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Removal of Cadmium from Aqueous Solutions by a Synthesized Activated Carbon

Mohsen Ansari [1, 2], Amir Hosein Mahvi [3], Mohammad Hossein Salmani [2], Mohammad Hassan Ehrampoush [2*], Mohammad Taghi Ghaneiyan [2], Mahboubeh Shiraniyan [2], Parvaneh Tallebi [2]

[1] Student Research Committee, Shahid Sadoughi University of Medical Sciences, Yazd, Iran.
[2] Environmental Science and Technology Research Center, Department of Environmental Health Engineering, School of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran.
[3] Solid Waste Research (CSWR) Center, Environmental Research Institute (ERI), Tehran University of Medical Sciences, Tehran, Iran.

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***Corresponding Author:**
Mohammad Hassan Ehrampoush

Email:
ehrampoush@ssu.ac.ir

Tel:
+983538209100

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ABSTRACT

Introduction: There are different methods for removal of cadmium from aqueous solutions. Adsorption based methods are among the bests. One of the most important aspects for adsorption techniques is the availability of an accessible and economical adsorbent. This study aims to investigate cadmium removal from aqueous solutions by walnuts shell waste.

Materials and Methods: Walnut Shell (WS) was used as a carbon and was activated by a chemical agent. The surface characteristics of the synthesized Activated Carbon (AC), kinetic and isothermic variation were investigated under laboratory conditions.

Results: The results showed that adsorption could be affected by the amount of adsorbent and pH. The adsorption of cadmium was in the maximum level when pH was 6. Between two investigated adsorption isotherms, Langmuir (R^2=0.98) and Freundlich (R^2 = 0.97) isotherms well described the cadmium adsorption on walnut shell produced activated carbon.

Conclusion: Walnut shell as an agricultural waste can be synthesized into a suitable absorbent to absorb cadmium from aquatic solutions.

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Introduction

In recent decades, increasing demands of industrial products lead to environmental pollution as a critical problem[1]. Cadmium is one of the most notorious toxic elements that could be used in many large industries, such as battery manufacturing industries [2]; pulp and paper industries [3], and etc. The serious adverse health effects of cadmium occur when it is released to the groundwater and other reservoirs [4]. Various natural and manmade release cadmium into the groundwater [5]. The natural processes include soil erosion, drainages from cadmium contacting soils and atmospheric depositions [6]. The manmade processes include industrial activities such as mining and metallurgical activities, combustion of fossil fuels, application of pesticides, and industrial effluents. Usually, cadmium is observed as Cd^{+2} in water resources and serious health effects (e.g. Cancers, Cadmium-induced renal damage, and etc.) occur due to exposure to it [7]. Cadmium as a nephrotoxic element damages kidneys and has adversely effects on bones indirectly or directly [8]. This element may also react with sulfur containing proteins and lead to nervous disorders, pancreas disorders, cardiovascular system disorders, skeletal limb abnormalities, and anemia [9]. Maximum contaminant level (MCL) of cadmium in industrial effluents and drinking water respectively established as 0.25 and 0.005 mg/l by the Iran Environmental Protection Agency (EPA) [10]. It is noteworthy that the US EPA also categorized cadmium as a teratogen and a probable human carcinogen [11]. Common treatment methods for cadmium removal include precipitation [12], membrane filtration [13], ion exchange, [14] and adsorption [15]. Each method has its advantages and disadvantages such as high investment and operating costs, excessive sludge production and inefficiency. On the other hand, the application of recycled adsorbents became a popular method in adsorption process [16]. Indeed, adsorption is an effective elimination method; hence activated carbon has been used as an appropriate adsorbent [17]. However, due to expensive costs and regeneration difficulties of the adsorbent, the application has been limited significantly in developing countries [18]. These limitations induced the researchers and executives for synthesis of applicable, effective, and economical adsorbents from recyclable materials. Over the last few years the application of agricultural wastes, such as date palm seed [19], charcoal ash [20], pomegranate peel [21], beans peel [22], poplar tree bark [23], and walnut shell [24] for treatment of industrial wastewaters by adsorption of heavy metals was considered as a successful and economical treatment method. These wastes have the suitable characteristics to be used as an adsorbent. Although, they are cheap and ubiquitous, their disposal need some solid waste management costs [25]. One of the most popular agricultural wastes for production of activated carbon is walnut shell. For example, in this field of study Jafari Mansuri et.al [24], Yu et.al [26], Cheng et. al [27] and Zafarani et. al [28] investigated the use of walnut shell as an adsorbent to remove contaminants from water environment. Walnut shells with high carbon content and low moisture content can be considered as one of the suitable substrates for activated carbon production [29]. Therefore, considering the limited resources of raw materials and the need for recycling wastes, (in particular waste and agricultural waste, and with an economical, efficient and environmentally friendly approach) this study aimed to investigate the production of activated carbon of walnut shells and its evaluation in removing binary cadmium.

Materials and Methods

Materials

All of the materials used in this study were manufactured by Merck, German corporation.

Absorbent Synthesis

The present study was carried out in a laboratory scale in School of Public Health, Yazd. The walnut shell was prepared from the Shabestar area in East Azarbaijan province, Iran. In order to prepare an absorbent, first, the walnut shell was crushed by milling and sieved using two sieves of 50 and 40 (microns). Then, the samples were washed twice with distilled water. After drying at ambient temperature, the samples pyrolysis is performed under vacuum in an electric furnace at 350 °C for 2 hours. This product was kept under the name of carbonized walnut shell (CWS). In order to prepare a modified chemical adsorbent, in line with previous studies on the chemical activation of natural adsorbents, the CWS was added to potassium hydroxide solution 0.7 M in the impregnation ratio of KOH to walnut shell (1 g of agent: 1 g of precursor) for 2 hours at 250 °C. The prepared material at this stage was called the Activated Carbon synthesized from Walnut Shell (ACWS). After completion of the chemical activation process, the ACWS was washed several times with distilled water without ion to remove the excess potassium hydroxide from ACWS.

Adsorbent Characteristics

The ACWS dataset parameters were determined in accordance with the following standards; such as moisture content and apparent density (AWWA standard) [30], ash content (ASTM D2866) [31], and iodine value (ASTM D4607-14) [32]. The specific surface area and the pore volume of ACWS were also determined by the BET method by the BELSORP Mini II machine. The X-ray powder diffraction (XRD) as a rapid analytical technique was primarily used for the identification phase of the crystalline material and it can provide information on unit cell dimensions. In this study the X-ray diffraction (XRD) was used by the Bruker AXS-D8 Advance device. One of its benefits is the lack of vacuum, which reduces the cost of construction and places it at a higher level than electronic techniques. Furthermore, the XRD is non-contact and non-destructive and requires no hard preparation [33]. The pH of the point of zero charge (pHzpc) was measured using the pH drift method. The pH of the sorbent in the diluted water was adjusted between 2 and 12 by adding 0.01 M NaOH and 0.01 M HCl; 0.2 g of the adsorbent was added to 50 cm^3 of the solution, and after 24 h, the final pH was measured [34].

Kinetic Study

The initial standard stock solutions of Cd(II) ion (about 1000 mg/L) were prepared by dissolution of $Cd(NO_3)^2{\cdot}4H_2O$ powder (Merck, Germany) in redistilled water. Then various concentrations of cadmium were prepared by diluting the stock solution using double-dissolving water. In the adsorption study of cadmium in the ACWS, a batch equilibration technique was used. Initially, the effect of time on cadmium adsorption in the ACWS was investigated. The initial concentration of cadmium in the single element solution was prepared to be at 100 mg/L, and the ACWS mass were around 0.2 g ± 0.03 g. The optimal pH in case of each metal ion was adjusted to 6. The kinetics solution was stirred on a shaker at room temperature 22 ± 2 °C at 120 rpm constant speed. The mixtures were filtered with 0.45 µm filters, and then the filtrates residue was measured using a spectrophotometer at a wavelength of 545 nm [34]. The kinetics data were optimized using Lagergren pseudo-first-order equation and pseudo-second-order equation. Finally, in this study the influencing factors on the cadmium adsorption such as pH, initial concentration of cadmium, and adsorbent dose were investigated.

Isotherms Study

The adsorption ability of cadmium on the ACWS was obtained according to the initial runs of adsorption isotherm. The adsorption isotherm was carried out at the initial pH of 6. During experiments, the cadmium concentration from 5 to 350 mg/L range was used. The adsorption analysis was consisting of 50 mL of solution and 0.2 g ± 0.03 g of the ACWS. Adsorption isotherms solution was stirred on a shaker with the temperature of 22 ± 2 °C and the equilibrium time of 24 h. In this study, Freundlich and Langmuir were used to fit the sorption isotherms.

The Langmuir absorption model is shown in the following equation:

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

In this equation, q_e is the amount of dye adsorbed per unit mass of adsorbent at equilibrium conditions (mg/g), C_e is the dye equilibrium concentration (mg/L), q_m is the monolayer capacity of the adsorbent (mg/g), and K_L is the Langmuir constant.

The Freundlich isotherm describes the adsorption on heterogeneous surfaces with different energy of adsorption onto the adsorbent surfaces sites and is expressed by the following equation:

$$q_e = K_f C_e^{1/n}$$

In this equation, K_f (mg/g).$(L/mg)^{1/n}$ and n are the Freundlich coefficients, K_f is related to adsorption capacity and n indicates the effect of concentration on the adsorption capacity.

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Results

Absorbent Characteristics

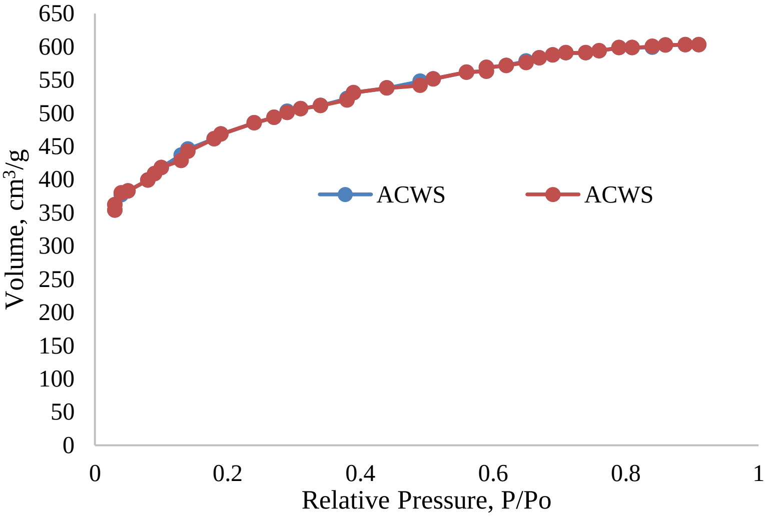
Characteristics of activated carbon prepared from walnut shell are described in Table 1. As it can be seen, apparent density, pH zero point of charge, ash content, iodine number, specific surface area, and pore volume of the ACWS were 0.78 (g/L), 7.3, 2.3 (%), 625 (mg/g), 1477 (m^2/g), 1.3 (cm^3/g), respectively.

The adsorption/desorption isotherms of the CWS and ACWS by the KOH are presented in Figure 1. The use of activating agent has a significant effect on the shape of the N_2 adsorption/desorption isotherms. Furthermore, Figure 2 illustrates the pore size distribution of the cavity structure of the ACWS and CWS. According to Figure 2, the pore size distribution of the ACWS and CWS are in the range of 2 nm to 4 nm in the mesoporous scale.

The XRD spectrum of carbonized walnut shell before and after activation is presented in Figure 3. This figure indicates that there was a tetragonal phase only for the ACWS. However, after the activation of carbonized walnut shell, the ACWS presented only the crystallinity phase, as shown in the diffraction peaks at 43.5º, 52.3º, and 72.8º. Moreover, there are diffraction peaks at 25º and 43º (101), which are assigned to the carbon phase as the graphite structure in the ACWS.

Table 1: Characteristics of activated carbon prepared from walnut shell

Characteristics	Unit	Value
Apparent density	g/L	0.78
pH $_{\text{zero point of charge}}$	-	7.3
Ash content	%	2.3
Iodine number	mg/g	625
Specific surface area BET	m^2/g	1604
Microporous	cm^3/g	0.684
Mesoporous	cm^3/g	0.196
Total volume	cm^3/g	0.880
Diameter	(nm)	2.19



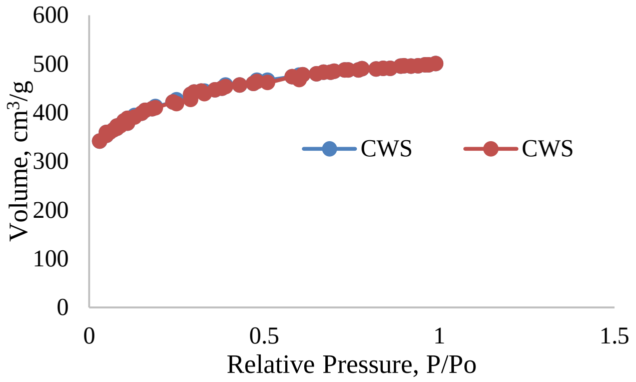


Figure 1: Adsorption and desorption isotherms N_2 at 77 ^{0}K of ACWS and CWS

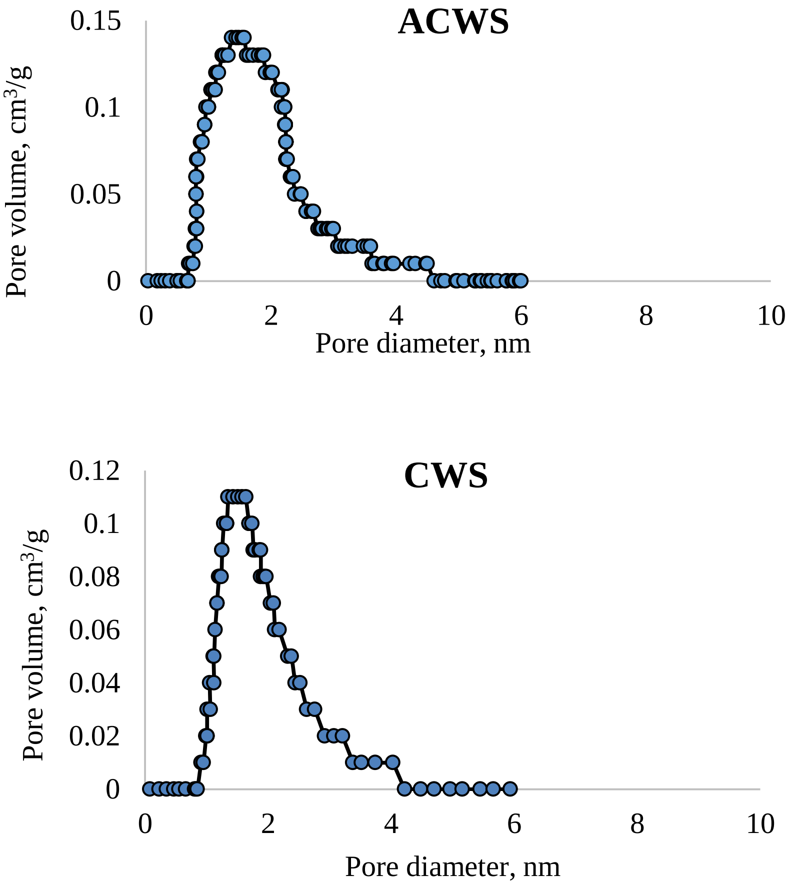


Figure 2: Pore size distribution of CWS and ACWS

Sorption Kinetic

The adsorption of cadmium on the ACWS was studied as a function of time, and the results are shown in Figure 3. The sorption kinetic analysis revealed that the percentage of Cd (II) adsorption increased with time (Figure 4).

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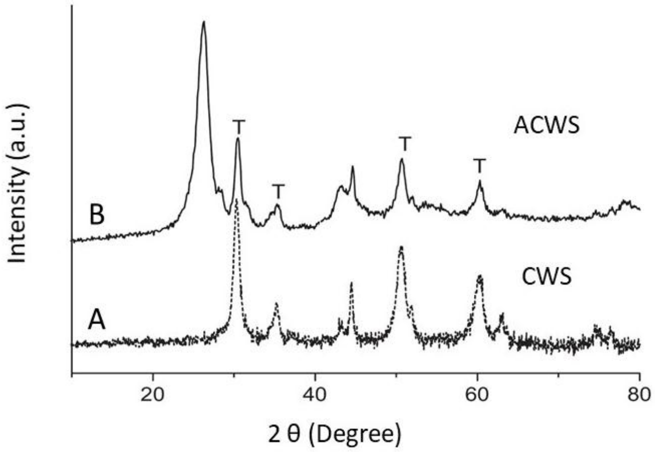

Figure 3: XRD patterns of activated carbon synthesized from walnut shell

Figure 4 indicates that the adsorption process of cadmium on the ACWS had two phases, which is in line with the previous research studies [35]. The first rapid step is attributed to the surface adsorption of cadmium on the ACWS. The following slow step is explained that the adsorbed cadmium was distributed from the outer to inner surfaces of ACWS [35].

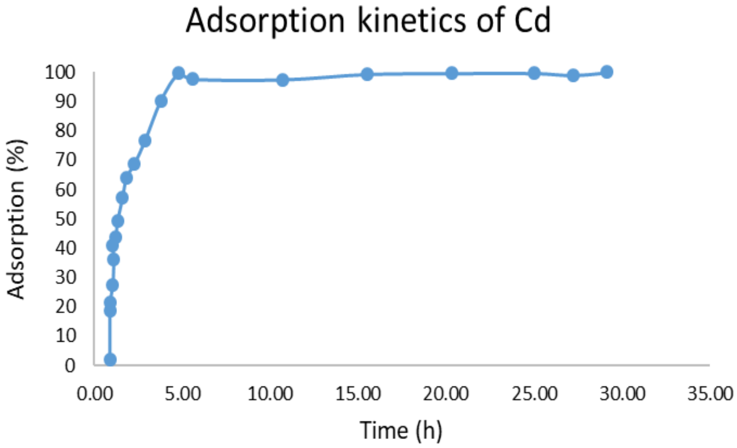

Figure 4: Adsorption kinetics of Cd (II) ions onto ACWS, m = 0.2 g, V = 50 mL, C= 100 mg/L, pH = 6, T = 22 ± 2 °C.

Effect of pH

The pH of the solution has some function such as determining the surface charge of the adsorbent, the degree of ionization and adsorption formation [17]. The effect of pH on cadmium adsorption by the ACWS is shown in Figure 5. This figure represents that the minimum and the maximum absorption levels of cadmium are observed at pH 2 and pH 6, respectively.

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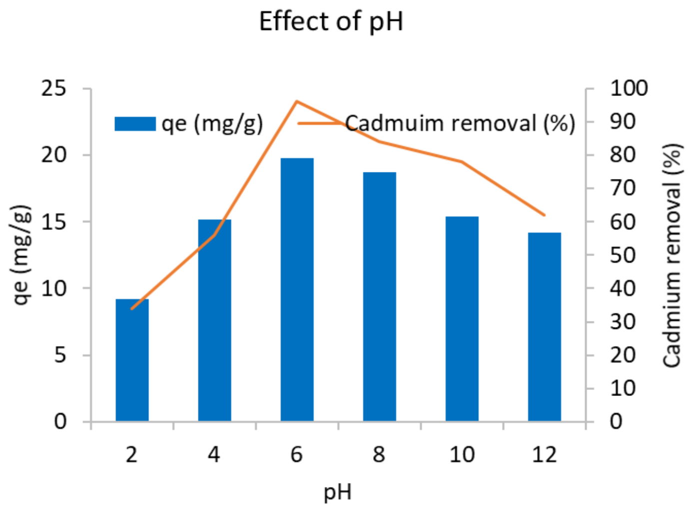

Figure 5: Effect of pH on the adsorption capacity and removal percentage of cadmium onto ACWS (dose of activated carbon = 0.5 g/L, Cd(II) = 25 mg/L, temperature = 22 ^{0}C)

Effect of Adsorbent Dose

The adsorption of cadmium as a function of adsorbent dose is shown in Figure 6. The experiment was carried out at V = 50 mL, Cd (II) = 25 mg/L, pH = 6, T = 22 ± 2 °C. The cadmium removal percentage increased significantly from 36.56 to 98.21 % when the adsorbent dose was increased from 0.25 to 1.25 g/L that was due to the substantial increase in available adsorption sites on the ACWS. As Figure 1 indicates, the adsorption capacity of cadmium was decreased from 19 to 9.2 mg/g with increasing the amount of the ACWS. A similar behavior was reported for the adsorption of Cr (VI) and Fe (II) from aqueous solution on walnut shell [36].

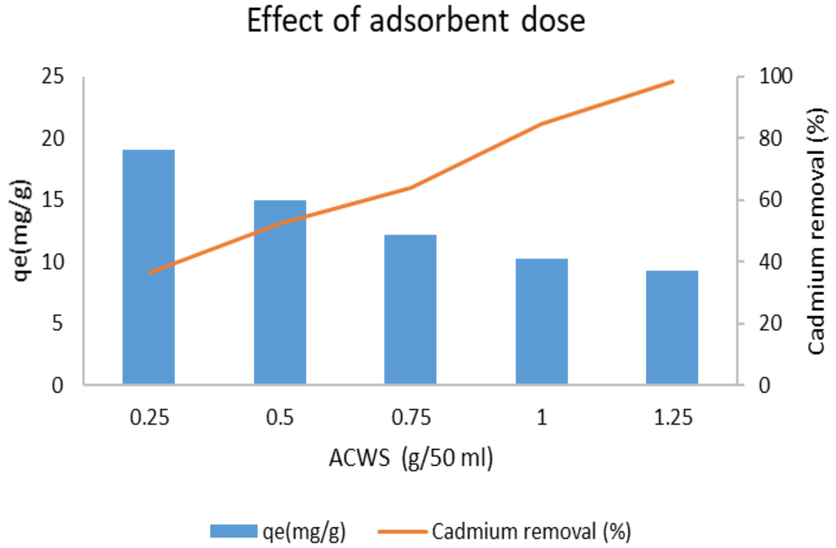

Figure 6: Effect of adsorbent dose on the adsorption capacity and removal percentage of cadmium onto ACWS (pH 6, temperature 22 °C Cd (II) = 25 mg/L

Adsorption Isotherms

Langmuir Isotherm

The adsorption isotherm is one of the important factors used in the design of absorption systems. In fact, the adsorption isotherm is explained as an interaction between the absorbent and the absorbed object. Therefore, it is considered as an essential factor in determining the absorbent capacity and

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optimizing the adsorption capacity. In the Langmuir isotherm, it is assumed that the single-layer adsorption is occurred in homogeneous sites on the adsorbent, in contrast to the Freundlich isotherm to describe heterogeneous systems.

The adsorption equilibrium data fitted with Langmuir and Freundlich models are shown in Figure 7. This figure shows a steep slope that specified the high efficiency of adsorbent at a low cadmium concentration and the slope decreased with increasing cadmium concentration. Furthermore, Constant parameters and correlation coefficients calculated for Langmuir and Freundlich models at different initial cadmium concentration for the ACWS are shown in Table 2. The determination coefficient (R^2) for cadmium adsorption was equal to 0.98, which indicated a good fit of Langmuir single-layer model for cadmium adsorption by the ACWS. In other words, the representation of the mathematical adaptation is very good, which may be due to the explanation of similar adsorption sites on the surface of the ACWS. Since Langmuir isotherm assumes the absorbing surface homogeneously.

Table 2: Isotherms parameters and determination coefficients (R^2)

Freundlich model			**Langmuir model**		
R^2	K_F	1/n	R^2	K_L(L/mg)	q_m(mg/g)
0.97	23.63	0.19	0.98	0.072	68.31

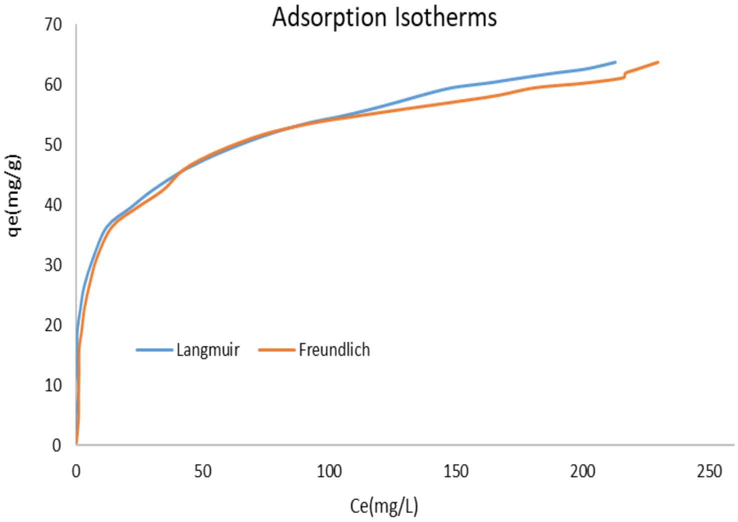

Figure 7: Freundlich and Langmuir isotherms for cadmium adsorption onto ACWS at different initial cadmium concentration (3 to 230 mg/l) (pH 6, temperature = 22 °C, dose of ACWS = 2 g/L)

Freundlich Isotherm

The results of the Freundlich model (Figure 7) showed that similar to the Langmuir slope, the slope of Freundlich model was sharp and showed the existence of high efficiency of the ACWS at a low cadmium concentration and the slope decreased with increasing cadmium concentration. As it is revealed in Table 2, R^2 for cadmium adsorption in the Freundlich model was equal to 0.97, which indicated a good fit of Freundlich model for cadmium adsorption by the ACWS.

Discussion

As a result, above the pH_{zpc} of 7.3, the ACWS has a negative charge and is capable of attracting captions. The quality of the ACWS is defined by various properties such as moisture content, ash content, and iodine number. In this study, the values related to moisture content, ash content, and iodine number were in the ranges that a high quality activated carbon needs them. The both isotherms of the CWS and ACWS are of type I in the IUPAC system. Based on the IUPAC classification, the porous media structure can contain holes smaller than 2 nm, called micro hollow (based on the average dimensions of the holes). Holes between 2 to 50 nm, are called meso holes, and holes larger than 50 nm, are called Macro [37]. This type of isotherm, often called Langmuir, is rarely seen in non-porous materials, and is suitable for compounds with high-density cavities (less than 2 nm). This indicates that the pore structure of samples is mostly microporous. As shown in Figure 1, the BET surface area of the ACWS was higher than that of CWS. This is related to the development of the high micropore volume and control of pore-size distributions due to use of activating agent. The type I of the IUPAC system indicates that the samples exhibit a pore size distribution on the micropore range which was confirmed by the micropore volumes in Table 1. As Figure 2 reveals, the pore volume (cm^3/g) in the ACWS was more than CWS. The results indicate that the ACWS is ideal for creating active sites to absorb multi-capacity metal contaminants. Therefore, the effect of the KOH was associated with stronger release of volatiles in the activation process and conversion to microspores [38]. Moreover, adding the KOH may prevent the formation of tar known as the pore-blocking agent; therefore, it can increase the surface area. This finding is in line with the studies of Zhanyong et al. [23], Lewicka [39], and Qiongfen et al. [40] who used the KOH as an activating agent.

The physical and chemical characteristics of a substance are related to the sorption kinetics, which also influence the adsorption process. As shown in Figure 3, the elemental composition of the ACWS showed a carbon phase as the graphite structure in the ACWS. Therefore, the surface of the ACWS can show a greater amount of polar groups responsible for binding the heavy metal ions [41].

Accordingly, Figure 4 shows that the adsorption kinetics of Cd (II) was slow and to reach the equilibrium state, the required contact time with the ACWS surfaces should be 6 h. According to pseudo–second–order data ($R^2 = 0.98$), the kinetic fitting plots were used to explain the time base mechanisms of adsorption process (Figure 8). Table 3 represents the kinetic parameters obtained for cadmium sorption kinetics. It can be seen that only the pseudo-second-order model provided the best fitting for all of the experimental data.

The regression coefficient can be extracted from Figure 4. The calculated regression coefficient show higher than 0.98 cadmium adsorption onto ACWS (Table 3). It was suggested (Kołodyńska et al., 2012) that the kinetics of metal ions following the pseudo-second-order model is controlled by a chemisorption process. The obtained second-order sorption kinetic is in agreement with other authors' findings [42-44].

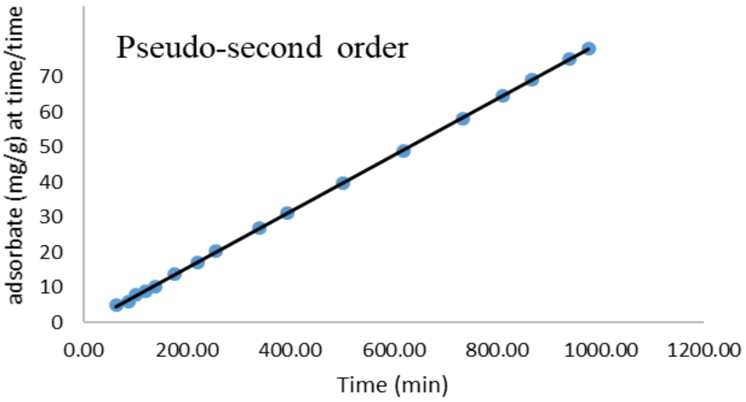

Figure 8: The kinetic fitting plots according to pseudo second order for ACWS

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Table 3: Kinetic models

Kinetic model					
Pseudo-first order		Pseudo-second order			ak
k_1	R^2	k_2	R^2	a_{eq}	
0.0036	0.671	0.06	0.98	20.61	22.89

The result of pH effects (Figure 5) was consistent with Elouear et al. that found the maximum adsorption of nickel and cadmium was at pH 6 and the metal ions removal was nearly constant for pH > 6 [45].

At lower pH_s, H_3O^+ ions compete with metal ions to the adsorption sites; therefore, absorbing metal ions increases with increasing pH from 2 to 6 [46]. The value of q decreases at high pH_s due to metal ions deterioration. Previous studies have shown that optimized pH values have been obtained for adsorption of metal ions from aqueous solutions under acidic conditions [47, 48]. In another study by Veemaraj Kannan, the absorption of cadmium bivalent capacity ions by activated carbon synthesized from the rubber tree in a pH range of 2 to 10 was studied. The results of their studies showed that by increasing the pH of the aqueous solution, the percentage of cadmium removal would increase and pH of about 7 would be the most suitable pH for the adsorption of cadmium by this natural absorbent [49]. The minimum metal adsorption at low pHs may be due to the high concentration and mobility of H^+ ions, which are preferably absorbed instead of metal ions [50]. At high pHs, cadmium adsorption increases as a result of the reduction in the number of H+ ions and the increase of negative charge ligands [51]. At pH below the pHzpc, the surface charge is absorbent; therefore, this positive charge on the ACWS is suitable for adsorption of bivalent cadmium cations. At pH higher than the pHzpc, pure charge on the surface of the ACWS in this study was negated, resulting in the absorption of bivalent cadmium cations. Meanwhile, at higher pH, hydroxyl ions increase in the solution and compete with cadmium ions to adsorb onto active sites of the ACWS and cadmium absorption decreases. Since the amount of adsorbent pHzpc used is 7.7, the reduction in adsorption efficiency in pH conditions above 7 is reasonable. Studies done by other researchers have shown that optimum pH for bivalent cadmium is between 5 and 7.

According to Table 2, the monolayer capacity of the adsorbent (q_m) for the ACWS was obtained 68.31 mg / g. Various studies presented the maximum absorption capacity of cadmium by other adsorbents. For example, Zubrik et al. calculated the maximum absorption capacity 107 mg of cadmium per gram of the activated carbon from agricultural waste [52]. In another study, Taghavi et al. investigated the efficiency of crystalline nanotubes carbon to remove component cadmium and showed a well-fitting Langmuir model ($R^2 = 0.994$) with q_m of 43.47 mg/g [53]. However, it should be noted that direct comparison of various studies is difficult because the experimental conditions are very different.

Conclusion

This study was conducted to produce a valuable absorbent of agricultural waste. Walnut shell has properties such as high carbon content, low humidity, availability, and successfully used as a cadmium adsorbent. Preparing activated carbon with less heat energy usage can be considered as a substitute for industrial activated carbon. The activated carbon derived from walnut shell was significantly effective in removing cadmium from the aquatic environment.

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Conflict of Interest

The authors declare that there is no conflict of interest.

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