Research Article
Assessment of Untreated Coffee Wastes for the Removal of Chromium (VI) from Aqueous Medium

Ilyasse Loulidi,1 Fatima Boukhlifi,1 Mbarka Ouchabi,2 Abdelouahed Amar,1 Maria Jabri,1 Abderahim Kali,1 and Chaimaa Hadey3

1Laboratory of Chemistry and Biology Applied to the Environment, Faculty of Sciences, Moulay Ismail University, BP 11, 201-Zitoune, Meknes, Morocco
2Laboratory of Catalysis and Corrosion of Materials, Chouaib Doukkali University, Faculty of Sciences El Jadida, BP. 20, El Jadida, Morocco
3Engineering Sciences and Trades Laboratory, ENSAM, University Moulay Ismail, Meknes, Morocco

Correspondence should be addressed to Ilyasse Loulidi; il.loulidi@gmail.com

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1.Introduction
Urbanisation, industrialisation, and globalisation are leading to increasing water pollution [1]. Water pollution is one of the most important issues facing scientists today. Among the major water pollutants, chromium is the highest priority toxic pollutant, according to the US Environmental Protection Agency [2]. In nature, chromium generally has two oxidation states, Cr(III) and Cr(VI) [3]. Cr(III) is less toxic and essential for the human body [4]. The toxicity of Cr(VI) is much higher than that of Cr(III). Cr(VI) is toxic, carcinogenic, and mutagenic and associated with reduced plant growth and changes in plant morphology [5]. Cr(VI) is generally used in the manufacture of pigments, in the treatment of metal surfaces, and in the chemical industry as an oxidising agent [6]. Untreated effluent from these industries may contain 10 to 100 mg/L of Cr(VI) [7].

According to current WHO standards [8], the permissible concentration of Cr(VI) in drinking water is 0.05 mg/L and 0.1 mg/L for surface water. For Cr(III), a concentration of 5 mg/L is the admissible limit. Therefore, the removal of Cr(VI) from wastewater is very important to make the environment safe and clean. For this purpose, several methods have been used, for example, filtration, electrochemical precipitation, and ion exchange [9]. These processes have many limitations such as the high cost, formation of toxic byproducts, and production of sludge [10]. Compared to all of them, adsorption has been proven to be efficient in economic and operational terms [11]. Commercial activated carbon cannot be used in the case of effluent treatment because of its high cost and its difficult regeneration [12]. For this reason, relatively effective, inexpensive, and readily available alternatives are in high demand today [13]. Research has focused on the use of waste
as a bioadsorbent, for example, waste potato peels [14], *Lathyrus sativus* husk [15], orange peels [16], tea waste [17], rice husk [18], citrus peels [19], *Cortaderia selloana* flower spikes [20], garlic straw [21], foxtail millet shell [22], Corn cobs [23], and olive cake waste [24]. However, there is a lack of studies on the use of spent coffee grounds (SCGs) as an adsorbent. Coffee is the world’s second most important commodity after petroleum and the largest agricultural product in terms of volume [25]. According to the International Coffee Organisation, world coffee production amounts to 7.4 billion kilos per year. The main producers are Brazil (40%), Vietnam (20%), Colombia (10%), Indonesia (7%), and also Ethiopia (5%). Almost all of these quantities are discharged as solid waste [26]. The valorisation of this residue presents very important environmental and socio-economic advantages. This study is part of this perspective and consists of examining the possibility of SCGs to remove Cr(VI) from aqueous mediums. The parameters of isotherms, kinetics, and thermodynamics are analysed, as well as the factors influencing adsorption. In addition, the regeneration of the SCGs and a cost estimate were made to show the cost-effectiveness of using the SCGs as an adsorbent.

2. Materials and Methods

2.1. Preparation and Characterisation of Adsorbent. SCGs used in this study were collected from a cafeteria in the city of Meknes (Morocco). The raw material was washed several times with hot distilled water (60°C) and then dried at 105°C in an oven for 24 hours. The dry product was then passed through a sieve to retain a grain size of <250 μm and was stored in clean, dry glass flasks. The adsorbent was used in all experiments without any further treatment. The adsorbent characterisation is an important factor in explaining the adsorption mechanism. The raw SCGs used in this study were subject to several measurements.

**FTIR:** chemical functional groups, present on the surface, were carried out by Fourier Transform Infrared Spectroscopy, using an infrared spectrometer (Shimadzu, JASCO 4100). The samples were analysed as very well dried KBr pellets of about 4% (w/w). The spectra were recorded from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹ and 16 scans per sample.

**TGA:** thermogravimetric analyses were carried out in the TA60 SHIMADZU equipment. The measurements were carried out on a 20 mg sample, between 25 and 600°C, with a linear increase of 10°C/min in the open air.

**XRD:** crystalline phases of the SCGs were evaluated by X-ray diffraction using a diffractometer (Brucker-AXS D8) with a copper tube (λ = 1.5406 Å). The radiation was generated at 40 mA and 40 kV. The diffraction angle of 2θ was measured at a step size of 0.02 and exposure of 1s at each step.

**pHₚzc:** point zero charge has been determined by the salt addition technique [27]. In a series of beakers containing 40 ml of NaCl solution (0.1 M) each, a mass of 0.2 g of SCGs has been added. The pH₁ was adjusted with a solution of HCl (0.1 M) and NaOH (0.1 M). The pH₁ values were measured after 24 hours. pHₚzc was obtained from the plot of ΔpH (=pH₁−pH₀) vs. pH₁ at ΔpH = 0.

2.2. Preparation of Cr(VI) Solutions. In this study, the analytical quality potassium dichromate K₂Cr₂O₇ (Sigma Aldrich. p.a. ≥ 99.0%; molecular weight 294.19 g/mol) was used to prepare a stock solution of Cr(VI) by dissolving 2.828 g in 1000 ml of distilled water. Experimental solutions, of the required concentrations, were obtained by diluting the stock solution with distilled water.

2.3. Adsorption Experiments. The adsorption tests were carried out in batch mode and at room temperature. A dose of SCGs was mixed with 20 ml of synthetic Cr(VI) solution in 50 ml beakers. Agitation was performed by a magnetic stirrer at 200 rpm. The effect of different parameters on the removal of Cr(VI) was studied by varying contact time (5–180 min), pH (1–8), adsorbent dose (0.5–7 g/L), and temperature (25–50°C). The adsorption kinetic studies are carried out on a solution with a concentration of 100 mg/L at pH 4 and the optimal adsorbent dose of 2.5 g/L and at different temperatures (20, 25, 30, and 40°C). Adsorption isotherm experiments were performed by contacting a fixed dose of SCGs (2.50 g/L) with 20 ml of Cr(VI) solution with different initial concentrations from 10 to 200 mg/L at pH 4 and temperature 25°C.

After each experiment, the adsorbent was separated from the solution by centrifugation at 3000 rpm for 20 min. The residual concentration of Cr(VI) in the solution was measured by a UV/visible spectrometer (Shimadzu, UV1240), using 1–5 diphenylcarbazide as a complexing agent in an acidic medium at wavelength 540 nm. The adsorbed amount of Cr(VI) 𝑞ₑ (mg/g) and the percent removal 𝑅ᵣ (%) were determined by the following equations [28]:

\[
q_e = \frac{(C_0 - C_t) V}{m},
\]

\[
R_t = \left(\frac{C_0 - C_t}{C_0}\right) 
\]

where \(C_0\) is the Cr(VI) initial concentration and \(C_t\) is the concentration at time \(t\) (mg/L), \(V\) is the solution volume (L), and \(m\) is the adsorbent mass (g).

\[
R^2 = \frac{\sum_{i=1}^{n} (q_{e,cal} - q_{e,exp})^2}{\sum_{i=1}^{n} (q_{e,cal} - q_{e,exp})^2 + \sum_{i=1}^{n} (q_{e,cal} - q_{e,exp})^2}. \]

In order to evaluate the performance and validity of kinetic and isotherm models, the coefficient of determination \((R^2)\) and the chi-square test \((\chi^2)\) were used [29]:

\[
\chi^2 = \frac{\sum_{i=1}^{n} (q_{e,exp} - q_{e,cal})^2}{q_{e,cal}},
\]

where \(q_{e,cal}\) and \(q_{e,exp}\) are the calculated and experimental adsorption capacities, respectively (mg/L).
3. Results and Discussion

3.1. Adsorbent Characterisation. FTIR analysis (Figure 1(a)) revealed that the SCGs have absorption bands typical of lignocellulosic materials. The broadest band of the spectrum, centred at 3441 cm\(^{-1}\), corresponds to the stretching of the O-H bonds [30] of the phenolic compounds composing the waste. The bands at 2934 cm\(^{-1}\) and 2852 cm\(^{-1}\) are attributed to the stretching vibration of the aliphatic C-H bonds [30]. The band at 1740 cm\(^{-1}\) is due to the stretching vibration of nonconjugated C=O bonds. These vibrations are mainly corresponding to the aldehyde, ketone, ester, and carboxylic acid functions of pectin and hemicelluloses and xanthene derivatives such as caffeine [31, 32]. According to the literature [31, 33], peaks around 1644, 1465, 1379, and 1242 cm\(^{-1}\) indicate the presence of COO, CO, and COO\(^{-}\) groups on the adsorbent surface. The other bands between 1200 and 1000 cm\(^{-1}\) are attributed to the stretching vibration of the C=O bonds of the aromatic compounds, the acetyl and carboxylic acid functions [34].

The TGA curves (Figure 1(b)) show the weight loss of a 20 mg sample of SCGs when exposed to heating from 20 to 600°C. The evolution can be divided into three steps. The first begins at about 60°C and corresponds to a slight weight loss of about 10.1% due to evaporation of water (dehydration of the sample), the second stage (290°C < T < 390°C) during which the greatest loss of mass occurs. In this stage, depolymerisation and decomposition of polysaccharides occur, resulting in a weight loss of 50.2%. The third and final stage corresponds to the carbonisation of the SCGs (390°C < T < 600°C) with a weight loss of 26.8%.

To evaluate the crystallinity of the SCGs, the cellulose spectra from the International Centre for Diffraction Data Database (ICDD) were used as a reference. The SCGs are mainly composed of cellulose, lignin, and hemicelluloses. These last two polymers being amorphous materials, the peaks situated at 15.7’ and 22.6’ on the X-ray diffractometry spectra (Figure 1(c)), are evidence of the crystallinity of the cellulose. These values are, respectively, characteristic of the (110) and (200) planes of cellulose [35]. In comparison, the DRX pattern is similar to that of other lignocellulosic wastes [36, 37].

The point zero charge pH\(_{pzC}\) is the pH value at which the surface charge of the adsorbent is zero [38], pH\(_{pzC}\) determines the working pH range to favour the electrostatic attraction between the adsorbent and the adsorbate. Figure 1(d) shows that the pH\(_{pzC}\) of the SCGs is equal to 5.3. This value is comparable to that reported by other researchers [32, 39].

3.1.1. Effect of Solution pH. The effect of pH on the adsorption of Cr(VI) was studied at an initial concentration of 100 mg/L and an adsorbent dose of 2.5 g/L. Figure 2(a) shows that the maximum elimination corresponds to a pH value of about 4 (88.8%), with decreasing values on either side of this pH. The effect of pH on metal adsorption is strongly related to these two main factors: the chemistry of the metal in solution and the ionic state of the surface functional group [41]. As the pH\(_{pzC}\) is equal to 5.3, so the surface is positive when the pH is below 5.3 and it is negative when the pH is above 5.3. Furthermore, Cr(VI) exists in solution in different ionic forms (Figure 2(b)). At pH = 2–5, the HCrO\(^+\) ions are predominant in the solution, diffusing and adsorbing more easily and in greater quantities due to the strong attraction exerted by the surface. At pH above 5 the surface of the adsorbent becomes negatively charged and there is an electrostatic repulsion which justifies the drop in Cr(VI) removal. Similar patterns have also been reported for the adsorption of Cr(VI) on various wastes [42–44]. This suggests that adsorption is controlled by electrostatic forces (physisorption).

3.1.2. Effect of Adsorbent Dose. The effect of adsorbent dose was studied in the range of 0.5 to 7 g/L for an initial Cr(VI) concentration of 100 mg/L and pH 4. The curve in Figure 3 shows that the increase in the adsorbent dose leads to an increase in the Cr(VI) removal rate, up to a dose of 2.5 g/L, where it remains unchanged. This may be due to the reduction of the concentration gradient between the Cr(VI) ions on the adsorbent surface and the Cr(VI) ions in the liquid solution. Therefore, the optimal dose is determined to be about 2.5 g/L. Nur-E-Lam [45] studied the removal of Cr(VI) from leather industry wastewater by adsorption on tea leaf waste. They showed that 14 g/L is required to adsorb 95.42% of Cr(VI). In another study, Hakan Çelebi [42] tested the efficiency of three tea wastes (black tea waste (WBT), green tea waste (WGT), and rooibos tea waste (WRT) in the adsorption of Cr(VI)); the experimental results showed that the optimal dose is 1 g/L, 1.5 g/L, 3.5 g/L for WBT, WGT and WRT, respectively.

3.1.3. Effect of Contact Time and Temperature. The results of the time effect on adsorption are shown in Figure 4. For the four temperatures, adsorption is carried out in two stages, the first stage being fast and the second slow. This type of two-phase adsorption is also mentioned in other studies [46–48]. Equilibrium is reached after 90 minutes for all temperatures. The curves also show that the increase in temperature is unfavourable to the removal of Cr(VI), indicating that the adsorption is exothermic [49].

3.2. Adsorption Kinetics. Pseudofirst-order (PFO) and pseudosecond-order (PSO) models were commonly used to fit the experimental data and to calculate kinetic parameters. Equations (5) and (6) represent the nonlinear form of the PFO and PSO models, respectively [50]:

\[
q_t = q_e \left(1 - e^{-k_1t}\right),
\]

\[
q_t = \frac{q_e^2k_2t}{1 + q_ek_2t},
\]

where \(q_t\) (mg·g\(^{-1}\)) and \(q_e\) (mg·g\(^{-1}\)) are the quantities of adsorbed Cr(VI) at the time \(t\) and at equilibrium, \(k_1\) (min\(^{-1}\))
Figure 1: (a) Determination of pHpzc for the SCGs; (b) FTIR spectra for SCGs (c) XRD diffractogram for SCGs; (d) TGA curve obtained for SCGs.

Figure 2: (a) The effect of pH. (b) Speciation diagram of Cr(VI). Source: [40].
and $k_2$ (g.mg$^{-1}$.min$^{-1}$) are the constants of pseudo-first-order and pseudo-second-order models, respectively.

The representation of the two models is given in Figure 5, and the values of the different kinetic parameters are shown in Table 1. A comparison of the values of the error functions $\chi^2$ and $R^2$, obtained for all temperatures, clearly shows that the pseudo-second-order model is the most suitable for describing the kinetics of adsorption. The value of the initial adsorption rate $h$ (mg.g$^{-1}$.min$^{-1}$), at different temperatures, was calculated using the following equation [51]:

$$h = K_2 \cdot q_{t=0}^{ij}.cal.$$  (7)

It can be seen from Table 1 that an increase in temperature leads to an increase in the initial rate of adsorption. In conjunction with other studies, the adsorption of Cr(VI) on other lignocellulosic wastes is of pseudosecond-order [52, 53].

The activation energy $E_a$ of Cr(VI) adsorption on the SCGs can be calculated from the Arrhenius equation (8) [54]:

$$\ln (K_2) = \ln (A) - \frac{E_a}{RT}$$  (8)

where $K_2$ is the pseudosecond-order rate constant (g.mg$^{-1}$.min$^{-1}$), $T$ is the absolute temperature (°K), $R$ is the perfect gas constant (8,314J.mol$^{-1}.K^{-1}$), $A$ is the pre-exponential factor (min$^{-1}$), and $E_a$ is activation energy (kJ.mol$^{-1}$)

By plotting $\ln (k_2)$ versus $1/T$ (figure not shown), $E_a$ was obtained from the slope of the linear plot. The value of $E_a$ is found equal to 10.92kJmol$^{-1}$. $E_a$ can give an idea of the type of adsorption. According to the literature [55], this adsorption is of the physisorption type.

### 3.3. Adsorption Isotherms.

In order to describe the phenomenon governing the retention of Cr(VI) on the SCGs and to calculate the maximum amount of adsorption, the study of the adsorption isotherm is essential. The adsorption isotherm is the relationship between the quantity adsorbed at equilibrium and the concentration remaining in the solution at constant temperature and pH. The experimental results were analysed by the Langmuir, Freundlich, and Temkin models, which are expressed by the following equations, respectively [56]:

$$q_e = q_mK_LC_e \left(1 + K_LC_e\right)^{-1},$$  (9)

$$q_e = K_FC_e^{1/n},$$  (10)

$$q_e = \frac{RT}{B} \ln (AC_e),$$  (11)

where $q_t$ (mg.g$^{-1}$) and $q_e$ (mg.g$^{-1}$) are the amounts of dye adsorbed at $t$ and equilibrium. $C_e$ (mg/L) is the equilibrium concentration; $q_m$ (mg/g) is the maximum adsorption capacity; $K_L$ (L/mg) is Langmuir’s constant; $K_F$ (mg.g$^{-1}$) (L.mg$^{-1}.mg^{-1}$) and $n$ are Freundlich’s constants. $A$ and $b$ are Temkin’s constants. $R$ is the universal gas constant (8,314J mol$^{-1}.K^{-1}$), and $T$ is the absolute temperature (°K).

Figure 6 shows the nonlinear curves of these models, and Table 2 shows the calculated nonlinear regression constants of these three models. According to the table, the Langmuir model has the largest value of $R^2$ and the smallest value of $\chi^2$. This indicates that the Langmuir model is the most adequate model to describe the Cr(VI) adsorption equilibrium on the SCGs. Retention is, therefore, on homogeneous adsorption sites without interaction and in the form of a monolayer [56]. The maximum Cr(VI) adsorption capacity on SCGs ($q_m = 42.9$ mg/g) is better than those reported in the literature for other adsorbents, as shown in Table 3.
Table 1: The pseudofirst-order and pseudosecond-order adsorption rate constants.

| Kinetic model     | Parameters | 298     | 303     | 313     | 323     |
|-------------------|------------|---------|---------|---------|---------|
|                   | $q_e$, exp (mg g$^{-1}$) | 35.52   | 35.02   | 34.66   | 33.98   |
| Pseudofirst-order | $k_1$ (min$^{-1}$) | 0.0521  | 0.0463  | 0.0440  | 0.0341  |
|                   | $R^2$      | 0.943   | 0.964   | 0.974   | 0.863   |
|                   | $\chi^2$  | 0.1026  | 0.0510  | 0.0331  | 0.1153  |
|                   | $q_e$, cal (mg g$^{-1}$) | 29.64   | 24.80   | 22.74   | 16.86   |
| Pseudosecond-order| $k_2$ (g mg$^{-1}$ min$^{-1}$) | 0.0037  | 0.0041  | 0.0045  | 0.0053  |
|                   | $R^2$      | 0.999   | 0.999   | 0.999   | 0.999   |
|                   | $\chi^2$  | 0.0014  | 0.0009  | 0.0008  | 0.0010  |
|                   | $h$        | 5.18    | 5.52    | 5.89    | 6.55    |

Figure 5: The plots of pseudofirst-order and pseudosecond-order model for Cr on SCGs for different temperatures.
The separation factor $R_L$ is characteristic of the Langmuir isotherm, and its value can be determined from the value of $K_L$, according to the following equation [61]:

$$R_L = \frac{1}{1 + K_L C_0},$$

where $K_L$ is the Langmuir constant and $C_0$ is the highest initial Cr(VI) concentration (mg/L).

The $R_L$ value of Cr(VI) adsorption on the SCGs is 0.014, indicating that the adsorption is favourable ($R_L < 1$).

### 3.4. Adsorption Thermodynamic

Temperature is an important factor affecting the adsorption process. This effect could be explained by the evaluation of thermodynamic parameters. These parameters include the Gibbs free energy change ($\Delta G^\circ$), standard enthalpy change ($\Delta H^\circ$), and standard entropy change ($\Delta S^\circ$) and have been calculated using the following equations [53]:

$$\ln(K_d) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT},$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ,$$

where $K_d = q_e/C_e$ is the distribution constant, $R$ is the universal gas constant (8.314 J/mol K), and $T$ is absolute temperature.

The thermodynamic study was carried out at 25, 30, 40, and 50°C. The tests were carried out on mixtures of 20 ml of solutions at a concentration of 100 mg/L and pH 4 with 2.5 g/L of SCGs. The values of $\Delta H^\circ$ and $\Delta S^\circ$ were determined from the slope and intercept at the origin of the ln (Kd) vs 1/T (Figure 7), respectively. These values are collected in Table 4. The negative value of $\Delta G^\circ$ for all temperatures indicates that the adsorption of Cr(VI) on the SCGs is spontaneous. The positive value of $\Delta H^\circ$ confirms that the adsorption is exothermic, while the positive value of $\Delta S^\circ$ reflects the decrease in disorder at the solution-solid interface during adsorption [62]. The results of many studies in the literature are consistent with the present study [36, 63].

### 3.5. Regeneration Studies

The desorption study allows confirming the mechanism of adsorption and the possibility of reusing the adsorbent and the adsorbate. The reversibility of the sorption is proportional to the nature of the binding established between the adsorbent and the adsorbate. The regeneration potential of the SCGs was tested using three different eluents: distilled water H$_2$O, NaOH (0.5 M), and HCl (0.5 M). A mass of SCGs (2.5 g) was mixed with 1 L of Cr(VI) solution with a concentration of 100 mg/L under stirring at pH 4 for 6 hours. After the adsorption experiment, the SCGs were collected by centrifugation at 3000 rpm for 20 min and dried in an oven at 105°C. Afterward, the mass of SCGs was transferred to different eluents. Desorption was carried out for 120 min with stirring (200 rpm). Consecutive adsorption-desorption cycles were repeated 4 times by the three eluents. The results are shown in Figure 8. It is very clear that HCl is the most efficient eluent for the regeneration of SCGs adsorbent. The loss in adsorbent efficiency between the first and fourth cycles can be attributed to the degradation of the material at these extreme acidity.
conditions and the progressive blocking of the active sites by impurities from the untreated adsorbent. Furthermore, the easy desorption of Cr(IV) shows that the adsorbent-adsorbate bond is weak and confirms that the adsorption is of the physisorption type.

3.6. Cost Estimation. Cost estimation of the biosorbent (SCGs) was made based on the methodology reported in recent works [64]. Table 5 shows that the production of 1 kg of SCGs costs only $0.91, which is 15 times less than the price of 1 kg of commercial activated carbon destined for water.
treatment [64]. Moreover, the regeneration of this adsorbent is easy and can be done by a simple acid wash since the adsorbent-adsorbate interactions are mainly of a physical nature.

4. Conclusion

This document highlights a new inexpensive adsorbent for the removal of Cr(VI) from the aquatic medium. The characterisation of the SCGs showed that it has a structure typical of lignocellulosic materials and its surface is rich in functions that serve as an adsorption site. The parameters influencing adsorption were studied, and the results show that 2.5g/L of SCGs is sufficient to remove 88.8% of Cr(VI) from a solution with an initial concentration of 100 mg/L, at pH 4 and temperature 298° K. Experimental data showed good agreement with the Langmuir isotherm and the pseudo-second-order kinetic model. The thermodynamic study indicated that the retention of Cr(VI) on the SCGs is feasible, spontaneous, and exothermic in nature. This was confirmed by the easy regeneration of SCGs by HCl. Finally, a cost estimate proved that SCGs are 15 times more economical than activated carbon. Taking all these results into account, it can be concluded that SCGs can be considered as an economical alternative to the more expensive adsorbents used for the removal of Cr(VI) in wastewater treatment processes.

**Data Availability**

No data were used to support this study.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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