

Cadmium Removal from Aqueous Solution by Adsorption on Spent Coffee Grounds

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Cadmium is a highly toxic element and can cause serious damages to the health of human beings. It is on the seventh position on the Agency for Toxic Substances and Disease Registry (ATSDR, 2015) list for dangerous elements. The Environmental Protection Agency (EPA) and the International Agency for Research on Cancer (IARC) have also recognized cadmium as a carcinogen. For all these reasons, in the recent years stringent limits have been set for this element both in industrial and drinking water. In this paper the potential of spent coffee grounds (SCG) for the removal of cadmium from contaminated water was investigated. Batch experiments were performed at different temperatures, i.e. 10, 25 and 40°C on untreated SCG. The size range of the SCG particles studied was $\leq 500 \mu\text{m}$. The results obtained showed that the equilibrium of cadmium on SCG was reached after 3 hours. The Langmuir isotherm provided the best correlation for the adsorption process, with a maximum adsorption capacity of 4.48 mg g^{-1} at 10 °C. Thermodynamic analysis confirmed the exothermicity and spontaneity of the phenomenon. Kinetic studies have revealed that the cadmium adsorption onto SCG followed a pseudo-second order kinetic model and the activation energy value calculated was of 14.5 kJ mol^{-1} , which have evidenced the physical nature of the process. Overall, this study strongly supports the use of SCG as an effective and economical adsorbent for the removal of cadmium from both industrial and drinking water.

1. Introduction

Heavy metals, because of their non-degradable, persistent and accumulative nature are toxic when present in trace amount. Since heavy metals are not biodegradable and have a long biological half-life, they accumulate within the organism, where they may cause poisoning, illnesses and neurological disorders (Lavecchia et al., 2016). The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes. Cadmium is the seventh element in the ranking of toxic priority, owing to its potential for causing acute and chronic metabolic disorders, such as serious renal damage, anemia, hypertension and itai-itai disease (Kamsolian et al., 2011; Yue et al., 2016). In fact, the World Health Organization (WHO) recommended limit dose of $5 \mu\text{g L}^{-1}$ ought not to be exceeded. The treatments used for the removal of heavy metals (Rossetti V.A. et al., 2002) such as copper, lead, cadmium, chromium and mercury are almost the same. They are: chemical precipitation (Ku and Jung, 2001) and electrochemical methods (Chen and Wang, 2008), mostly used in the past two decades for direct or indirect (Petrucci et al., 2012) wastewater treatment. Their disadvantage is the cost. Nowadays, adsorption is identified as an effective and economic method for the heavy metal wastewater treatment. One of its major advantage is that adsorbents can be reused: adsorption is sometimes reversible and the adsorbent can be regenerated using a desorption process and is also preferred due to its efficiency of removal from dilute solutions (Azouaou et al., 2010). The use of activated carbon (AC) (De Filippis et al., 2013) and silico-aluminous materials (Ippolito et al., 2016) is very common but also expensive. From an economical point of view new low-cost adsorbents, such as agricultural wastes (rice, tea, coffee waste, fruit peels) have been studied (Dhir, 2014; Zuorro et al., 2013). The advantages of using bio-adsorbents are low cost, biodegradability

and no disposal problems. The use of SCG to remove lead from aqueous solution was described in a previous work (Lavecchia et al., 2016). In this paper the equilibrium, kinetics and thermodynamic of the cadmium adsorption onto the SCG were analyzed in order to estimate the typical phenomenon parameters.

2. Experimental

2.1 Materials and Methods

Cadmium chloride (CAS No.10108-64-2) with purity >99% was purchased from Carlo ErbaS.p.A. (Milan, Italy). Synthetic cadmium solutions were prepared by adding an appropriate amount of cadmium chloride to distilled water. Spent coffee grounds (SCG) were obtained from an industrial plant located in Ciampino (Roma, Italy). The adsorbent was preliminary ground and sieved by ASTM No. 35 sieve (nominal mesh opening $\leq 500 \mu\text{m}$). The resulting material was dried at 40°C in an electric oven for several hours in order to avoid microbiological alteration, obtaining a final humidity of 6,97%. Then it was cooled in air to room temperature, stored in closed containers and kept in the dark until its use. One g of the ground adsorbent was contacted with 100 mL of cadmium solution at different initial concentrations for different time intervals under agitation of 300 rpm. After that, the samples were filtered on paper and the residual cadmium concentration was measured. The same procedure was used for all the tests. In these experiments the liquid-to-solid ratio was set at 100 mL g^{-1} and the initial cadmium concentration was varied between 5 and 100 mg L^{-1} . The interval times ranged between 0.5 and 24 h. Batch experiments were performed at three different temperatures, i.e. $10^\circ \pm 2^\circ\text{C}$, $25 \pm 2^\circ\text{C}$ and $40^\circ\text{C} \pm 2^\circ\text{C}$. The concentration of cadmium in the aqueous solution was determined by an X-ray fluorescence spectrometer (TRACeR IV, Bruker AXS, Germany). Standard cadmium solutions at concentration ranging from 2 to 300 mg L^{-1} were used to construct the calibration curve (ASTM, 2008; Kaiser and Wright, 2011).

2.2 Adsorption equilibrium study

The equilibrium concentration of cadmium in the liquid phase (c_e) and in the adsorbed phase (q_e) were calculated according to Eq.1:

$$q_e = \frac{V_L}{m} (c_0 - c_e) \quad (1)$$

where V_L is the volume of the aqueous solution, m is the mass of adsorbent, c_0 e c_e are the initial and the equilibrium cadmium concentrations. Different models were used to analyze the equilibrium data (DjatiUtomo and Hunter, 2009): Langmuir (Eq. 2), Freundlich (Eq. 3) and Dubinin-Radushkevich (D-R) (Eq. 4).

$$q_e = \frac{q_{max} b c_e}{1 + b c_e} \quad (2)$$

$$q_e = K_F c_e^{1/n} \quad (3)$$

$$q_e = q_{exp} \exp\left(-B \left(RT \ln \left(1 + \frac{1}{c_e}\right)\right)^2\right) \quad (4)$$

In Eq.2 q_{max} is the maximum adsorption capacity (mg g^{-1}), corresponding to a complete monolayer on the adsorbent, and b is the Langmuir constant (L mg^{-1}), which can be related to the affinity of the adsorbing species for the adsorption sites on the solid. In Eq.3 K_F is the Freundlich adsorption capacity (mg g^{-1}) and n is a dimensionless constant that represents the adsorption intensity. It is generally stated that values of n in the range 2–10, 1–2 and <1 indicate, respectively, good, moderate and poor adsorption characteristics. In Eq.4 B ($\text{mol}^2 \text{kJ}^{-2}$) is a constant related to the adsorption energy, R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the gas constant, and T (K) is the absolute temperature. The constant B gives the mean free energy E (kJ mol^{-1}) of adsorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution. It can be computed from the following relationship:

$$E = \frac{1}{(2B)^{0.5}} \quad (5)$$

This parameter gives information about the adsorption nature. Values of $E < 8 \text{ kJ mol}^{-1}$ indicates physical adsorption meanwhile a magnitude of E between 8 and 16 kJ mol^{-1} evidences a chemisorption process (Azouaou et al., 2010).

2.3 Adsorption kinetics and activation energy

The kinetics of adsorption was studied by using two empiric models: pseudo-first order and pseudo-second order models (Azouaou et al., 2010; Dávila-Guzmán et al., 2011; Yen et al., 2016). Both of them take into account the amount of solute adsorbed which is an important information for determining the batch reactor volume. The pseudo-first order model or Lagergren model is described by the following equation:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (6)$$

integration of Eq.6 using $t=0, q=0$ and $t=t, q=q_t$ as boundary conditions is reported in Eq.7.

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

where k_1 is the rate constant of the pseudo-first order model (h^{-1}). The pseudo-second order model and its integration, using the same boundary conditions, are shown in Eq.8 and Eq.9, respectively.

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where k_2 is the rate constant of the pseudo-second order model ($\text{g mg}^{-1}\text{h}^{-1}$). The activation energy was calculated by using the linearized form of Arrhenius equation:

$$\ln k = \ln A_0 - \frac{E_a}{RT} \quad (10)$$

where A_0 is the independent temperature factor ($\text{g mg}^{-1} \text{h}^{-1}$), R and T as defined previously, and the rate constant k assumes the k_2 value from the pseudo-second order kinetic model which provided the best fitting for the kinetic study. Generally, low activation energies ($5\text{--}40 \text{ kJ mol}^{-1}$) are characteristic of the physical adsorption, while high ones ($40\text{--}800 \text{ kJ mol}^{-1}$) suggest chemisorption (Azouaou et al., 2010)

2.4 Thermodynamic study

The thermodynamic parameters can be determined by using the equilibrium constant K_e , which depends on the temperature. The change in the standard free energy, ΔG° , the standard enthalpy, ΔH° , and the standard entropy, ΔS° , were calculated by using the following equations:

$$\Delta G^\circ = -RT \ln K_e \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

Combining Eq.11 and Eq.12 van't Hoff equation is obtained:

$$\ln K_e = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

3. Results and discussion

X-ray Fluorescence spectroscopy (XRF) analysis of SCG was carried out in order to have a characterization and composition of the adsorbent used. The results of SCG characterization are reported in a previous work (Lavecchia et al., 2016). Potassium, calcium, sulfur and phosphorus were the elements present in higher amounts.

3.1 Equilibrium studies

The time needed to reach the equilibrium was of the order of 3 h and it was independent of the initial cadmium concentration, as shown in Figure 1. From that time onwards there is not variation in the Cd^{2+} concentration measured in the solutions after filtration, and a plateau is obtained.

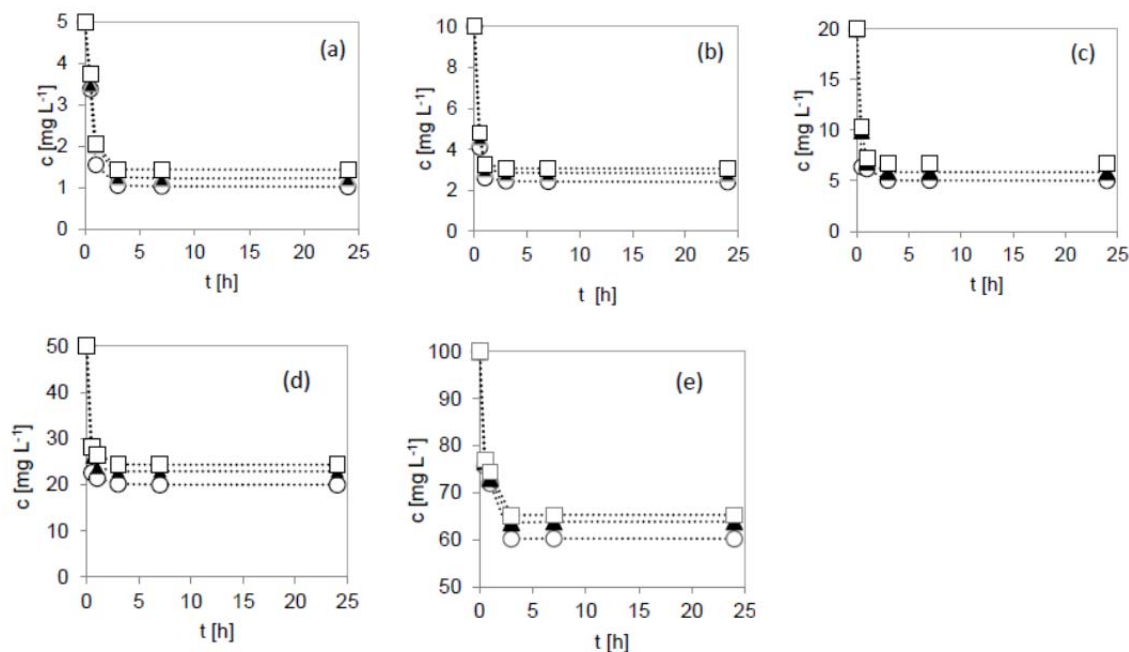


Figure 1: Cadmium concentration decay curves at the different studied temperatures: 10°C (\circ), 25°C (\blacktriangle) and 40°C (\square). Different cadmium concentration starting values were used: (a) 5 mg L⁻¹, (b) 10 mg L⁻¹, (c) 20 mg L⁻¹, (d) 50 mg L⁻¹ and (e) 100 mg L⁻¹.

The parameters appearing in the Eq. (2) to (5) were obtained by fitting the experimental data to the linearized form of each equation. Langmuir equation provided the best fit to the data at all the studied temperatures (high R^2 value) as shown in Figure 2, in which is reported the data fitting of the run performed at 10°C, identified in our test as the most favorable temperature for cadmium adsorption. The parameters collected in this case are $q_{max} = 4.48 \text{ mg g}^{-1}$ and $b = 0.09 \text{ L mg}^{-1}$ for the Langmuir equation, $K_F = 0.46 \text{ mg g}^{-1}$ and $n = 1.74$ for the Freundlich equation and $q_{max} = 2.37 \text{ mg g}^{-1}$, $B = 0.80 \text{ mol}^2 \text{ kJ}^{-2}$ and $E = 0.79 \text{ kJ mol}^{-1}$ for the D-R equation.

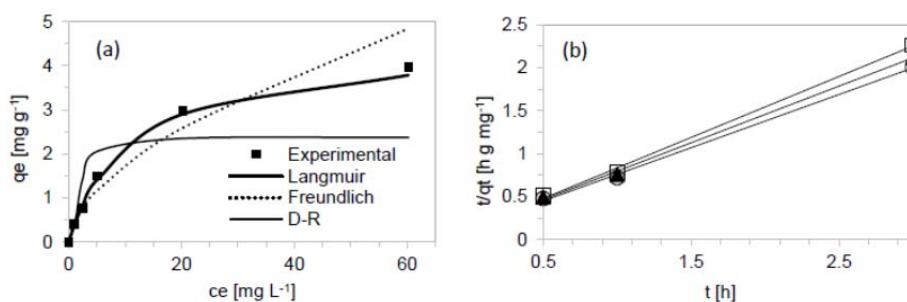


Figure 2: (a) Comparison of adsorption model responses for cadmium adsorption on SCG at $T=10^\circ$; (b) Pseudo-second order plot for cadmium adsorption ($c_0=20 \text{ mg L}^{-1}$) on SCG at the different studied temperatures: 10°C (\circ), 25°C (\blacktriangle) and 40°C (\square).

To confirm that, in Figure 3 and Table 1 are displayed the adsorption isotherms and adsorption parameters, respectively. The highest value of q_{max} is reached at 10°C, as already mentioned.

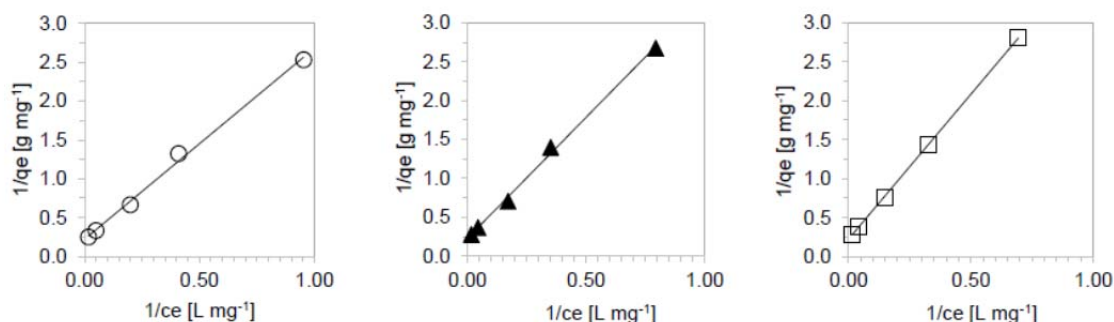


Figure 3: Langmuir plot for cadmium adsorption on SCG at the different studied temperatures. 10°C (○), 25°C (▲) and 40°C (□).

Based on these results, it can therefore be inferred that cadmium adsorption on SCG is well described by the Langmuir model. This result is in agreement with those of Azouaou et al. (2010), who studied the adsorption of cadmium on the SCG; of Dávila-Guzmán et al. (2011), who investigated the biosorption of lead on the same material and of Yen et al. (2016) who investigated the adsorption of cadmium on the SCG by Taguchi optimization. The maximum adsorption capacity found in the work is in accordance with the value estimated by Yen et al. (2016) and three times lower than that found by Azouaou et al. (2010).

3.3 Adsorption kinetics and activation energy

Figure 2b shows the plot of the experimental data using the linearized form of the pseudo-second order model, at an initial concentration of 20 mg L⁻¹ and at the different studied temperatures. From the R² values we can conclude that the Ho model gives the best fit to the data and we could estimate the k₂ values (Table 2).

Table 1 Langmuir and pseudo-second order coefficients.

T [°C]	Langmuir			Pseudo-second order		
	q _{max} [mg g ⁻¹]	b [L mg ⁻¹]	R ²	q _e [mg g ⁻¹]	k ₂ [g mg ⁻¹ h ⁻¹]	R ²
10	4.484	0.091	0.996	1.62	2.69	0.998
25	4.342	0.074	0.997	1.52	3.12	0.998
40	4.440	0.060	0.999	1.41	3.96	0.997

These results are in agreement with those of Azouaou et al. (2010) and of Yue et al. (2016). Otherwise, the q_e values obtained with this model were similar to the experimental values of q_e.

Based on these results, we can conclude that the cadmium adsorption onto the SCG follows a pseudo-second order kinetics. Moreover, utilizing Arrhenius equation, an activation energy value of 14.5 kJ mol⁻¹ was obtained, this result confirms the physical nature of the process.

3.4 Thermodynamic study

From this study we obtained the following values: ΔG°=-21.74 kJ mol⁻¹, ΔH°=-9.95 kJ mol⁻¹, ΔS°=0.042 kJ mol⁻¹ K⁻¹. The negative results for ΔG° and ΔH° confirmed the spontaneity and the exothermicity of the process, while the positive value of ΔS° indicated a much more chaotic distribution of Cd²⁺ in the solid phase compared with the bulk phase. In this case, where the Langmuir isotherm is the model that best described the data, K_e assumes the value of the parameter b of Langmuir, according to the model's mathematical deduction.

4. Conclusions

The SCG examined in this study showed promising properties as low-cost and effective adsorbent materials for the removal of cadmium from water. Obtained experimental data showed that adsorption equilibrium of cadmium on SCG is well described by the Langmuir equation, which evidences a monolayer-type adsorption. The cadmium adsorption on to the SCG follows a pseudo-second order kinetics, while evaluation of thermodynamic parameters demonstrates that the process is exothermic and spontaneous. Furthermore, evaluation of activation energy indicated the physical nature of the adsorption process. Future research should be directed at studying the adsorption mechanism both batch and continuous mode, and assessing the suitability of SCG for the removal of other metal or organic contaminants from water.

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