Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics

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ABSTRACT

Adsorption can be used as a cost effective and efficient technique for the removal of toxic heavy metals from wastewater. Waste materials with no further treatment such as coffee grounds from cafeterias may act as adsorbents for the removal of cadmium. Batch kinetic and equilibrium experiments were conducted to study the effects of contact time, adsorbent dose, initial pH, particle size, initial concentration of cadmium and temperature. Three adsorption isotherm models namely, Langmuir, Freundlich and Dubinin–Radushkevich were used to analyse the equilibrium data. The Langmuir isotherm which provided the best correlation for Cd^{2+} adsorption onto coffee grounds, shows that the adsorption was favourable and the adsorption capacity found was equal to $15.65\,mg\,g^{-1}$. Thermodynamic parameters were evaluated and the adsorption was exothermic. The equilibrium was achieved less than 120 min. The adsorption kinetic data was fitted with first and second order kinetic models. Finally it was concluded that the cadmium adsorption kinetic onto coffee grounds was well fitted by second order kinetic model rather than first order model. The results suggest that coffee grounds have high possibility to be used as effective and economical adsorbent for Cd^{2+} removal.

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1. Introduction

The excessive release of heavy metals into the environment is a major concern worldwide. Heavy metals contamination of water is a serious threat to the globe ecosystem. Strict environmental protection legislation and public environmental concerns lead the search for novel techniques to remove heavy metals from industrial wastewater. Various processes of heavy metals elimination are used, we can cite: precipitation, electro precipitation, electro coagulation, cementing and separation by membrane, the solvent extraction and the exchange of ions on resins. Adsorption is considered quite attractive in terms of its efficiency of removal from dilute solutions. Although, the use of commercially available activated carbon and zeolites [1] of different grades is still very popular, but it is very expensive. Thus, there is a growing demand to find relatively efficient, low cost and easily available adsorbents for the adsorption of cadmium, particularly if the adsorbents are the wastes. The researchers were oriented towards no expensive adsorbents which are the vegetable wastes such as: waste of tea [2], degreased coffee beans [3], sawdust [4], the tree fern [5], chitosan [6], the olive oil waste [7,8], the orange juice waste [9],

the orange barks [8], the algae [10], plants dried [11] and olive stone waste [8,12]. The present study was carried out to show the potential of adsorption of cadmium on a vegetable material which is coffee grounds coming from cafeterias and constitute a waste. The aim of this study was to found an untreated waste with a better maximum capacity of adsorption which can be used in next step in fixed bed and later in pilot scale.

2. Materials and methods

2.1. Preparation of the adsorbent

The adsorbent used in this study was coffee grounds coming from cafeterias and constitute a waste. It was used with no further treatment just only dried at the ambient air and then sieved by applying the TAYLOR norm.

2.2. Preparation of the metal solution

The cadmium solution is prepared by dissolving cadmium nitrate $(Cd(NO_3)_2 \cdot 4H_2O)$ in distilled water. The initial concentration varies from 10 to $700\,mg\,L^{-1}$. The initial pH of the solution is adjusted by using a solution of HNO_3 or NaOH.

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2.3. Metal adsorption experiments

The adsorption experiments were carried out in batch at room temperature. A given mass of adsorbent was added to cadmium solution and the entirety was agitated during a certain time. The samples were carried out at quite time intervals, filtered through filter paper (Double Boxing rings 102).

Cadmium analysis was realised by atomic absorption spectrophotometer (PERKIN ELMER, A 800) with a wavelength of 228.8 nm, a slit of 0.5 and one flame of the air–C_2H_2 type.

The quantity of metal adsorbed at equilibrium was calculated by the following expression:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where m is the mass of adsorbent (g), V is the volume of the solution (L), C_o is the initial concentration of metal (mg L^{-1}), C_e is the equilibrium metal concentration (mg L^{-1}) and q_e is the metal quantity adsorbed at equilibrium (mg of Cd g^{-1} of adsorbent).

For the calculation of the cadmium rate adsorption (Re) we used the following expression:

$$Re(\%) = \frac{(C_o - C_r)100}{C_o} \tag{2}$$

where C_r is the residual concentration of cadmium in the solution (mg L^{-1})

2.4. Calculation of adsorption isotherms parameters

The tests concerning the study of the adsorption equilibrium were carried out for metal concentrations varying from 10 to 700 mg L^{-1} using 1 L of cadmium solution. During adsorption, a rapid equilibrium is established between the quantity of metal adsorbed on the adsorbent (q_e) and metal remaining in solution (C_e). The isotherms data were characterized by the Langmuir (3), Freundlich (4) and Dubinin–Radushkevich (D–R) (8) equations:

$$q_e = \frac{q_{max}bC_e}{1 + bC_e} \tag{3}$$

$$q_e = K_F C_e^n \tag{4}$$

where (b, q_{max}) and (K_F, n) are empirical constants of Langmuir and Freundlich isotherms, respectively, that will be calculated from the linear forms of Eqs. (3) and (4):

$$\frac{1}{q_e} = \frac{1}{q_{max}b}\frac{1}{C_e} + \frac{1}{q_{max}} \tag{5}$$

$$\ln q_e = \ln K_F + n \ln C_e \tag{6}$$

The Langmuir isotherm equation is valid for monolayer sorption on to surface containing finite number of identical sorption sites. The essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant separation factor, R_L, defined by:

$$R_L = \frac{1}{(1 + bC_0)} \tag{7}$$

The values of R_L indicate the type of Langmuir isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). The equation of Freundlich is based on the adsorption on heterogeneous surfaces [10]. This equation does not give any information about the maximum capacity of adsorption contrary to the Langmuir model.

The Dubinin–Radushkevich (D–R) isotherm is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential. The D–R equation is:

$$q_e = q_{max} \exp\left(-B\left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2\right) \tag{8}$$

where B is a constant related to the adsorption energy, R (8.314 J mol^{-1} K^{-1}) is the gas constant, and T(K) is the absolute temperature. The constant B (mol^2 kJ^{-2}) gives the mean free energy E (kJ mol^{-1}) of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship:

$$E = \frac{1}{(2B)^{0.5}} \tag{9}$$

This parameter gives information about chemical or physical adsorption. With the magnitude of E, between 8 and 16 kJ mol^{-1}, the bisorption process follows chemical ion-exchange, while for the values of $E < 8$ kJ mol^{-1}, the biosorption process is of a physical nature. The linear form of this model is expressed by:

$$\ln q_e = \ln q_{max} - Be^2 \tag{10}$$

where

$$e = RT \ln\left(1 + \frac{1}{C_{eq}}\right) \tag{11}$$

2.5. Adsorption kinetics

The knowledge of adsorption velocity is important information for designing batch adsorption systems [10]. The kinetics of adsorption was studied by using two kinetic models: pseudo-first order and pseudo-second order models. These models take into account the adsorbed quantities that will enable us to determine the reactor volume.

2.5.1. Pseudo-first order model

The model of the pseudo-first order used is that of Lagergren given by the following equation:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{12}$$

The integration of Eq. (12) in the conditions ($t = 0$, $q_t = 0$) and ($t = t$, $q = q_t$) gives:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{13}$$

where k_1 is the velocity constant of the pseudo-first order (min^{-1}).

2.5.2. Pseudo-second order model

In 1995, Ho has proposed a law of the pseudo-second order velocity that illustrates the velocity dependence on the capacity of adsorption in the solid phase and its no dependence on the concentration of the adsorbed substance [5]. Its expression is given by:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{14}$$

By integrating Eq. (14) into the boundary conditions ($t = 0$, $q = 0$) and ($t = t$, $q = q_t$), we obtain:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \tag{15}$$

where k_2 is the velocity constant of the pseudo-second order (g mg^{-1} mn^{-1}).

2.6. Thermodynamic study

Thermodynamic parameters can be determined using the equilibrium constant K (q_e/C_e) which depends on temperature. The change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) associated to the adsorption process was calculated using the following equations:

$$\Delta G^\circ = -RT \ln K \tag{16}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is temperature (K).

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{17}$$

According to Eq. (17), ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of $\ln K$ versus $1/T$ yields respectively.

The activation energy can be determined from the Arrhenius equation:

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \tag{18}$$

where k_2 is the rate constant pseudo-second order of adsorption (g mg^{-1} mn^{-1}), k_0 is the independent temperature factor (g mg^{-1} mn^{-1}), R is the gas constant (J mol^{-1} K^{-1}) and T is the solution temperature (K). A plot of $\ln k_2$ versus $1/T$ gives a straight line, and the corresponding activation energy was determined from the slope of linear plot.

3. Results and discussions

3.1. Characterisation of adsorbent

Some chemical and physical characteristics of coffee grounds are presented in Table 1.

Table 1
Physical and chemical properties of coffee grounds.

Mean diameter (µm)	389.18
Moisture (%)	1.89
Organic compounds (%)	96.15
Mineral compounds (%)	1.96

3.1.1. Analysis of coffee grounds by SEM/EDX

In order to know the surface structure of coffee grounds, morphological analysis was performed by scanning electron microscopy (SEM) using a Philips XL 20 WELTON JOANNE, 1950. Fig. 1 shows the structure of coffee grounds and indicates that coffee grounds have a porous and homogenous structure with a deep pore.

The energy dispersive X-ray microanalysis (SEM/EDX) of the coffee grounds shown in Table 2 indicates mainly the presence of oxygen (58.59%) and carbon (33.75%) but also of some heteroatoms, such as K, Na and Si originating from the wood precursor [13].

3.1.2. X-ray fluorescence analysis

The chemical composition of coffee grounds was determined using X-ray fluorescence (XRF) spectrometer (Bruker-Axs: SRS 3400) and listed in Table 3.

The results indicate mainly the presence of potassium, phosphore, magnesium and calcium. The analysis supported the existence of sulphur and suggested the absence of nitrogen, similar results have been reported by Kaikake et al. [3]. The presence of Fe, Cl, Cu and the other elements may be due to the cistern water used in cafeteria for the preparation of coffee drinking. The results confirm the presence of the elements Ca, Na, Mg, Al, P, S and K found in the SEM/EDX analysis.

3.1.3. X-ray diffractometry (XRD) analysis

X-ray diffraction (XRD) analysis was carried out with X-ray diffractometer (X'PERT PROMODEL) using Cu Kα radiation. Patterns were recorded from 5° to 70° 2θ at a scan rate 1° min^{-1}. The XRD patterns for untreated coffee grounds are shown in Fig. 2.
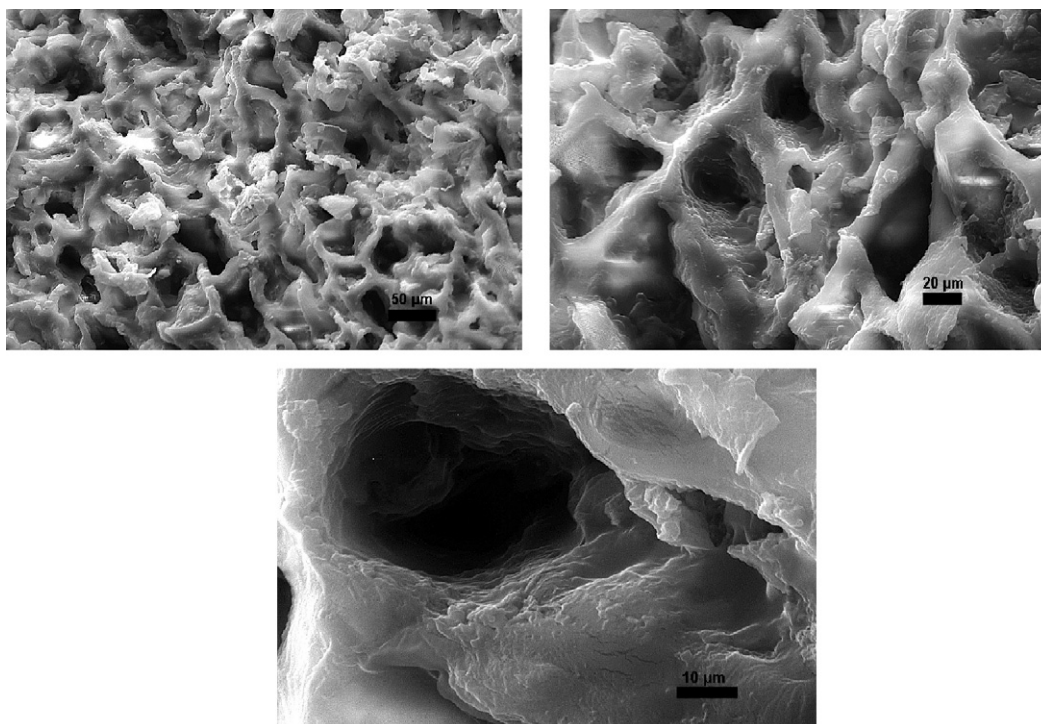

Fig. 1. Scanning electron microscopy of coffee grounds at different magnifications

Table 2
Elemental composition of coffee grounds.

Element	C	Ca	O	Na	Mg	Al	Si	P	S	K
(%)	33.75	0.42	58.59	2.72	1.19	0.68	0.48	0.72	0.65	0.80

Table 3
Chemical composition of coffee grounds.

| Element	K_2O	P_2O_5	MgO	CaO	SO_3	SiO_2	Na_2O	Fe_3O_3	Cl	Al_2O_3	CuO	Sr
%(w)	34.40	22.98	15.89	12.51	4.27	3.22	2.92	1.76	0.89	0.82	0.18	0.011
Element	Mn	Zn	Pb	Ti	Ni	Nb	Rb	Co	Cr	Ba
%(w)	0.08	0.058	0.03	0.03	0.02	–	0.024	–	0.0063	–
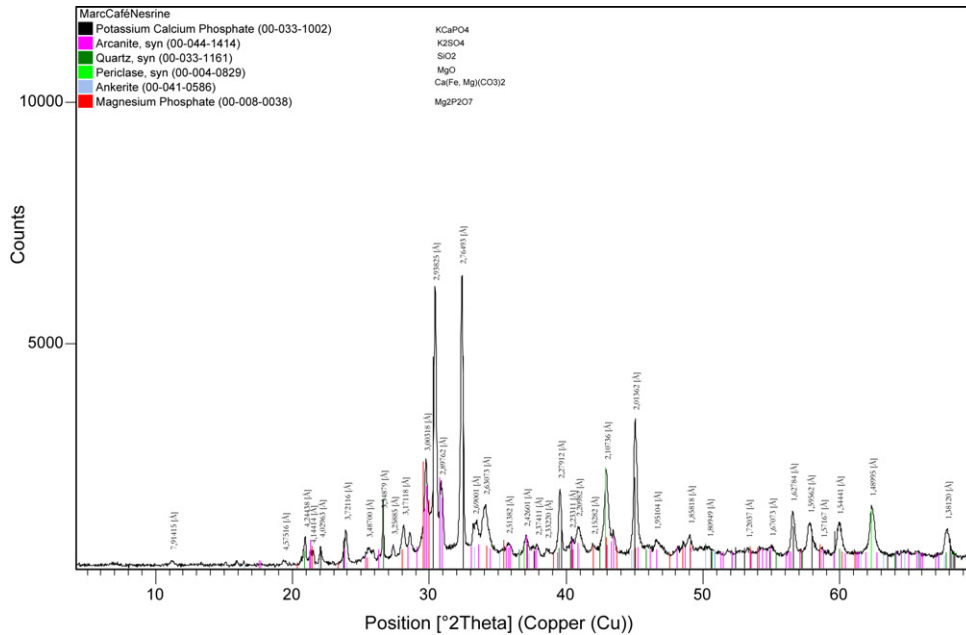
Fig. 2. XRD pattern of coffee grounds.

The main characteristic peaks at 2.76, 2.93, 2.01 and 1.62 indicate the presence of potassium, calcium, and phosphate. Other characteristic peaks show the presence of other phases like arcanite, quartz, periclase, ankerite and magnesium phosphate. The presence of these phases is well confirmed by the X-ray fluorescence analysis.

3.1.4. FTIR spectral analysis

In order to determine which functional groups were responsible for metal uptake, an FTIR analysis in solid phase was performed on the biomass in a KBr disk. FTIR spectra were obtained for adsorbent solid samples before and after the adsorption process. As shown in Fig. 3, the broad bands observed at 3435 and 3429 cm^{-1} was assigned to the stretching of O–H group due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin. The O–H stretching vibrations occur within a broad range of frequencies indicating the presence of free hydroxyl groups and bonded O–H bands of carboxylic acids [14,15]. The band at 2924 cm^{-1} indicates symmetric or asymmetric C–H stretching vibration of aliphatic acids [14,16]. The absorption peaks at 1744 and 1745 cm^{-1} was assigned to the resulting carboxyl linkage derived from xanthine derivatives such as caffeine [3]. Bands in the range of 1383 cm^{-1} is attributed to COO^{-} symmetric stretching vibration. According

to literature [17,18,3], the bands in the 1200–900 cm^{-1} range are assigned to m(S=O), showing the existence of sulphur [17]. FTIR spectra of Cd^{2+}sorbed on coffee grounds showed that the peaks expected at 3435, 2925, 1744, 1383, 1163 and 609 cm^{-1} had shifted, respectively to 3429, 2925, 1745, 1383, 1162 and 609 cm^{-1} due
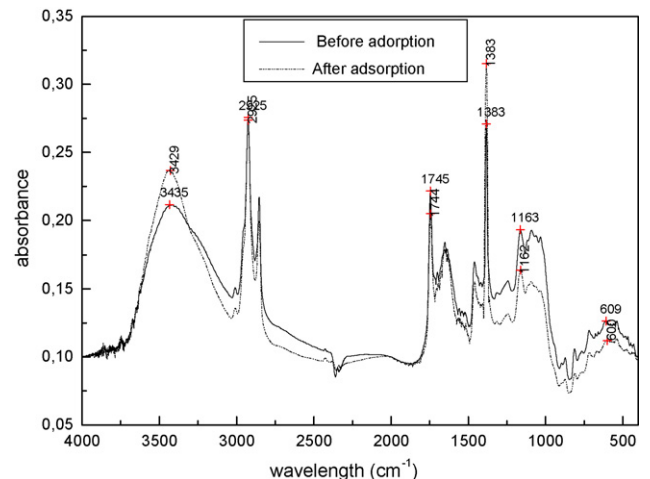
**Fig. 3.** FTIR spectra of coffee grounds before and after adsorptions.
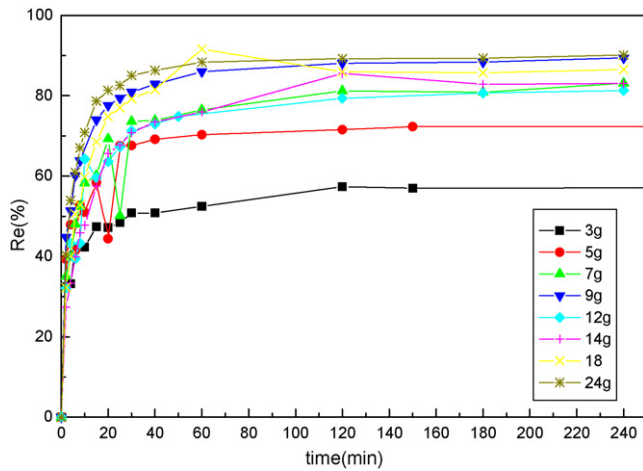
Fig. 4. Effect of contact time on the rate of adsorption of cadmium for different mass of adsorbent. pH 7, $[Cd]_0 = 100\,mg\,L^{-1}$, $d_p = 0.63–0.85\,mm$, $T = 20\,°C$

to Cd^{2+} sorption. These shifts may be attributed to the changes in counter ions associated with carboxylate and hydyroxylate anions, suggesting that acidic groups, carboxyl and hydroxyl, are predominant contributors in metal ion uptake [14,19].

3.2. Effect of operating parameters

3.2.1. Effect of contact time

The effect of contact time was studied for several mass of the adsorbent. The initial cadmium concentration was fixed at $100\,mg\,L^{-1}$, the agitation velocity at $384\,tr\,mn^{-1}$, the ambient temperature ($20\,°C$), solution pH at 7 and the particles diameter were included between 0.63 and 0.85 mm. Fig. 4 shows a rapid initial uptake rate of cadmium at the beginning until 1 h and, thereafter, the adsorption rate became practically constant. The variation in the extent of adsorption may be due to the fact that initially all sites on the surface of sorbent were vacant and the solute concentration gradient was relatively high. Consequently, the extent of cadmium species uptake decreases with the increase of contact time, which is dependent on the decrease in the number of vacant sites on the surface of coffee grounds. Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid. Then, as lower adsorption would follow, as the availed adsorption site gradually decreases, which is consistent with studies reported before [20,21]. According to the results obtained from different mass of adsorbent, the equilibrium time found is 120 min.
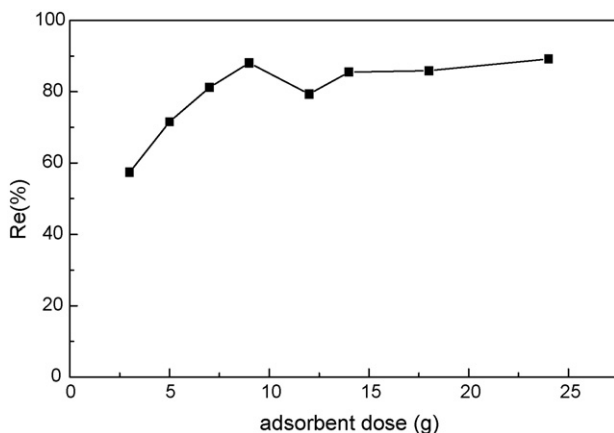
Fig. 5. Effect of adsorbent dose on the rate of adsorption pH 7, $[Cd]_0 = 100\,mg\,L^{-1}$, $d_p = 0.63–0.85\,mm$, $T = 20\,°C$.
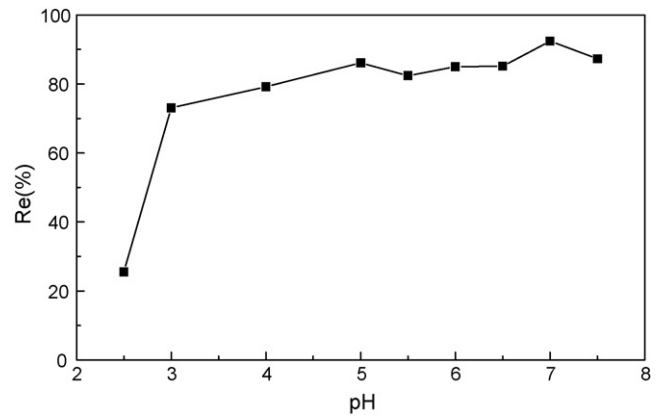
Fig. 6. Effect of initial pH on the rate of adsorption $m = 9\,g$, $[Cd]_0 = 100\,mg\,L^{-1}$, $d_p = 0.63–0.85\,mm$, $T = 20\,°C$.

3.2.2. Effect of adsorbent dosage

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The effect of coffee grounds dose, varying from 3 to 24 g, onto Cd^{2+} adsorption is depicted in Fig. 5. It is apparent that the percent removal of metal ions increases with increasing weight of coffee grounds until 9 g. However, once almost all Cd^{2+} is adsorbed, the contribution of additional coffee grounds will be insignificant. With increasing adsorbent dosage, more surface area is available for adsorption due to increase in active sites on the adsorbent then making easier penetration of metal ions to the sorption sites. The insignificant increase in uptake of Cd^{+2} at coffee grounds dosage higher than 9 g may be attributed to the presence of excess/surplus metal-binding sites on coffee grounds than the available Cd^{+2} ions present in solution at the fixed concentration of $100\,mg\,L^{-1}$. These observations are in agreement with others reported in the literature for the sorption of metal ions by different biological materials [14,22,23] and by clay [24]. From these results the optimal adsorbent dose obtained is equal to 9 g.

3.2.3. Effect of solution pH

Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent [25,26]. It has been identified as the most important variable affecting metal adsorption onto adsorbent, this partly because hydrogen ions themselves are strongly competing with adsorbate [10,27–29]. To characterize the effect of pH on Cd(II) adsorption using coffee grounds, set of batch equilibrium adsorption experiments were conducted modifying the pH from 2.5 to 7.5. The results obtained are presented in Fig. 6. The variation of the initial pH leads to a high increase of adsorption rate of cadmium (25–73%) when the pH value varies from 2.5 to 3. After this pH, we observe a low increase of the rate of cadmium adsorption on the coffee grounds until pH 7.5 (73–92%), an optimal value of pH 7 was found. At pH values less than 7, metals are in their free ionic form and as such the sharp increase in metal uptake. This leads to the hypothesis that the cell wall functional groups and their associated ionic state are responsible for the extent of adsorption. Biosorbent materials primarily contain weak acidic and basic functional groups. It follows from the theory of acid–base equilibria that, in the pH range 2.5–7, the binding of heavy metals cations is determined primarily by the state of dissociation of the weak acidic groups. Carboxyl groups (–COOH) are the important groups for metal uptake by biological materials [10,30,31]. At pH 7, there are lower numbers of competing hydrogen ions and more ligands are exposed with negative charges, resulting in greater cadmium sorption. But for pH greater
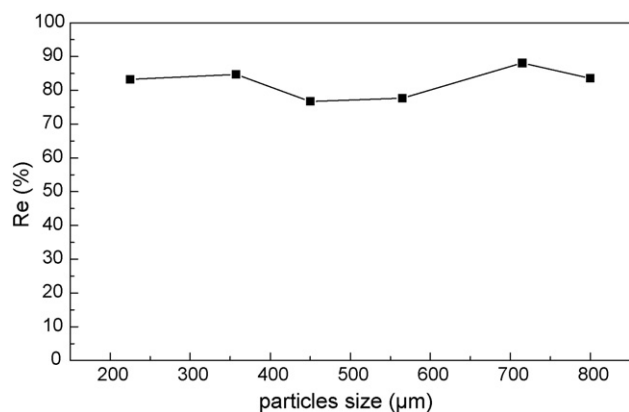
Fig. 7. Effect of particles size on the rate of adsorption pH 7, $[Cd]_0 = 100\,mg\,L^{-1}$, $m = 9\,g$, $T = 20\,°C$.

Fig. 9. Effect of temperature on the rate of adsorption pH 7, $m = 9\,g$, $[Cd]_0 = 100\,mg\,L^{-1}$.

than 7, a decrease in adsorption was observed for cadmium, this might be due to the lower polarity of cadmium ions at higher pH values. The minimal adsorption at low pH may be due to the higher concentration and high mobility of H+ ions, which are preferentially adsorbed rather than metal ions [32,33]. At higher pH values, the lower number of H+ with higher negative surface charge results in more cadmium adsorption.

3.2.4. Effect of particle size of the adsorbent

The other effective parameter on molecules adsorption is particle size of adsorbent. Maximum uptake of adsorption is a function of specific surface or external surface of adsorbent [6]. A series of experiments were performed in the range of particles size [225–800 μm] as function of contact time. According to Fig. 7 we observe that the rate of cadmium adsorption was not remarkably affected by the change in the particle size (change in surface area) of the coffee grounds. This state can indicate that the adsorption takes place at the surface of the adsorbent and the functional groups are probably responsible for the adsorption of cadmium on the coffee grounds. Similar behaviour has been found by Bozic et al. [34] in the adsorption of copper. In the following experiments we use coffee grounds coming from cafeterias as a waste without any sieving.

3.2.5. Effect of the initial concentration of cadmium

The effect of the initial cadmium concentration on the cadmium adsorption rate was investigated in the range [10–700 mg L−1] for three media (pH 7, 4, 2.5). The results presented in Fig. 8 show that the percentage of removal decreased with increasing initial
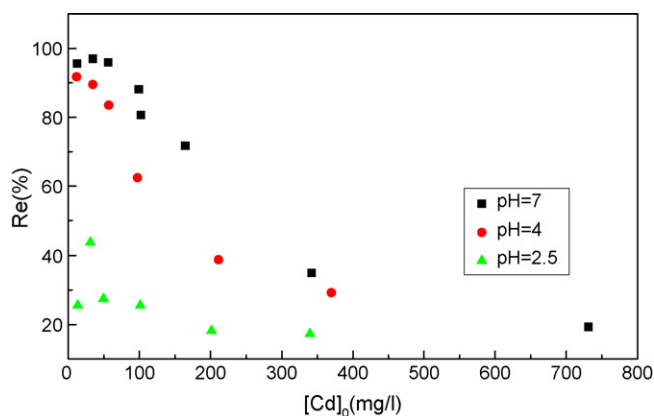
cadmium concentration and the best results were obtained for pH 7. The lower uptake at higher concentration resulted from an increased ratio of initial number of moles of cadmium to the available surface area; hence fractional adsorption becomes dependent on initial concentration. For a given adsorbent dose the total number of available adsorption sites is fixed thereby adsorbing almost the same amount of adsorbate, thus resulting in a decrease in the removal of adsorbate corresponding to an increase in initial adsorbate concentration (saturation of the adsorbent). Similar results were also reported by other researchers [20,35].

3.2.6. Effect of temperature

To investigate the effect of the temperature (20, 30, 40 and 50 °C) on the Cd(II) adsorption, the experiments were conducted at constant concentrations of Cd(II) (100 mg L−1) and different times. The results are given in Figs. 9 and 10. As can be seen from these figures, the adsorption of Cd(II) onto the surface of coffee grounds taken place quickly for three temperatures until first 10 min. It is seen that adsorption rate is constant in 120 min by increasing times at all of studied temperatures. The absorbed amount of Cd(II) ions slightly decreases when increasing temperature from 20 to 50 °C. The observed decrease in the adsorption capacity with an increase of temperature indicated that low temperatures is in favour Cd(II) ions removal by adsorption onto coffee grounds. This may be due to a tendency for the Cd(II) ions to escape from the solid phase to the bulk phase with an increase in the temperature of the solutions. This effects suggested that an explanation of the adsorption mechanism associated with the removal of Cd(II) ions onto coffee grounds involves a physical process in this situation, in which

Fig. 8. Effect of initial concentration of cadmium on the rate of adsorption for different pH media: $m = 9\,g$, $T = 20\,°C$.

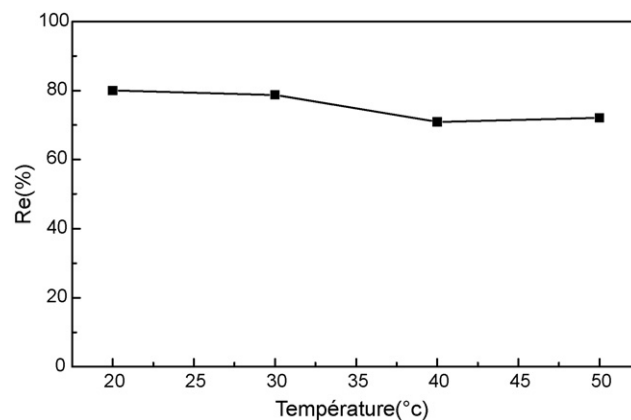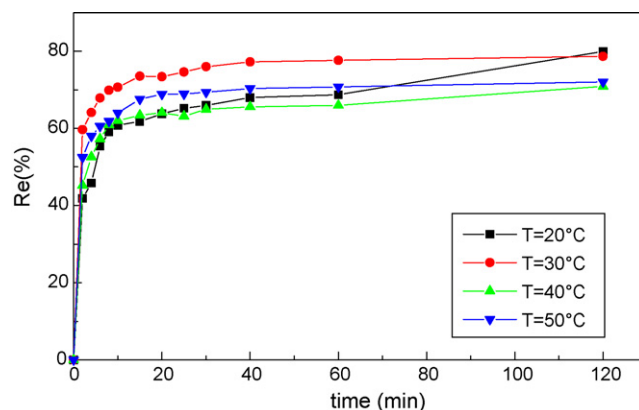**Fig. 10.** Effect of contact time on the rate of adsorption for different temperatures. pH 7, $m = 9\,g$, $[Cd]_0 = 100\,mg\,L^{-1}$.

Table 4
Isotherm constants for cadmium adsorption onto coffee grounds.

Media	Langmuir				Freundlich			Dubinin–Radushkevich			
	q_{max} (mg g^{-1})	b (L mg^{-1})	R_L	r^2	K_F	n	r^2	q_{max} (mg g^{-1})	B (mol^2 kJ^{-2})	E (kJ mol^{-1})	r^2
pH 7	15.65	0.097	0.093	0.996	3.262	0.295	0.786	11.08	3×10^{-4}	1.290	0.921
pH 4	12.19	0.055	0.154	0.978	1.692	0.370	0.919	7.09	6×10^{-4}	0.912	0.795
pH 2.5	10.46	4.949	0.002	0.756	0.111	0.728	0.898	3.49	4×10^{-2}	0.111	0.823

adsorption arises from the electrostatic interaction, which is usually associated with low adsorption heat [36]. This means that the adsorption process has an exothermic character. Similar behavior has been found by Sari et al. [24].

Additionally, it was seen that the equilibrium time was observed to be independent from the temperature.

3.3. Adsorption isotherms

In order to describe the uptake of cadmium by coffee grounds biomass, the isotherms data were analysed using three models, Langmuir, Freundlich and Dubinin–Radushkevich (D–R). The various constants of the three models were calculated and were represented in Table 4.

By comparing the correlation coefficients, it can be concluded that Langmuir isotherm provides a good model for the sorption system, which is based on monolayer sorption on to surface containing finite number of identical sorption sites. The maximum adsorption capacity increases with increasing pH, this result was previously found (optimal value of pH adsorption was found equal to 7). The maximum adsorption capacity of cadmium found was 15.65 mg g^{-1}, the value of the dimensionless parameter R_L indicates that the adsorption is favourable ($0 < R_L < 1$) and the value of the free energy estimated from the DR model $E < 8$ kJ mol^{-1} indicating that adsorption process is of physical nature. The comparison
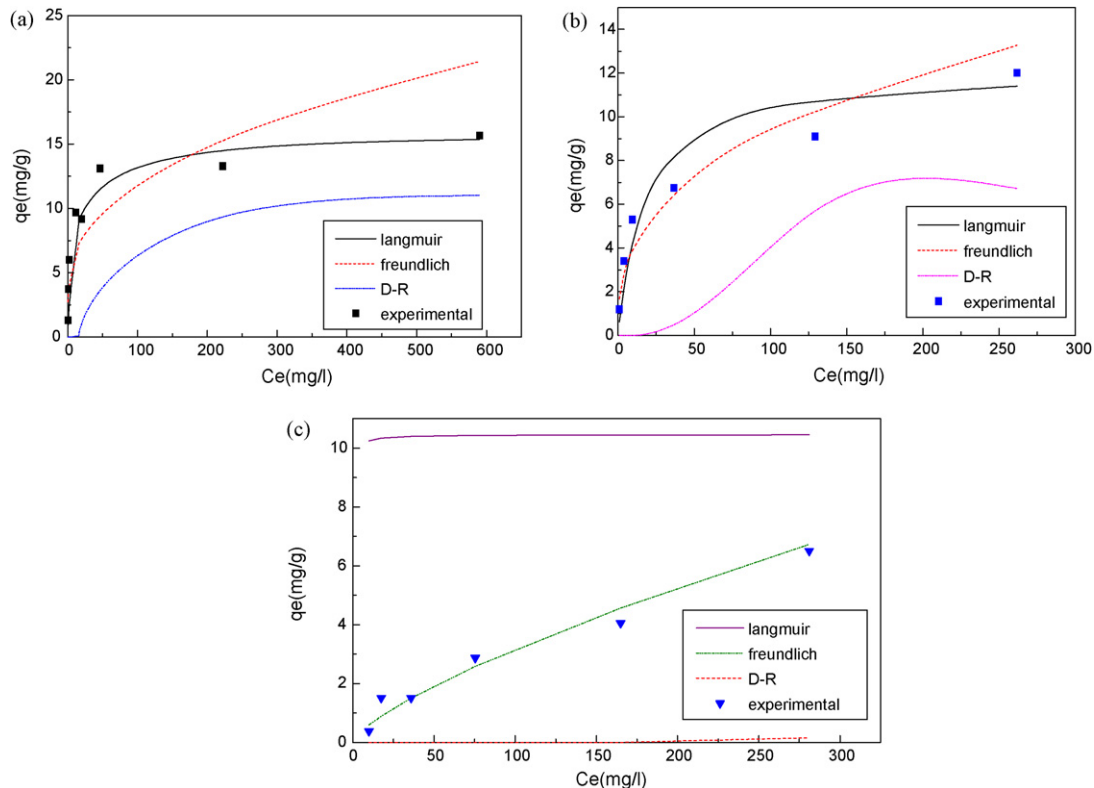
Table 5
Comparison of adsorption capacity of coffee grounds with various adsorbents.

Adsorbents	q_{max} (mg g^{-1})	References
Olive cores	7.73	[12]
Olive cake	10.56	[7]
S. anthophorbium	18.90	[11]
L. arboresens	11.50	[11]
Olive wastes	6.56	[8]
Olive cores	12.56	[8]
Degreased coffee beans	6.72	[3]
Bagasse fly ash	6.19	[37]
Commercial activate carbon F.400	8.21	[38]
Oxidized granular activated carbon	5.73	[39]
Coffee grounds	15.65	Present study

of adsorption capacity of the coffee grounds with that of various adsorbents is given in Table 5.

The coffee grounds has a high adsorption capacity as comparable with that of the other adsorbents. Therefore, considering the low cost of this natural adsorbent (waste), it can be used as an alternative material to minimize the concentration of Cd(II) in wastewater.

The isotherm profiles of cadmium adsorption at various pH values are shown in Fig. 11. It is obvious that the experimental results are well represented by the Langmuir isotherm for pH 7. However for pH 2.5 and 4, the metal adsorption obeys to the Freundlich isotherm.

Fig. 11. Experimental and adjusted isotherms for adsorption of cadmium with coffee grounds at different pH. $m = 9$ g, $T = 20\,^\circ$C, (a) pH 7, (b) pH 4, (c) pH 2.5

Table 6
Kinetic constants for cadmium adsorption onto coffee grounds.

T (°C)	Pseudo-first order model		Experience	Pseudo-second order model		
	k_1 (mn^{-1})	r^2	q_e (mg g^{-1})	q_e (mg g^{-1})	k_2 (g mg^{-1} mn^{-1})	r^2
$T = 20$ °C	0.0248	0.620	7.77	7.72	0.0298	0.993
$T = 30$ °C	0.0584	0.804	8.94	9.01	0.0957	0.999
$T = 40$ °C	0.0319	0.551	7.96	7.97	0.0611	0.998
$T = 50$ °C	0.0559	0.762	7.95	8.01	0.1035	1.000

3.4. Kinetic study

In order to define the kinetics of the cadmium adsorption, the parameters for the adsorption process were studied for contact time ranging between 2 and 240 min for different temperature (20, 30, 40 and 50 °C), by monitoring the percent removal of cadmium by adsorbents. Results presented in Fig. 10, show that the removal rate of Cd(II) ions was extremely rapid in first few minutes regardless the effect of temperature. The sorption equilibrium was achieved in 120 min. The kinetic data was fitted to the Lagergren pseudo-first order model and Ho pseudo-second order kinetic model. The kinetic rate constants obtained from first order and second order pseudo-kinetic models are given in Table 6. Though, the pseudo-second order kinetics possess high correlation coefficient value (0.99–1) than the pseudo-first order one (0.55–0.80). So, it can be concluded that cadmium sorption onto coffee grounds seems to be more pseudo-second order.

3.5. Thermodynamic parameters

A study of temperature dependence during adsorption process gives valuable information about the enthalpy and entropy changes accompanying adsorption processes [17,40].

The thermodynamic parameters such as Gibbs free energy ($\Delta G°$), enthalpy change ($\Delta H°$), entropy change ($\Delta S°$) and activation energy E_a were estimated to evaluate the feasibility and the nature of adsorption process. The value of enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were found to be respectively -11.884 kJ mol^{-1} and -47.036 J mol^{-1} K^{-1}. The negative value of $\Delta H°$ for Cd(II) removal confirms that the metal adsorption process was exothermic in nature. The negative value of ($\Delta S°$) implied that Cd(II) in bulk phase (aqueous solution) was in a much more chaotic distribution compared to the relatively ordered state of solid phase (surface of adsorbent). Similar results have been found in previous works [24,39]. Moreover, Gibbs free energy change ($\Delta G°$) was between 1.896, 2.367, 2.837 and 3.307 kJ mol^{-1} for temperatures of 293, 303, 313 and 323 K respectively. The positive $\Delta G°$ values indicated that the adsorption was not spontaneous thermodynamically. In addition, this result was in well agreement with that obtained from D–R isotherm (1.29 kJ mol^{-1}). Generally, low activation energies (5–40 kJ mol^{-1}) are characteristic of physical adsorption, while high ones (40–800 kJ mol^{-1}) suggest chemisorptions [17,41]. In this study, $E_a = 31.828$ kJ mol^{-1} for the adsorption of Cd^{2+} onto coffee grounds, indicating that the rate-limiting step in the adsorption process, might be a physically controlled type.

4. Conclusion

The good capacity of untreated coffee grounds to remove Cd(II) from aqueous solution was demonstrated in this study, highlighting its potential for effluent treatment processes.

The kinetic experiments show that the adsorption is rapid and maximum adsorption capacities achieved in 120 min. The effect of several parameters on the removal of cadmium such as adsorbent dose, initial pH of the solution, particle size of the adsorbent, initial concentration of Cd(II) and temperature have been stud-

ied. The particle size has no effect on the removal of cadmium, this result is very important and conducts us to use this adsorbent directly as a waste without any treatment. The adsorption process is a function of the adsorbent concentration, pH, metal ion concentration and temperature, the optimal parameters found are: adsorbent dose = 9 g, pH 7 and ambient temperature (20 °C). FTIR spectra showed that the principal functional sites taking part in the sorption process included carboxyl and hydroxyl groups. For pH value of 7, Langmuir isotherm model is in good agreement with the experimental data as compared to Freundlich and D–R models. The maximum adsorption capacity was found equal to 15.65 mg g^{-1} and the adsorption process is favourable and of physical nature. However, the Freundlich model fits well the experimental data for pH values of 4 and 2.5. For all the temperatures studied, the rate of adsorption was found to follow the pseudo-second order kinetics. The thermodynamic constants, $\Delta G°$, $\Delta H°$ and $\Delta S°$ of the adsorption process showed that adsorption of cadmium was exothermic and not spontaneous thermodynamically. The results indicate that coffee grounds may be used as an inexpensive, effective and easily used adsorbent without any treatment for the removal of cadmium from aqueous solutions.

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