 cm^{-1}, which is characteristic of the C–O or N–O symmetric stretch. The medium absorption band at 1,410 cm^{-1}was assigned to the aromatic ring of the APPH. The PPH and APPH both contain –OH and C–O functional groups, which could be involved in chemical bonding and may be responsible for adsorption [29]. This phenomenon can be explained as oxygen atoms present on carbonyl and hydroxyl groups containing lone pair of electrons, which act as Lewis bases and form coordination bonds with the metal ions [30].

3.1.2. XRD patterns

X-ray diffraction is one of the most useful techniques for examining the structure (crystalline and amorphous) of materials. XRD of activated carbon showed that the amorphous solids have a large

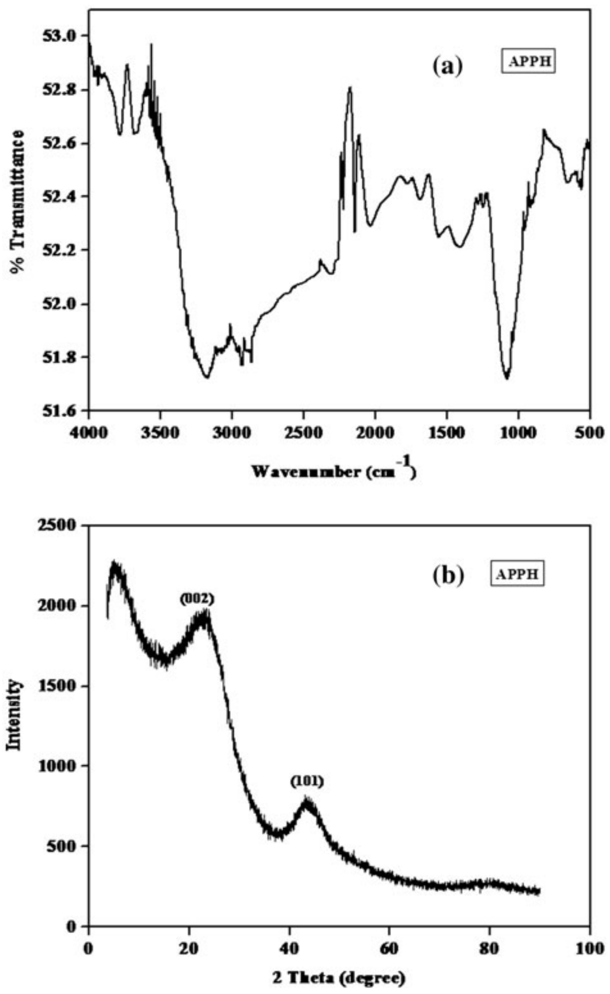

Fig. 1. (a) FT-IR spectrum of APPH and (b) XRD spectrum of APPH.

internal surface area and pore volume [31]. Fig. 1(b) shows the XRD pattern of the activated carbon, indicating a shape of symbolic amorphous carbon and showed broad asymmetric peaks at 23° 2θ and 44° 2θ, which were assigned to the (0 0 2) plane and (1 0 1) plane of carbon. The results are consistent with the results reported earlier [32]. In addition, XRD indicated that APPH was amorphous and due to its nature, metal ions can easily penetrate its surface.

3.1.3. SEM and TEM analysis

Textural analysis is important for examining the reactive sites on the surface of functionalized materials and are indicative of the potential of the materials for applications in adsorption. SEM of APPH revealed a cracked and uneven surface morphology, which is an adequate morphology for metal ion adsorption (Fig. 2(a–b)). TEM (Fig. 2(c–d)) revealed mesoporosity with a uniform pore size, which is similar to that reported elsewhere [33]. The amorphous form of APPH revealed the presence of a mesoporous structure. This structure should contribute extensively to the diffusion of metal ions to adsorbent surfaces, which favors the efficient removal of metal ions. SEM-EDAX showed that the APPH contained 79.50% carbon and 20.50% oxygen. The BET surface area and pore volumes of PPH and APPH were 415.82, 893 m^2 g^{-1}, 0.73, and 0.41 cm^3 g^{-1}, respectively.

3.2. Effect of pH

The metal solution pH plays a key role in the adsorption process. In the aqueous phase, pH governs the speciation of metals and the dissociation of active functional sites on the sorbent. Therefore, metal sorption is critically linked to pH, which affects the surface charge of the adsorbent as well as the degree of ionization [34].

The effects of pH on the adsorption of Cu(II) and Cd(II) ions were studied at different pH ranging from 2.0 to 9.0 using two adsorbents at a constant metal ion concentration of 50 mg L^{-1} and 0.2 g of adsorbent mass. The dependence of metal uptake on pH is related to both the surface functional groups present on the biomass and the metal chemistry in solution. The adsorption of M(II) ions can be explained by the exchange properties of the husks due to the presence of their various functional groups. Metal species (M (II) = Cu^{+2} or Cd^{+2}) remain in deionized water in the forms of M^{+2}, M(OH)$^{+}$, and M(OH)$_2$. Up to pH 4.0, the solubility of M(OH)$_2$ is appreciable. Therefore, M^{+2} is the main adsorbate species in solution [35].

From Fig. 3 at lower pH (pH < 3) the adsorption was quite low because the sorbent surface was surrounded by hydronium ions (H$_3$O$^+$), which prevented the metal ions from approaching the binding sites on the sorbent [36]. From Fig. 3, the maximum percentage removal of Cu(II) and Cd(II) ions were 94.98 and 94.80% at pH 5.0 and 96.44 and 95.59% at pH 6.0 onto PPH and APPH, respectively. The removal efficiency of both adsorbents increased dramatically with increasing pH 2.0–3.0. Above pH 3.0, the removal efficiency of both adsorbents decreased. The adsorption of Cd(II) and Cu(II) can also be explained based on the pH$_{pzc}$ of the adsorbents. The pH at the PZC of PPH and APPH are 3.52 and 4.58, respectively, the surface charges of the adsorbents were neutral and the electrostatic forces between the metal ions and the surface of the sorbents were balanced. A pH deviation from PZC causes a disturbance in this

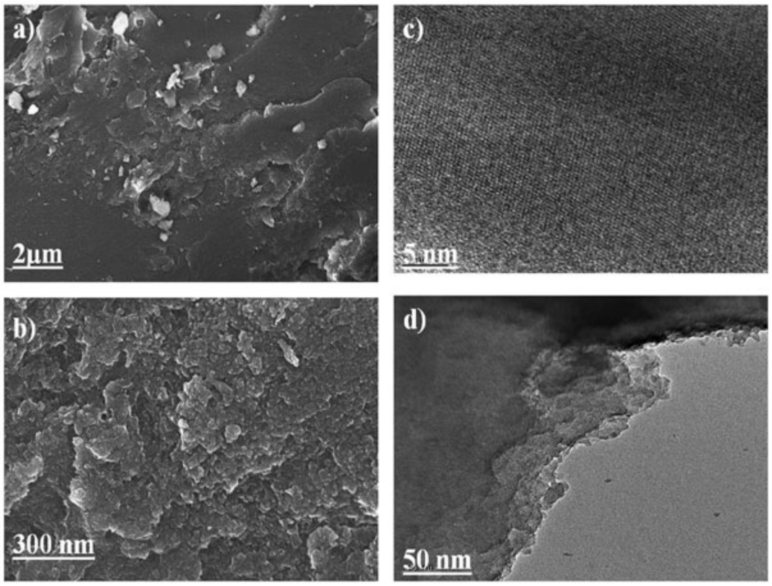

Fig. 2. (a–b) SEM images of APPH, (c–d) TEM images of APPH.

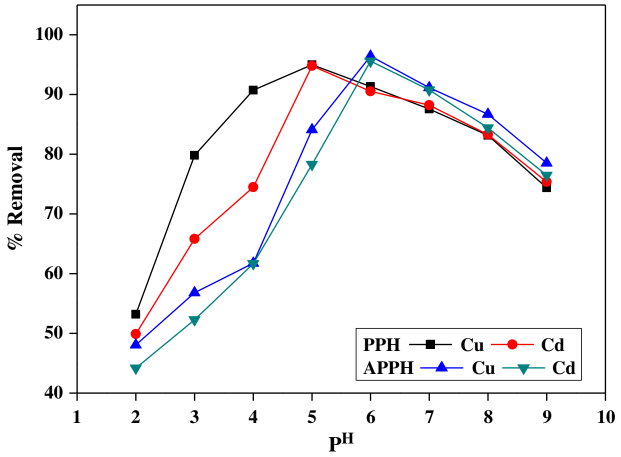

Fig. 3. Effect of pH for Cu(II) and Cd(II) removal onto PPH and APPH.

balance. At pH < PZC, the adsorbents surface charge is positive, which results in electrostatic repulsion with metal ions and causes low sorption. At pH > PZC, the surface charge of the adsorbents becomes negative and metal ions in solution are attracted onto the surface. The maximum sorption is likely to occur at pH greater than PZC when the adsorbent has a net negative charge [37].

Another optimistic clarification of the adsorption mechanism regarding the PZC can be given as the rule of PZC correlating with the adsorption behaviors of the adsorbent for metal ions and the pH dependence of metal uptake can depend on the nature of the adsorbents. The adsorbents used were agricultural byproducts, which contain carboxyl groups as their major functional groups [17], the pK_a of the carboxyl group was approximately 3 [38]. At low pH, the carboxylic groups will be present as molecules and at higher pH values, they exist as ions. As a result, the anionic form of the carboxylate attract the cation of the metal and form a complex and cause more removal [17,38]. As compared to the PZC of used adsorbents, the PZC of APPH is higher than the PZC of PPH, according to the above explanation the sorption capacity of APPH is greater than the sorption ability of PPH, and the results are shown in Fig. 3.

3.3. *Effect of adsorbent dose*

The dosage is an important parameter in adsorption studies because it determines the capacity of a adsorbent for a given initial concentration of metal ions in solution. The effects of the adsorbent dose on copper and cadmium adsorption were examined at an initial concentration of 50 mg L^{-1}, whereas the adsorbent doses was varied from 0.1 to 0.9 g with all other parameters kept as constant. Fig. 4 shows the effect of the adsorbent dose on the percentage removal of Cu(II) and Cd(II). From the figure, it can be observed that increasing the adsorbent dose increased the percentage removal of Cu(II) and Cd(II). At 0.4 g of weight of PPH the removal percentage of Cu(II) and Cd(II) observed are 85.69 and 82.51%, whereas at the

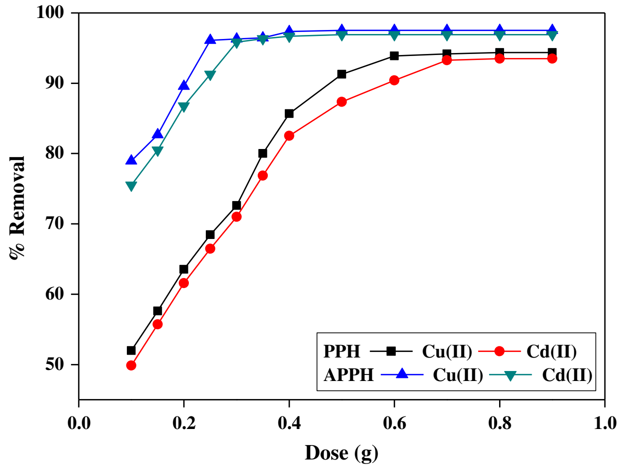

Fig. 4. Effect of dose for Cu(II) and Cd(II) removal onto PPH and APPH.

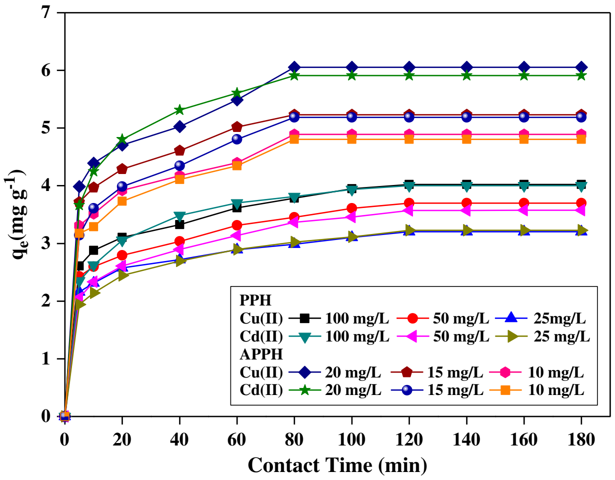

Fig. 5. Effect of contact time for Cu(II) and Cd(II) removal onto PPH and APPH.

same weight of APPH the removal percentage of the same metals are found to be 97.35 and 96.69%. At about 0.6 g weight of PPH the percent removal reached 93% only, the much difference in the removal of metal ions may depend on the nature and the surface area of the sorbents. Further increase in sorbent mass beyond 0.4 g did not result in further increase in the fraction deletion of metal ions for APPH and 0.6 g for PPH. This tendency can be explained as the result of the partial aggregation of adsorbent mass at a higher sorbent mass concentration, which results in a decrease in the effective surface area for adsorption [17]. Due to the activation APPH has more surface area when compared to PPH, hence the sorption capacity of APPH is more than the PPH. Generally, the higher the surface area, the larger is its adsorptive capacity. It has been reported that the activated carbons contain highly developed pore structures characterized by large surface area [39]. Therefore, the optimal quantity of adsorbent mass selected was 0.4 and 0.6 g for APPH and PPH, respectively, for the remainder of the experimental studies.

3.4. Effect of the contact time

The adsorption capacity of two sorbents toward Cu(II) and Cd(II) as a function of time at three different initial sorptive concentrations and a constant adsorbent dose was studied. The data was collected within the time period of 0−160 min. Fig. 5 shows that the increase in agitation time (0–40 min) increased the uptake of metal ions. Equilibrium for the removal of the selected metal ions on both adsorbents reached in 60 min. The rate of uptake was rapid in the early stages up to 50 min, and decreased until equilibrium. The adsorption of metal ions from aqueous solution was linear within 60 min for Cu(II) and Cd(II) metals. This behavior can be attributed to utilization of the available adsorbing sites on the surface of the adsorbent. After this phase, the sorption of metal ions was almost negligible. This might be due to the extremely slow diffusion of metal ions from the surface film into the micropores, which are the least accessible sites for adsorption. In the later stage, sorption is likely to be an attachment-controlled process due to the less available sorption sites.

3.5. Adsorption kinetics

The adsorption kinetics can be explained by several models, in these studies, the pseudo-first-order Lagergren equation [40], pseudo-second-order rate [41], and Weber–Morris intraparticle [42] diffusion models were considered by examining the kinetics at different initial metal ion concentrations.

The first two models were based on the assumption that the adsorption rate is proportional to the number of free sites available. The linear forms of the pseudo-first-order, pseudo-second-order rate, and Weber–Morris models are expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

$$q = k_{\mathrm{id}} t^{1/2} + c \tag{4}$$

where q_e (milligrams per gram) and q_t (milligrams per gram) are the adsorption amount at equilibrium and time t (minutes), respectively. k_1 (per minute) and k_2 (grams per milligram per minute) are the pseudo-first and pseudo-second-order model rate constants, respectively. K_{id} is the Weber–Morris intraparticle diffusion rate constant (milligrams per gram per square-root minute) and C is the thickness of the boundary layer.

Here, linear plots of $\log(q_e – q_t)$ vs. t were used to evaluate the data and determine the rate constant and q_e from the slope and intercept, respectively. Table 1 lists all the parameters of the kinetic models of Cu(II) and Cd(II) adsorption on PPH and APPH.

The theoretical values ($q_{e,\mathrm{cal}}$) for the three series of experiments under three initial concentrations are much lower than the corresponding experimental data ($q_{e,\mathrm{exp}}$) suggesting that the adsorption process did not fully follow the pseudo-first-order adsorption rate expression. From Eq. (2), plots of t/q_t vs. t, q_e and k_2 were evaluated at all experimental concentrations, and are shown in Fig. 6(a–b). From Table 1, the values of the linear regression correlation coefficient reached 0.999 for the pseudo-second-order kinetic models, which were closer to unity than those of the other models. Moreover, the calculated equilibrium adsorption was also much closer to the experimental values in the pseudo-second-order model, whereas the $q_{e,\mathrm{cal}}$ obtained from the pseudo-first-order kinetic models did not agree with $q_{e,\mathrm{exp}}$. Therefore, the pseudo-second-order kinetic model is the most appropriate one.

3.5.1. Intraparticle diffusion

In addition, there is the possibility of prevalent intraparticle diffusion of sorbate ions from the surface to the pores of the sorbent. According to Eq. (4), a plot of q_{t} vs. $t^{0.5}$ should be a straight line with a slope k_{id} and intercept C when the adsorption mechanism follows the intraparticle diffusion process. In general, the adsorption process is controlled by three diffusion steps: (a) transport of the solute from the bulk of the solution to the film, (b) transfer from the film to the adsorbent surface, and (c) diffusion from the surface to the internal sites [17].

From Fig. 7, the plots showed multi-linearity with three distinct regions. The initial curved region corresponds to the external surface uptake. The second stage is related to the gradual uptake, reflecting intraparticle diffusion as the rate limiting step, and the final plateau region indicates the equilibrium uptake, which means that the molecule takes up their positions within the pores of the sorbent. Thereafter, the adsorption development was saturated with time [43].

3.6. Equilibrium adsorption isotherm modeling

Identifying the appropriate isotherm model is important for better understanding the complex adsorption mechanism. The adsorption of Cu(II) and Cd(II) were studied in the concentration range, 10–80 mg L^{-1}, between 293 and 313 K, keeping other parameters as constant. In the present study, three extensively accepted Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models were analyzed.

3.6.1. Langmuir isotherm

The Langmuir model [44] assumes that adsorption occurs at specific homogeneous sites on the sorbent and is used successfully in many monolayer adsorption processes. This model can be expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

where q_e is the amount of metal ions adsorbed per unit mass of adsorbent in (mg g^{-1}), C_e is the equilibrium concentration of the metal ion in solution (mg L^{-1}), q_m is the maximum metal uptake, and K_L is the Langmuir adsorption constant (L mg^{-1}) related to the free energy of adsorption.

The essential characteristics of the Langmuir isotherm can be expressed conveniently in terms of a dimensionless term [45], R_L, which is a constant separation factor or equilibrium parameter for a given isotherm. This is defined as:

$$R_L = 1/(1 + bC_0) \tag{6}$$

where C_0 is the initial concentration of the metal ion.

3.6.2. Freundlich isotherm

The Freundlich model [46] can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption, the model is given by the following equation:

$$q_e = k_f C_e^{1/n} \tag{7}$$

where k_f and n are the Freundlich's constants and the characteristic of the system, indicating the adsorption capacity and adsorption intensity, respectively.

Table 1
Kinetic parameters of Pseudo-first-order kinetic, Pseudo-second-order kinetic, and Weber–Morris models for Cu(II) and Cd(II) onto PPH and APPH

Initial metal ion concentration (mg L^{-1})	Pseudo-first-order kinetics				Pseudo-second-order kinetics			Weber–Morris		
	$q_{e,\mathrm{exp}}$ (mg g^{-1})	$q_{e,\mathrm{cal}}$ (mg g^{-1})	K_1 (×10^{-2} mg g^{-1})	R^2	$q_{e,\mathrm{cal}}$ (mg g^{-1})	K_2 (×10^{-2} mg g^{-1})	R^2	$q_{e,\mathrm{cal}}$ (mg g^{-1})	K_{id} (mg g^{-1} $m^{-1/2}$)	R^2
PPH										
Cu(II)										
10	4.802	1.898	3.477×10^{-2}	0.9956	5.015	4.056×10^{-2}	0.9984	2.967	0.1962	0.9008
30	5.547	2.505	3.615×10^{-2}	0.9697	5.841	2.957×10^{-2}	0.9974	3.216	0.2481	0.9005
50	6.034	2.722	3.776×10^{-2}	0.9707	6.341	2.875×10^{-2}	0.9978	3.546	0.2663	0.8969
Cd(II)										
10	4.843	2.490	4.030×10^{-2}	0.9939	5.122	3.200×10^{-2}	0.9981	2.609	0.2417	0.8857
30	5.360	3.052	4.168×10^{-2}	0.9621	5.711	2.550×10^{-2}	0.9972	2.717	0.2851	0.8894
50	6.000	3.407	4.974×10^{-2}	0.9946	6.333	2.843×10^{-2}	0.9988	3.249	0.3040	0.8494
APPH										
Cu(II)										
10	4.891	1.277	2.372×10^{-2}	0.7392	5.144	3.791×10^{-2}	0.9988	1.240	0.5240	0.8153
15	5.228	1.757	4.053×10^{-2}	0.7691	5.452	2.975×10^{-2}	0.9991	1.474	0.4401	0.7790
20	6.052	1.697	2.072×10^{-2}	0.4397	6.385	3.933×10^{-2}	0.9995	1.476	0.4199	0.8264
Cd(II)										
10	4.897	1.538	4.030×10^{-2}	0.7078	5.083	4.405×10^{-2}	0.9987	1.141	0.4196	0.8322
15	5.183	5.512	4.168×10^{-2}	0.6341	5.711	2.965×10^{-2}	0.9988	1.146	0.4623	0.8497
20	5.990	1.967	4.974×10^{-2}	0.7041	6.246	2.157×10^{-2}	0.9990	1.444	0.5206	0.8221

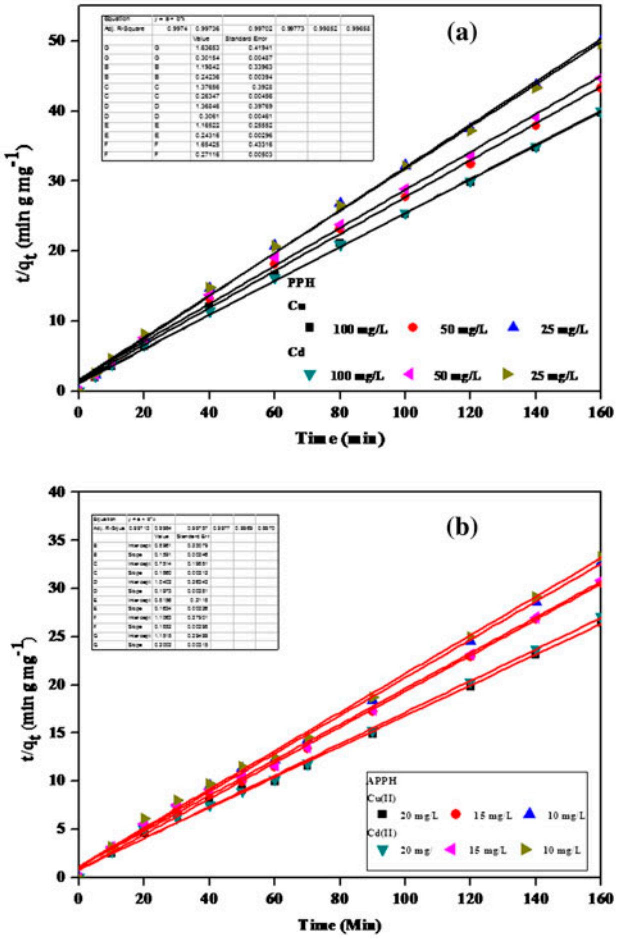

Fig. 6. Pseudo-second-order graphs for Cu(II) and Cd(II) removal onto (a) PPH and (b) APPH.

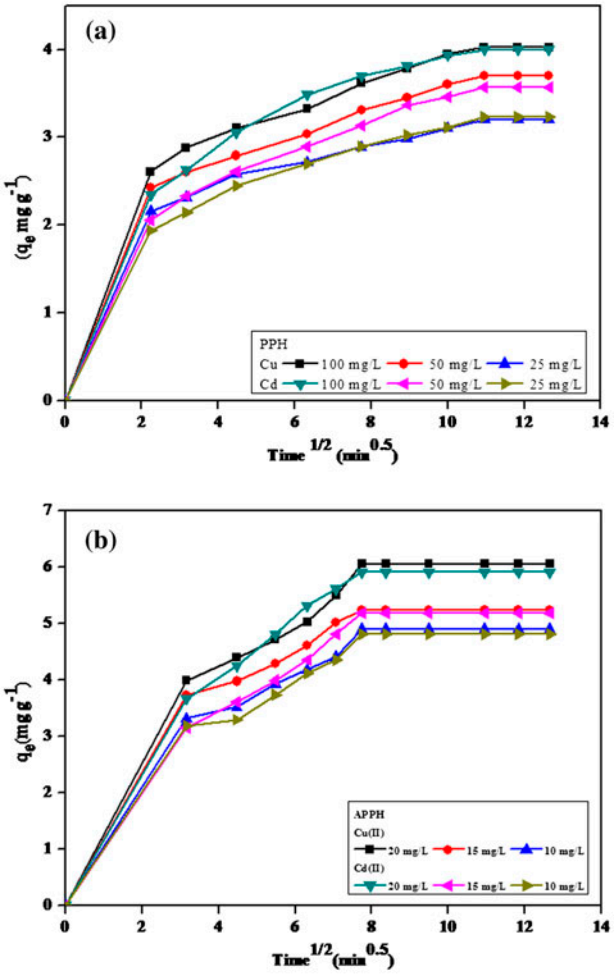

Fig. 7. Weber–Morris graphs for Cu(II) and Cd(II) removal onto (a) PPH and (b) APPH.

3.6.3. Dubinin–Radushkevich (D-R) isotherms

The Dubinin–Radushkevich isotherm equation [47] is represented as:

$$q_e = Q_m \exp\left(-K\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2\right) = Q_m \exp(-K\varepsilon^2) \quad (8)$$

where Q_m is the maximum amount of ions that can be adsorbed per unit weight of adsorbent (mg g^{-1}), ε is the polanyi potential, which is equal to $RT\ \ln(1 + 1/C_e)$, where R and T are the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}) and the absolute temperature, respectively. K (L g^{-1}) is the equilibrium constant obtained by multiplying the Langmuir constant, q_m and K_L [48].

Table 2 lists the Langmuir, Freundlich, and Dubnin–Radushkevich isotherms constants of Cu(II) and Cd(II) adsorption onto PPH and APPH. The R_L value indicates the type of the isotherm. R_L values between 0 and 1.0 indicates a favorable isotherm, whereas $R_L > 1.0$ indicates an unfavorable isotherm. The isotherms are linear or irreversible if R_L values are equal to 1.0 or 0, respectively. The respective R_L values for Cu(II) and Cd(II) were 0.03 and 0.03 on PPH, and 0.09 and 0.1 onto APPH, which indicates favorable adsorption onto the selected adsorbents.

The K_f and $1/n$ values of Cu(II) and Cd(II) were 8.24, 7.98, 9.13, and 8.72, and 0.27, 0.27, 0.36, and 0.34 onto PPH and APPH, respectively. The fitness of the models was indicated by the coefficient of determination (R^2) and the chi-square (χ^2) test. From Table 3, the R^2 values were greater than 0.98 and the χ^2 values were less than the remaining two models for the Langmuir isotherm. Therefore, the adsorption isotherm data was fitted better to the Langmuir isotherm model than the Freundlich and D–R models.

Table 2
Isothermal parameters for Cu(II) and Cd(II) adsorption onto PPH and APPH at various temperatures

			Langmuir		Freundlich		D–R	
Metal ion		Temp. (K)	q_e (mg g^{-1})	b (L mg^{-1})	k_f (mg g^{-1})	$1/n$	Q (mg g^{-1})	K
PPH								
	Cu(II)							
		293	17.85	0.5329	7.05	0.288	15.27	0.0015
		303	19.63	0.5468	7.53	0.277	15.55	0.0018
		313	20.83	0.5801	8.24	0.271	17.21	0.0014
	Cd(II)							
		293	16.87	0.6344	6.97	0.306	15.53	0.0016
		303	17.25	0.6699	7.21	0.278	15.94	0.0017
		313	19.81	0.5338	7.98	0.276	16.59	0.0014
APPH	Cu(II)							
		293	32.57	0.2489	10.79	0.321	27.59	0.0113
		303	34.38	0.2685	9.43	0.357	30.85	0.0103
		313	37.39	0.1905	9.13	0.369	32.41	0.0069
	Cd(II)							
		293	31.62	0.2725	10.25	0.298	26.79	0.0114
		303	33.59	0.2983	9.18	0.319	29.27	0.0071
		313	35.83	0.1585	8.72	0.349	31.92	0.0062

Although the ionic radius of cadmium (0.98 Å) is higher than that of copper (0.73 Å), the adsorbents exhibited slightly higher physical affinity for Cu(II) ions than for Cd(II) ions. This suggests that the adsorption capacity of the adsorbent depends on its nature [38]. Therefore, the adsorption capacity of Cu(II) is higher than Cd(II). A similar trend was reported in previous studies [39].

3.7. Thermodynamics

Thermodynamic estimates can offer insight into the type and mechanism of the adsorption process by determining the thermodynamic parameters, such as the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). The parameters were calculated using the following well-known equations:

Table 3
R^2 and χ^2 values of Langmuir, Freundlich, and D–R isotherms at various temperatures for PPH and APPH

			Langmuir		Freundlich		D–R	
Metal ion		Temp. (K)	R^2	χ^2	R^2	χ^2	R^2	χ^2
PPH	Cu(II)							
		293	0.9813	0.81	0.9304	3.36	0.8556	4.72
		303	0.9668	1.54	0.9573	3.46	0.8539	6.94
		313	0.9692	0.55	0.9781	3.52	0.8686	6.69
	Cd(II)							
		293	0.9769	0.85	0.9683	3.94	0.8597	5.06
		303	0.9896	0.86	0.9572	3.50	0.8649	5.73
		313	0.9879	0.69	0.9463	3.68	0.8938	6.25
APPH	Cu(II)							
		293	0.9941	1.01	0.9627	7.24	0.9004	11.23
		303	0.9925	2.56	0.9598	5.63	0.9137	12.83
		313	0.9876	0.79	0.9699	5.70	0.9251	14.31
	Cd(II)							
		293	0.9989	1.21	0.9685	8.02	0.9314	12.67
		303	0.9675	1.94	0.9793	5.66	0.9257	14.42
		313	0.9991	0.59	0.9698	5.58	0.9325	13.57

Table 4
Thermodynamic parameters for the adsorption of Cu(II) and Cd(II) ions onto PPH and APPH at various temperatures

Adosorbents	Metal ions	Temperature (K)	$-\Delta G^\circ$ (KJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔH° (KJ mol^{-1})
PPH	Cu(II)	293	5.48		
		303	5.97	28.04	13.70
		313	6.40		
	Cd(II)	293	5.77		
		303	6.16	28.39	13.80
		313	6.41		
APPH	Cu(II)	293	5.09		
		303	5.10	25.72	13.02
		313	5.59		
	Cd(II)	293	5.24		
		303	5.63	25.57	12.98
		313	5.82		

$$\Delta G^\circ = -RT\ln K, \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{ and } \ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

where R is the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T is the absolute temperature, and K (L g^{-1}) is an equilibrium constant obtained by multiplying the Langmuir constant, q_m and K_L.

Table 4 lists the thermodynamic parameters of Cu(II) and Cd(II) adsorption. The small negative and dissimilar values of ΔG° confirmed the spontaneity of the adsorption process with increasing temperature, and the positive value of ΔH° suggests that adsorption is endothermic in nature. The magnitude of ΔH° determines the type of adsorption, whether the process is physical or chemical. Generally, the magnitude of the ΔH° value lies in the range of 2.1–20.9 and 20.9–41.84 kJ mol^{-1}, which is indicative of physical and chemical adsorption, respectively [49].

The positive value of ΔS° suggests increased randomness at the solid/solution interface during the

Table 5
Comparison of maximum adsorption capacity of various biosorbents for Cu(II) and Cd(II) ions

Adsorbent	q_e (mg g^{-1})	Temp. (K)	pH	References
Cu(II)				
AC (*Cicer arietinum*)	18.37	273	7.0	[18]
Sunflower hulls	57.14	303	5.0	[23]
Acivated carbon	9.50	303	8.0	[39]
Banana peel	8.24	293	6.4	[50]
Sugarcane bagasse	9.48	293	6.0	[50]
Sawdust	37.17	303	6.6	[51]
Wheat straw	7.05	273	5.0	[52]
PPH	20.83	313	5.0	Present work
APPH	37.39	313	6.0	Present work
Cd(II)				
AC (*Cicer arietinum*)	18.00	273	8.0	[18]
Rice straw	27.87	293	5.5	[53]
Rice straw	13.88	298	5.0	[53]
Orange peel	35.71	298	7.0	[54]
Heartwood powder of Areca catechu	10.66	303	6.0	[55]
Coffee husk	6.90	298	4.0	[56]
Fennel Biomass	26.59	323	4.3	[57]
PPH	19.81	313	5.0	Present work
APPH	35.83	313	6.0	Present work

adsorption of metal ions onto the adsorbent. These studies show that the adsorbents used have selectivity and higher adsorption capacity for Cu(II) and Cd(II) removal when compared to most of the adsorbents reported in the literature (Table 5) [13,18,23,39,50–57]. Because of these advantages, agro-waste derived PPH and APPH could be used as an effective and low-cost adsorbent for the removal of Cu(II) and Cd(II) from aqueous solutions.

3.8. Desorption and regeneration

Desorption studies can determine the recovery of the metal from waste and recycling of the sorbent. Therefore, studies were carried out to assess the potential of chemical regeneration for adsorbents using hydrochloric acid at concentrations of 0.01, 0.05, 0.10, 0.15, and 0.20 N HCl. The results showed (figure not shown) that the desorption increased with increasing HCl concentration until 0.2 N, but was constant at higher concentrations. The desorbed percentages were 85.37 and 87.4% for Cu(II), 81.29 and 83.5% for Cd(II) from PPH and APPH, respectively. The reusability of the adsorbents is good after four consecutive adsorption–desorption cycles without any significant loss in adsorption ability based on all results.

4. Conclusions

In the present study, PPH and APPH were used as adsorbents. APPH was produced from PPH by chemical activation with H_2SO_4 and heating in a N_2 atmosphere. The various characterization methods were used to determine the functional groups, surface area, morphology, and state of the adsorbents. Sorption studies, such as pH, adsorbent mass quantity, contact time, and temperature, were found to be effective on the adsorption process. Kinetic studies showed that the pseudo-second-order model was more suitable. The isothermal studies showed that the Langmuir model isotherm was more suitable than the Freundlich and D–R isotherms. Thermodynamic studies confirmed that the adsorption process was spontaneous and exothermic. The results suggested that agricultural waste derived PPH and APPH can act as effective surface sorbents for the selected metal ions from aqueous solutions. Compared to PPH, the activated PPH has potential for selective metal removal. Therefore, they can be used as a substitute for commercial activated carbon for the removal of heavy metals from water and wastewater.

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