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Research Article

Evaluation of Activated Carbons Prepared from Bioprecursors for the Removal of Cadmium and Chromium (VI)

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Trace metals found in industrial effluents are highly toxic pollutants, and these include cadmium and chromium (VI). The objective of this work is to remove cadmium and chromium (VI) on activated carbons, prepared from biomaterials such as nuclei of *Ziziphus lotus* and coffee grounds. The characterization of adsorbents was performed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results of the characterization showed an important porosity on the activated carbon's surface, with sizes between 6 and 50 μm. Similarly, the adsorption results showed that the adsorption process is very rapid and that the increase in contact time and temperature improves the efficiency of the Cd and Cr(VI) removal process. Indeed, abatement rates (R%) of 80% for Cr(VI) and 60% for Cd were obtained after 80 minutes of adsorption on activated carbon prepared from *Ziziphus lotus*, whereas activated carbon obtained from coffee grounds allows a reduction rate of about 50% for Cr(VI) and Cd. Hence, it seems clearly that the activated carbon of *Ziziphus lotus* is more effective than that of coffee grounds, especially for the Cr(VI) adsorption. The kinetic modeling of the adsorption process followed the pseudo-second-order model, and the Freundlich model has better explained the adsorption isotherm for Cd and Cr(VI). The thermodynamic study showed that adsorption was spontaneous and endothermic.

1. Introduction

All natural resources are dependent on water as the most essential element. Indeed, it is essential and necessary for the man's survival and health. Therefore, most countries in the world struggle with managing water resources, which are of great importance. However, these resources are under increasing pressure globally due to agricultural and industrial activities and high drinking water consumption. The discharge of untreated or partially treated effluents is currently affecting these water resources, which can lead to pollution of surface and groundwater waters and have a direct impact on ecosystems [1]. Furthermore, wastewater can be made up of several compounds, either solid or dissolved [2]. These micropollutants include metallic trace elements (MTEs), used in many industrial sectors. Due to the toxicity of many MTEs in industrial effluents, even at low concentrations, adverse health and environmental effects

may occur [3–5]. The direct and indirect toxic effects of MTEs have been highlighted by numerous studies, which showed that they can cause various health problems in the respiratory, digestive, and urinary systems [6, 7].

Although some heavy metals play an important role in biological systems, they are generally toxic to living organisms depending on the dose and duration of exposure [8]. In toxicology, it is well known that high rates of any compound can have negative impacts and cause toxicity. Indeed, essential heavy metals are necessary in trace amounts in the body but become toxic above certain limits or threshold concentrations, while nonessential heavy metals (Cr, Cd, Pb, and Hg) can be toxic even at very low concentrations [9]. Moreover, unlike organic matter, which can be degraded, MTEs accumulate in water, soil, pond bottoms, and even living organisms [10, 11]. Rapid industrialization has thus led to an expansion of manufacturing and environmental contamination, mainly by heavy metals, particularly in developing countries. Therefore, metal contamination problems are becoming increasingly common worldwide, and numerous studies have been carried out on metal toxicity, particularly in regions where anthropogenic activities are significant.

Chromium is a naturally occurring heavy metal and is considered a major environmental pollutant due to its toxicity for ecological, nutritional, and environmental reasons [12]. Cr exists in the aqueous environment mainly in the oxidation states of Cr(VI) and Cr(III). The discharge of Cr-containing effluents into municipal sanitary sewers has become a matter of concern in recent decades [13]. These toxic chromium ions are generally produced by industries such as pigment and paint manufacture, textile processing, and leather tanning. Indeed, due to its advantages for tanneries, textile, wood processing, and food processing, chromium is one of the most commonly used heavy metals in industry. One of the most dangerous and toxic form of this MTE is chromium (VI) due to its high solubility, which enhances tremendously its mobility in ecosystems [14].

The treatment of wastewater containing various MTEs has, therefore, a great importance in the environment preservation. In this sense, several treatment techniques have been used for wastewater purification to remove chemical contaminants, including the oxidation processes, chemical precipitation, ion exchange, coagulation/flocculation processes, reverse osmosis, membrane filtration, adsorption, and solvent extraction [15]. Unfortunately, most of these methods are sometimes costly and inefficient, particularly when contaminants are present in low or trace concentrations, such as heavy metal ions present at concentrations up to 100 mg/l [16]. Thanks to its economic, environmental, and technical advantages very important to eliminate soluble, insoluble, and biological contaminants, adsorption remains the most commonly used method for treating certain micropollutants such as dyes, trace metals, pesticides, and pharmaceuticals [17]. Since this process was introduced, activated carbon has been most widely used because of its high ability of adsorption depending mainly on its activation, preparation, and purification processes [18]. Many researchers are still struggling to select inexpensive and available precursors for activated carbon production, which has been widely studied [19]. To this end, adsorption using an adsorbent manufactured from biomass may be an interesting and promising solution.

In this context, the present study focuses on the elimination of cadmium (Cd) and chromium (VI) (Cr(VI)) by active carbon prepared from the nuclei of *Ziziphus lotus* and coffee grounds. These residues are widely available and are renewable sources for the environment. The recovery of these residues has significant environmental and socioeconomic benefits. The obtained active coals were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The kinetic models of the pseudo-first-order and the pseudo-second-order, as well as the Langmuir and Freundlich isotherms, are studied to explain the mechanisms and the efficiency of the process of elimination of contaminants under study.

2. Materials and Methods

2.1. The Activated Carbon Preparation. The process of preparation of activated carbon using the nucleus of *Ziziphus lotus* (NZL) and coffee grounds (GC) as raw materials follows several steps, according to Touzani et al. [20, 21]. Step 1: The NZL and GC are washed, dried, and then crushed into fine particles; step 2: Chemical activation of the NZL and GC by sulfuric acid (H_2SO_4) for 24 h; step 3: The carbonization of the paste obtained after chemical activation is made at 500°C for 2 h; and step 4: The active carbons obtained are sieved with a sieve smaller than 100 μm. The activated carbon produced from NZL and GC, according to the steps described above, is named CA1 and CA2, respectively. These two carbons will be used to eliminate Cd and Cr(VI).

Moisture was measured by weighing a mass quantity of CA1 and CA2 before and after drying at 110°C for one hour. The moisture content obtained was 2.5% and 3% for CA1 and CA2, respectively.

The rate of ash (TC) was measured by weighing the final mass after incineration at 500°C of a 1 g mass of CA1 and CA2 followed by its cooling. The ash content of 2.2% and 2.9% was obtained for CA1 and CA2, respectively.

The prepared CA1 and CA2 were characterized by analytical techniques, including scanning electron microscopy (SEM) by a Quanta 200 model SEM equipped with a tungsten filament electron gun and X-ray diffraction (XRD) undertaken by an XPERT-PRO type XRD within a scan area between 5 and 120° 2θ.

2.2. Experimental Adsorption of Cd and Cr(VI)

2.2.1. Adsorbate Preparation. The Cd stock solution was obtained by solubilizing 10 g of eight hydrated cadmium sulphate ($3CdSO_4$, 8 H_2O) in 1 liter of distilled water, while the Cr(VI) stock solution (at 1000 mg/l potassium dichromate) was prepared by dissolving 2.829 g of potassium dichromate $K_2Cr_2O_7$ in 1 liter of distilled water. Then, the other concentrations used for adsorption tests are obtained by successive dilutions.

2.2.2. Contact Time's Effect. Contact time is one of the most important factors during chemical reactions. In a closed reactor, a 100 ml volume of one of the concentrations of cadmium or chromium (VI) is brought into contact with 0.1 g of activated carbon, under an agitation of 300 r/min. After every 10 min of contact, the suspension is centrifuged 5 min at 5000 rpm. The Cd concentration was determined by inductively coupled plasma mass spectrometry (ICP-AES) at the "Cité d'Innovation" in Fez. In addition, the concentration of Cr(VI) was determined by an UV/visible spectrophotometer (UV 240 Shimadzu mode) using 1–5 diphenylcarbazide as a complexing agent in an acid medium (H_2SO_4) at the wavelength of 540 nm in the laboratory of natural resources and environment of the Polydisciplinary Faculty of Taza.

The effect of contact time on the removal rate of adsorbates was studied during a time interval of 10–280 min for each of the initial following concentrations of 25, 40, 50, and 75 mg/l for Cd and Cr(VI) in the presence of 0.1 g of activated carbon (CA1 and CA2) at ambient temperature. The abatement rate $R(\%)$ was calculated from the following equation:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100, \quad (1)$$

where C_0 (mg/l) is the initial adsorbate concentration and C_t (mg/l) is the adsorbate concentration in solution.

2.2.3. Temperature's Effect. To evaluate the effect of temperature on the adsorption capacity of the various pollutants on the adsorbent, a quantity of 0.1 g of activated carbon with concentration of 25 mg/l for the metallic elements Cd and Cr(VI) was placed in the batch system for 60 minutes. The adsorption temperatures studied were 25–50°C. Finally, the residual concentrations (C_e) were determined for each adsorbate.

2.2.4. Kinetics of Adsorption. The adsorption mechanism and the transfer mode of solutes from the liquid to the solid phase are covered in kinetics. Simplified kinetic models are approved to understand the adsorption mechanism and are commonly well adjusted by a pseudo-first-order kinetic model [22] and a pseudo-second-order kinetic model [23]. These two classical models were tested to study the adsorption kinetics of the investigated pollutants Cd and Cr(VI) on the activated carbons produced (CA1 and CA2).

2.2.5. Pseudo-First-Order. The pseudo-first-order model is defined according to Das et al. [24] as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_1.t}{2.303}, \quad (2)$$

where q_e and q_t are the quantities of the adsorbed ion ($mg{\cdot}g^{-1}$) at equilibrium and time t, respectively, while k_1 is the constant of equilibrium velocity for this model (min^{-1}).

2.2.6. Pseudo-Second-Order. The present model is defined according to Raoul et al. [25].

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}, \quad (3)$$

where k_2 is the pseudosecond-order adsorption rate constant (g/mg·min).

2.2.7. Adsorption Isotherms. Adsorption isotherms can describe an adsorption process. Langmuir and Freundlich isotherms are used to study the adsorption of Cd and Cr(VI) on activated carbons.

The amount of an adsorbed solute is calculated according to Ojemaye et al. [26].

$$q_e = \frac{(C_0 - C_e).V}{m}, \quad (4)$$

where q_e is the quantity of solute adsorbed at equilibrium per adsorbent's unit weight (mg/g); C_0 is the initial concentration of solute (mg/l); C_e is the equilibrium concentration of solute (mg/l); m is the adsorbent mass (g); and V is the solution volume (l)

The Langmuir model [27] is described mathematically by the following equation:

$$q_e = \frac{q_{max} K_L Ce}{1 + K_L C_e}. \quad (5)$$

This equation is often written in the linear form as follows [28]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e, \quad (6)$$

where q_e and q_{max} are the equilibrium and the maximum adsorption capacities (mg/g), respectively. K_L is the characteristic Langmuir constant, corresponding to the concentration at equilibrium of the adsorbate solution per unit mass of solid (mg/l).

The Freundlich model [29] is described as follows:

$$q_e = K_f * C_e^{1/n}. \quad (7)$$

It can also be expressed in the logarithmic form [30].

$$\log q_e = \log k_f + \frac{1}{n} \log C_e, \quad (8)$$

where q_e is the amount of the material adsorbed per unit mass of adsorbent at equilibrium (mg/g). This is the equilibrium concentration (mg/l), K_f is the capacity of the adsorbent adsorption, and n is the intensity of sorption of adsorbent-adsorbate.

2.2.8. Thermodynamic Study. The thermodynamic equilibrium constant K_d, enthalpy (ΔH_0), entropy (ΔS_0), and the variation of Gibbs free energy (ΔG_0) are among the most important thermodynamic parameters involved in the

establishment of an adsorption system. Thus, to assess the adsorption process's feasibility and nature [31], the thermodynamic parameters were determined as follows [32].

$$K_d = \frac{q_e}{C_e},$$
$$\Delta G_0 = \Delta H_0 - T\Delta S_0, \quad (9)$$
$$\Delta G_0 = -RT\,\mathrm{Ln}K_d,$$

where k is the equilibrium constant (l/mg), R is the gas constant (8.314 J/mol·K), and T is the absolute temperature (K).

Plotting $\ln K_d$, a function of $1/T$, a line having a slope of $-\Delta H_0/R$ and an intercept of $\Delta S_0/R$ is obtained. Subsequently, the standard thermodynamic parameters of adsorption (ΔG_0, ΔH_0, and ΔS_0) are calculated.

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM). Scanning electron microscopy (SEM) enables to determine the activated carbon's morphology and external porosity. The porosity increase enables to enhance the active site's number, thus offering several advantages to the adsorption process [33] and promoting the fixation of the studied metal elements (Cd and Cr(VI)). The results of the SEM analysis of CA1- and CA2-activated carbons are presented in Figures 1(a) and 1(b), respectively. These results show that the surface of the active coals CA1 and CA2 have a very porous morphology with pores of different sizes ranging from 6 to 50 μm and having different cavity shapes. Indeed, the presence of cavities in activated carbons results from the activating agent reaction during the chemical activation process of the precursor by sulfuric acid, followed by pyrolysis. This suggests that the activation process has led to the development of pores and the modification of the produced carbons structure. Thus, the formation of cavities on the surface of the coal seems to result from the evaporation of the activator during carbonization, leaving the space previously occupied by this agent. Moreover, the porous structure can also develop after the evaporation of most of the volatile organic matter, resulting in a fractured activated charcoal surface with large pores.

This is in agreement with other research works, such as the optimization of the preparation conditions of activated carbon from *Diplotaxis harra* biomass and removal of heavy metals carried out by Tounsadi et al. [34] and the production of mesoporous-activated carbon from Indonesian *Schleichera oleosa* by the combination of pyrolysis and H_2SO_4 activation by Neolaka et al. [35], for Pb(II) adsorption in aqueous solution.

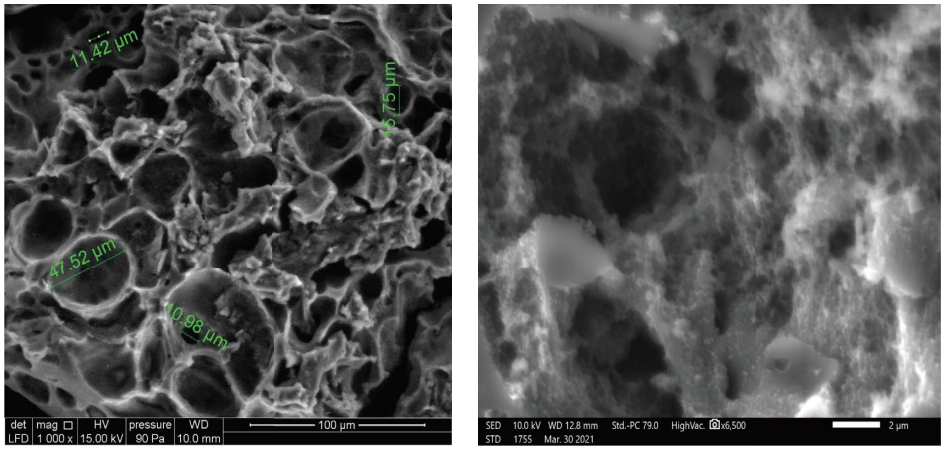
Similarly, it appears from the elementary analysis (Table 1) that the CA1- and CA2-activated carbons contain very interesting carbon percentages of 88.98% and 92.35%, respectively, as well as low oxygen percentages, especially for CA2 (6%), which means that carbonization at 500°C has a significant effect on the elements composition on the activated carbons' surface. The presence of trace sulfur is also observed, which is due to the use of sulfuric acid (H_2SO_4) as an activating agent.

3.2. X-Ray Diffraction (XRD). X-ray diffraction (XRD) is used to identify the crystalline or amorphous structure of materials. Figures 2(a) and 2(b) of the X-ray diffraction of CA1 and CA2 show very wide diffraction peaks. Thus, a large peak at about $2\theta = 25°$ indicates the presence of carbon [36]. Moreover, the absence of an acute peak reveals an essentially amorphous structure for both CA1 and CA2 materials [37]. Similarly, there are noise signals corresponding to ash powder in the activated carbons.

3.3. Effect of Contact Time. The contact time and the initial concentration of adsorbates play a very important role in the adsorption process. Indeed, the concentration of adsorbates represents the driving force of mass transfer between the solid/liquid phases. Figure 3 represents the evolution of the abatement rate (R%) as a function of time (T) for Cd and Cr(VI) at different concentrations of 25, 40, 50, and 70 mg/l by adsorption on activated carbons CA1 and CA2, respectively. Results show that abatement rates (R %) of 80% and 60% were obtained for Cr(VI) and Cd, respectively, after 80 minutes of adsorption on activated carbon prepared from *Ziziphus lotus*, whereas reduction rates for both Cr(VI) and Cd did not exceed 50%, with activated carbon obtained from coffee grounds. Hence, the activated carbon of *Ziziphus lotus* seems to be more effective than that of coffee grounds, especially for the Cr(VI) adsorption.

On the other hand, the adsorption curves of Cd and Cr(VI) on the CA1 and CA2 show the same gaits with a metal retention that increases with the increase of the contact time and reaches a saturation phase at about 120 minutes, the time from which retention becomes almost constant. In fact, two kinetic phases can be observed in the Cd and Cr(VI) adsorption process on CA1 and CA2, a rapid phase that can be attributed to the high number of active sites available on the surface of activated carbons, which increases the mass transfer potential and makes it more important. As adsorption progresses, the accumulation of metallic element molecules on the surface of the adsorbents hinders diffusion of the molecules into the pores, which results in slower speed and adsorption capacity.

3.4. Effect of Temperature. The effect of solution temperature on the removal of Cd and Cr(VI) by CA1 and CA2 was studied to determine the effect of temperature on adsorption capacity and process. The results obtained show that the adsorption capacity of Cd and Cr(VI) on CA1 and CA2 increases with increasing temperature (Figure 4). It goes from 4.1 to 4.3 and from 3.68 to 3.97 for Cd and Cr(VI) on CA1, respectively, and from 2.98 to 3.25 and from 2.6 to 3 for Cd and Cr(VI) on CA2, respectively, when the solution temperature increases from 293 K to 323 K. This can be attributed mainly to the penetration of Cd and Cr(VI) molecules into micropores or apparent surface cavities, as it

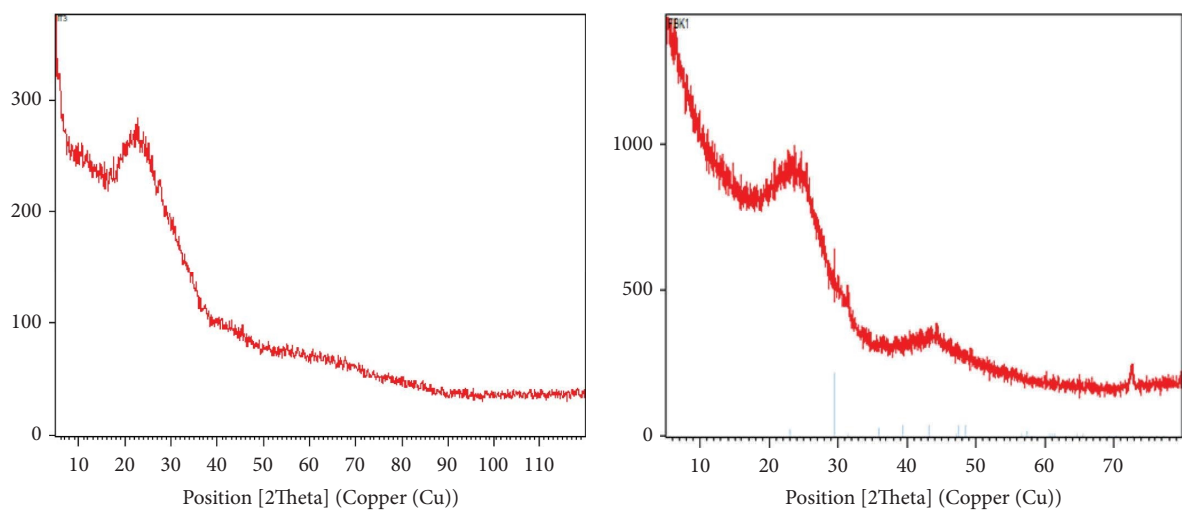


(a) (b)

Figure 1: Image of (a) CA1 and (b) CA2 observed by scanning electron microscopy (SEM).

Table 1: Elemental analysis of CA1 and CA2 by SEM.

Elements	Atom (%)	
	CA1	CA2
C	88.98	92.35
O	10.70	6.65
S	0.24	0.63
Na	—	0.11
K	0.09	0.20
Mg	—	0.07



(a) (b)

Figure 2: X-ray diffraction of (a) CA1 and (b) CA2.

can be attributed to the creation of new active sites at higher temperatures [8, 38]. In addition, a greater affinity between the adsorbate and active sites can be created due to an increase in the chemical interaction between adsorbate and adsorbent at a higher temperature.

3.5. Adsorption Kinetics. The correlation coefficients and kinetic parameters of the two diffusion models are presented in Table 2. These results show that the values of the correlation coefficients R^2 of the pseudo-first-order model are lower than those obtained for the pseudo-second-order

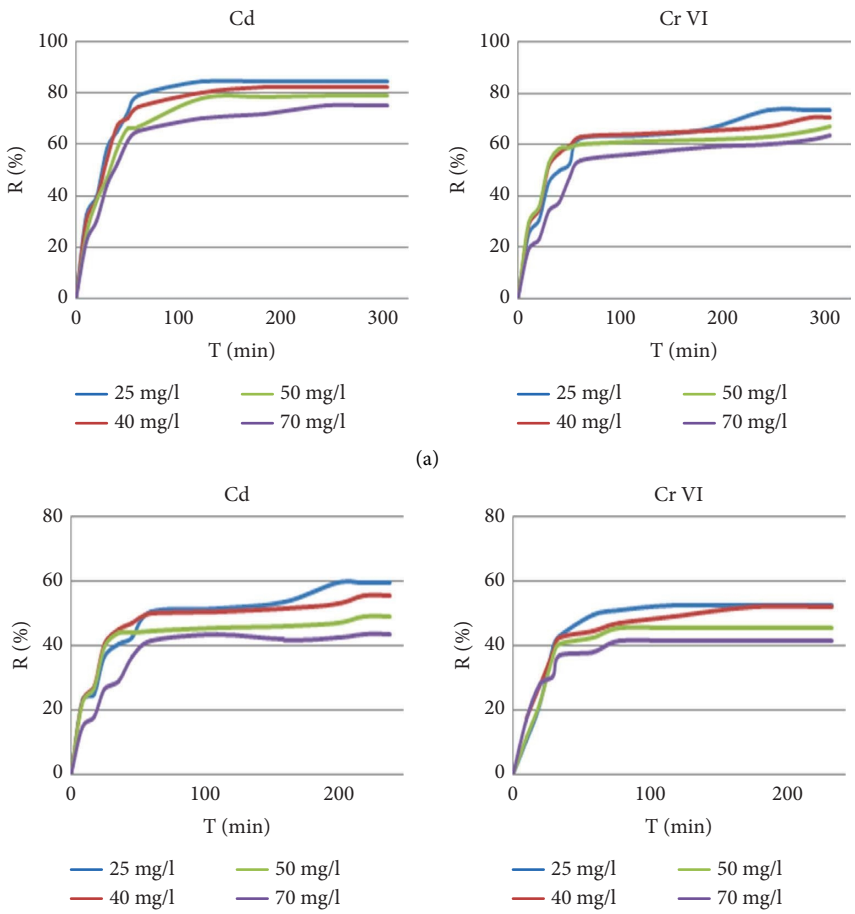


Figure 3: Abatement rates (R%) of Cd and Cr(VI) at different concentrations (25, 40, 50, and 70 mg/l), respectively, by CA1 (a) and CA2 (b).

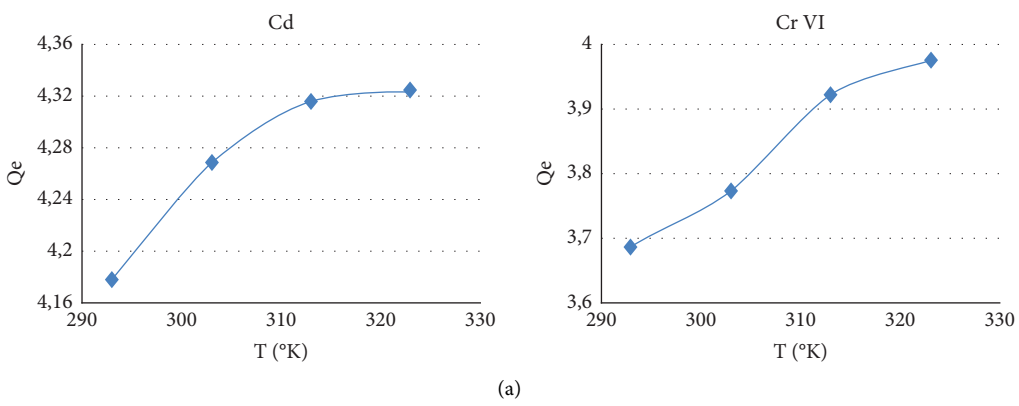
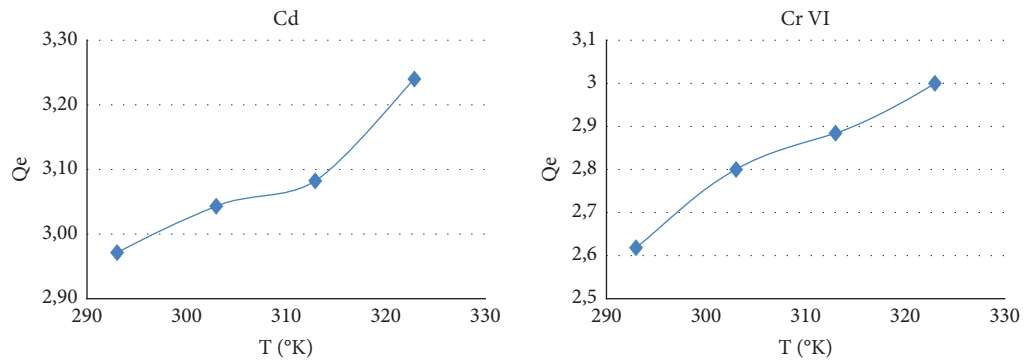


Figure 4: Continued.



(b)

Figure 4: Effects of temperature on the adsorption capacity of Cd and Cr(VI) on CA1 (a) and CA2 (b).

Table 2: Adsorption kinetics parameters of Cd and Cr(VI) on CA1 and CA2.

Adsorbent	Element	CC (mg/l)	$q_{e,\ exp}$ (mg/g)	Pseudofirst order			Pseudosecond order		
				$q_{e,\ cal}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e,\ cal}$ (mg/g)	K_2 (g·mg^{-1}·min^{-1})	R^2
CA1	Cd	25	4.178	4.550	0.041	0.949	4.244	2.945	0.995
		40	6.597	5.781	0.023	0.912	7.043	2.353	0.994
		50	7.966	7.430	0.032	0.902	8.072	2.392	0.991
		70	11.070	11.041	0.030	0.922	11.448	1.489	0.994
	Cr(VI)	25	3.687	2.438	0.039	0.921	3.817	1.799	0.999
		40	5.644	2.710	0.041	0.828	5.780	0.669	0.999
		50	6.750	2.523	0.032	0.634	6.897	0.591	0.999
		70	8.938	6.607	0.046	0.968	9.259	0.716	0.999
CA2	Cd	25	2.971	2.661	0.023	0.913	3.165	0.014	0.993
		40	4.214	4.130	0.044	0.983	4.464	0.012	0.997
		50	4.695	4.864	0.058	0.961	4.778	0.009	0.997
		70	5.920	6.580	0.035	0.946	6.179	0.007	0.999
	Cr(VI)	25	2.618	3.819	0.060	0.954	2.959	0.015	0.975
		40	4.144	5.188	0.044	0.959	4.464	0.014	0.997
		50	4.529	11.858	0.145	0.623	4.950	0.013	0.996
		70	5.767	5.188	0.044	0.959	6.098	0.010	0.997

CC: concentration of element; $q_{e,\ exp}$: equilibrium adsorbed capacity; k_1: pseudo-first-order constant; K_2: pseudo-second-order constant; R^2: correlation coefficient.

model, which are very close to the unit for the adsorption of Cd and Cr(VI) on CA1 and CA2 activated carbons. In addition, the quantities theoretically adsorbed at equilibrium calculated from the pseudo-second-order model for all studied concentrations (25, 40, 50, and 70 mg/l) are fairly close to the experimental results for Cd and Cr(VI). Furthermore, the velocity constants K_2 decrease as the initial metal concentrations increase, indicating that the adsorbates studied reaches equilibrium more quickly at low initial concentrations than at higher concentrations [39]. More specifically, the pseudo-second-order model represents the involvement of valence forces by electron exchange between adsorbate and adsorbent [40]. These results confirm that the pseudo-second-order model is better suited to the adsorption of Cd and Cr(VI) on CA1 and CA2.

3.6. Adsorption Isotherms. The modeling of the Cd and Cr(VI) adsorption isotherms was done using the Langmuir and Freundlich models. The model constants K_L and K_F and the correlation coefficients (R^2) obtained from the two models are listed in Table 3. The Langmuir model reveals that the maximum adsorbed quantity values are 23.256 mg/g for Cd and 17.857 mg/g for Cr(VI) on CA1. Similarly, the K_L constant values for Cd are higher than those for Cr(VI),

Table 3: Langmuir and Freundlich isotherms for adsorption of Cd and Cr(VI) on CA1 and CA2.

Adsorbent	Element	Langmuir			Freundlich		
		q_{max} (mg/g)	K_L	R^2	K_F	$1/n$	R^2
CA1	Cd	23.256	0.051	0.904	1.211	0.868	0.937
	Cr(VI)	17.857	0.039	0.992	1.096	0.652	0.997
CA2	Cd	8.849	0.047	0.984	1.032	0.482	0.995
	Cr(VI)	10.526	0.029	0.946	1.640	0.612	0.967

q_{max}: maximum adsorption capacity; K_L: Langmuir constant; K_F: Freundlich constant; $1/n$: coefficient of the Freundlich equation; R^2: correlation coefficient.

Table 4: Thermodynamic parameters of Cd and Cr(VI) adsorption on CA1 and CA2 at different temperatures.

Adsorbent	Element	R^2	ΔH_0 (kJ/mol)	ΔS_0 (kJ/mol·K)	ΔG_0 (kJ/mol)			
					293	303	313	323
CA1	Cd	0.903	6.102	24.136	−7.064	−7.305	−7.547	−7.788
	Cr(VI)	0.975	8.937	25.681	−7.515	−7.772	−8.029	−8.286
CA2	Cd	0.909	11.191	14.358	−5.196	−5.339	−5.483	−5.626
	Cr(VI)	0.982	8.597	15.447	−4.517	−4.672	−4.826	−4.981

indicating that the adsorption energy of Cd is higher compared to that of Cr(VI) on the two materials studied. The Freundlich model presents R^2 values close to unity in comparison with the Langmuir model, suggesting that the Freundlich model presents a good fit to the experimental data of Cd and Cr(VI) adsorption on CA1 and CA2. This shows that adsorption is a multilayer process, involving interactions between the studied metals' molecules and the activated carbons surface.

3.7. Adsorption Thermodynamics. In order to study the thermodynamic behavior of Cd and Cr(VI) adsorption on CA1 and CA2, thermodynamic parameters such as Gibbs free energy (ΔG_0), enthalpy (ΔH_0), and entropy (ΔS_0) were calculated using the expressions mentioned above. Table 4 presents the thermodynamic parameters ΔG_0, ΔH_0, and ΔS_0 of adsorption of Cd and Cr(VI) on CA1 and CA2.

(i) Feasibility and spontaneity

Negative ΔG_0 values for all cases indicate that the adsorption is feasible and spontaneous under the studied conditions. This means the process proceeds naturally without external energy input and reaches equilibrium in a way that minimizes the total system free energy.

Increasing absolute values of ΔG_0 with temperature suggest that spontaneity is enhanced at higher temperatures. This aligns with the expected increased kinetic energy of adsorbate molecules at higher temperatures, making them more likely to overcome the energy barrier for adsorption.

(ii) Endothermic nature

Positive ΔH_0 values indicate that the adsorption process is endothermic. This means it absorbs heat from the surrounding environment. This aligns with the expectation that breaking bonds in the solution and forming new bonds with the adsorbent surface require energy input. The increase in quantity adsorbed with temperature is consistent with the endothermic nature. Higher temperatures provide more energy for overcoming the adsorption barrier, allowing more molecules to stick to the adsorbent.

(iii) Entropy change

A positive ΔS_0 contributes favorably to the driving force for spontaneity, as increasing entropy generally leads to lower free energy.

Overall, our analysis aligns with established principles of thermodynamics in adsorption processes [41]. Moreover, physisorption can be considered as the predominant adsorption process.

3.8. Performance of the Prepared CA1 and CA2. The development of activated carbon materials has been widely reported by researchers as adsorbents for heavy metals such as Cr(VI), Pb(II), Cu(II), Cd, Zn, and Hg [42]. In general, agricultural resources and bioresources rich in cellulose and hemicellulose are used as precursors in the production of activated carbon. However, in order to assess the MTE removal preferences studied on CA1 and CA2, a comparative study of this work was conducted with other relevant studies (Table 5) using the adsorption capacity (q_{max}) as the comparative parameter. The results show that the adsorption capacity obtained in this study is comparable to that obtained in the previous work. Furthermore, it is important to point out that the biomaterials used in this study are very abundant, so *Ziziphus lotus* is a species found in several biotopes in arid and semiarid regions and occupies various geographical areas of Morocco [20]. Whereas, coffee grounds represent waste, resulting from coffee consumption, which can have a great added value. For this reason, CA1- and CA2-activated carbons offer a real advantage as new agent or the depollution of industrial effluents loaded with MTEs.

Table 5: Comparison of Cd and Cr(VI) q_{max} with various adsorbents.

Adsorbent	Element	Adsorption capacity (mg/g)	References
Sugarcane bagasse	Cr(VI)	64.52	[43]
Spartina alterniflora	Cd(II)	47.85	[44]
Eichhornia crassipes root	Cr(VI)	36.34	[45]
Terminalia arjuna nuts	Cr(VI)	28.4	[46]
Viticultural industry wastes	Cd(II)	75.61	[47]
Bael fruit shell	Cr(VI)	17.27	[48]
Rice husks	Cr(VI)	62.9	[49]
Pterocladia capillacea	Cr(VI)	66	[50]
Long-root *Eichhornia crassipes*	Cd	1.22	[51]
Fox nutshell	Cr(VI)	74.95	[52]
Aloe vera waste leaves	Cr(VI)	59.88	[53]
Jacobi	Cd	24.69	[54]
Ziziphus lotus nuclei	Cd	23.25	Current work
	Cr(VI)	17.85	
Coffee grounds	Cd	8.84	
	Cr(VI)	10.52	

4. Conclusion

This work aims to study the removal of cadmium and chromium (VI) on activated carbons prepared from biomaterials such as the nucleus of *Ziziphus lotus* and coffee grounds. Activated carbon was obtained using a chemical activation process with sulphuric acid (H_2SO_4), followed by carbonization carried out at 500°C during 2 h. The results of the SEM characterization revealed the presence of a porous and amorphous structure on the surface of the prepared activated carbons (CA1 and CA2). The adsorption results for MTEs (Cd and Cr(VI)) show that the adsorption process is influenced by a number of parameters such as the initial concentration, contact time, and temperature. The kinetic modeling of adsorption follows the pseudo-second-order model. Similarly, the adsorption isotherm data were better adjusted with the Freundlich model. The thermodynamic parameters (ΔG_0, ΔS_0, and ΔH_0) indicate that the adsorption process of the contaminants studied is an endothermic process and that the quantity adsorbed at equilibrium increases with increasing temperature. These results show that *Ziziphus lotus* and coffee grounds can be considered as an interesting source of the raw material for the preparation of high-quality activated carbon which can be used to decontaminate effluents containing trace metals.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References

[1] E. Corcoran, Ed., *Sick Water: The central Role of Wastewater Management in Sustainable Development: a Rapid Response Assessment*, UNEP/Earthprint, Nairobi, Kenya, 2010.

[2] M. A. Alsheyab and S. Kusch-Brandt, "Potential recovery assessment of the embodied resources in Qatar's wastewater," *Sustainability*, vol. 10, no. 9, p. 3055, 2018.

[3] M. S. Islam, S. Han, M. K. Ahmed, and S. &Masunaga, "Assessment of trace metal contamination in water and sediment of some rivers in Bangladesh," *Journal of Water and Environment Technology*, vol. 12, no. 2, pp. 109–121, 2014.

[4] M. A. A. Wijayawardena, M. Megharaj, and R. Naidu, "Exposure, toxicity, health impacts, and bioavailability of heavy metal mixtures," *Advances in Agronomy*, vol. 138, pp. 175–234, 2016.

[5] N. Yavar Ashayeri and B. &Keshavarzi, "Geochemical characteristics, partitioning, quantitative source apportionment, and ecological and health risk of heavy metals in sediments and water: a case study in Shadegan Wetland, Iran," *Marine Pollution Bulletin*, vol. 149, Article ID 110495, 2019.

[6] L. T. Gibson, "Mesosilica materials and organic pollutant adsorption: part B removal from aqueous solution," *Chemical Society Reviews*, vol. 43, no. 15, pp. 5173–5182, 2014.

[7] T. Rasheed, M. Bilal, F. Nabeel, M. Adeel, and H. M. Iqbal, "Environmentally-related contaminants of high concern: potential sources and analytical modalities for detection, quantification, and treatment," *Environment International*, vol. 122, pp. 52–66, 2019.

[8] F. Batool, J. Akbar, S. Iqbal, S. Noreen, and S. N. A. Bukhari, "Study of isothermal, kinetic, and thermodynamic parameters for adsorption of cadmium: an overview of linear and nonlinear approach and error analysis," *Bioinorganic Chemistry and Applications*, vol. 2018, Article ID 3463724, 11 pages, 2018.

[9] H. Ali, E. Khan, and I. Ilahi, "Environmental chemistry and ecotoxicology of hazardous heavy metals: environmental

persistence, toxicity, and bioaccumulation," *Journal of Chemistry*, vol. 2019, Article ID 6730305, 14 pages, 2019.

[10] L. Järup, "Hazards of heavy metal contamination," *British Medical Bulletin*, vol. 68, no. 1, pp. 167–182, 2003.

[11] Q. Q. Chi, G. W. Zhu, and A. Langdon, "Bioaccumulation of heavy metals in fishes from Taihu Lake, China," *Journal of Environmental Sciences*, vol. 19, no. 12, pp. 1500–1504, 2007.

[12] C. Kornhauser, K. Wróbel, K. Wróbel et al., "Possible adverse effect of chromium in occupational exposure of tannery workers," *Industrial Health*, vol. 40, no. 2, pp. 207–213, 2002.

[13] S. Mishra and R. N. Bharagava, "Toxic and genotoxic effects of hexavalent chromium in environment and its bioremediation strategies," *Journal of Environmental Science and Health, Part C*, vol. 34, no. 1, pp. 1–32, 2016.

[14] P. Sharma, S. P. Singh, S. K. Parakh, and Y. W. Tong, "Health hazards of hexavalent chromium (Cr (VI)) and its microbial reduction," *Bioengineered*, vol. 13, no. 3, pp. 4923–4938, 2022.

[15] M. Abbas, Z. Harrache, and M. &Trari, "Removal of gentian violet in aqueous solution by activated carbon equilibrium, kinetics, and thermodynamic study," *Adsorption Science and Technology*, vol. 37, no. 7-8, pp. 566–589, 2019.

[16] E. Ramos-Ramírez, N. L. G. Ortega, C. A. C. Soto, and M. T. O. Gutiérrez, "Adsorption isotherm studies of chromium (VI) from aqueous solutions using sol–gel hydrotalcite-like compounds," *Journal of Hazardous Materials*, vol. 172, no. 2-3, pp. 1527–1531, 2009.

[17] A. R. Bagheri, M. Ghaedi, A. Asfaram et al., "Modeling and optimization of simultaneous removal of ternary dyes onto copper sulfide nanoparticles loaded on activated carbon using second-derivative spectrophotometry," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 65, pp. 212–224, 2016.

[18] M. Yousefi, S. M. Arami, H. Takallo et al., "Modification of pumice with HCl and NaOH enhancing its fluoride adsorption capacity: kinetic and isotherm studies," *Human and Ecological Risk Assessment: An International Journal*, vol. 25, no. 6, pp. 1508–1520, 2019.

[19] Q. X. Liu, Y. R. Zhou, M. Wang et al., "Adsorption of methylene blue from aqueous solution onto viscose-based activated carbon fiber felts: kinetics and equilibrium studies," *Adsorption Science and Technology*, vol. 37, no. 3-4, pp. 312–332, 2019.

[20] I. Touzani, K. Fikri-Benbrahim, H. Ahlafi, B. Ihssane, and O. Boudouch, "Characterization of *Ziziphus lotus*' activated carbon and evaluation of its adsorption potential," *Journal of Environmental and Public Health*, vol. 2022, Article ID 8502211, 12 pages, 2022.

[21] I. Touzani, K. Fikri-Benbrahim, O. Boudouch, and R. Elkacimi, *Charbon actif préparé à base du noyau du NBEG ZIZIPHUS LOTUS (sidr) et son procédé de fabrication, (MA 49232 B1)*, Moroccan Office of Industrial and Commercial Property, Casablanca, Morocco, 2022.

[22] B. Damiyine, A. Guenbour, and R. &Boussen, "Adsorption of rhodamine B dye onto expanded perlite from aqueous solution: kinetics, equilibrium and thermodynamics," *Journal of Materials and Environmental Science*, vol. 8, pp. 345–355, 2017.

[23] N. Fayoud, S. A. Younssi, S. Tahiri, and A. &Albizane, "Kinetic and thermodynamic study of the adsorption of methylene blue on wood ashes," *Journal of Materials and Environmental Science*, vol. 6, no. 11, pp. 3295–3306, 2015.

[24] B. Das, N. K. Mondal, R. Bhaumik, P. Roy, K. C. Pal, and C. R. Das, "Removal of copper from aqueous solution using alluvial soil of Indian origin: equilibrium, kinetic and thermodynamic study," *Journal of Materials and Environmental Science*, vol. 4, no. 4, pp. 392–409, 2013.

[25] T. T. D. Raoul, A. S. Gabche, K. J. Mbadcam, N. G. Ndifor-Angwafor, and N. J. &Nsami, "Kinetics and equilibrium studies of adsorption of phenol in aqueous solution onto activated carbon prepared from rice and coffee husks," *International Journal of Engneering and Technological Research*, vol. 2, pp. 166–173, 2014.

[26] M. O. Ojemaye, O. O. Okoh, and A. I. &Okoh, "Adsorption of Cu^{2+} from aqueous solution by a novel material; azomethine functionalized magnetic nanoparticles," *Separation and Purification Technology*, vol. 183, pp. 204–215, 2017.

[27] I. Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum," *Journal of the American Chemical Society*, vol. 40, no. 9, pp. 1361–1403, 1918.

[28] R. M. Ali, H. A. Hamad, M. M. Hussein, and G. F. &Malash, "Potential of using green adsorbent of heavy metal removal from aqueous solutions: adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis," *Ecological Engineering*, vol. 91, pp. 317–332, 2016.

[29] H. M. F. Freundlich, "Over the adsorption in solution," *Journal of Physical Chemistry*, vol. 57, no. 385471, pp. 1100–1107, 1906.

[30] H. Nourmoradi, M. Avazpour, N. Ghasemian et al., "Surfactant modified montmorillonite as a low cost adsorbent for 4-chlorophenol: equilibrium, kinetic and thermodynamic study," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 59, pp. 244–251, 2016.

[31] F. M. S. Kernels, "Adsorption du méthylorange sur un biosorbant à base de noyaux de mangue," *Larhyss Journal*, vol. 36, pp. 145–156, 2018.

[32] F. Mekhalef Benhafsa, S. Kacha, A. Leboukh, and K. D. &Belaid, "Étude comparative de l'adsorption du colorant Victoria Bleu Basique à partir de solutions aqueuses sur du carton usagé et de la sciure de bois," *Revue des Sciences de l'Eau*, vol. 31, no. 2, pp. 109–126, 2018.

[33] R. Davarnejad, S. Afshar, and P. &Etehadfar, "Activated carbon blended with grape stalks powder: properties modification and its application in a dye adsorption," *Arabian Journal of Chemistry*, vol. 13, no. 5, pp. 5463–5473, 2020.

[34] H. Tounsadi, A. Khalidi, M. Abdennouri, and N. Barka, "Activated carbon from Diplotaxis Harra biomass: optimization of preparation conditions and heavy metal removal," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 59, pp. 348–358, 2016.

[35] Y. A. Neolaka, Y. Lawa, J. Naat et al., "Indonesian Kesambi wood (Schleichera oleosa) activated with pyrolysis and H_2SO_4 combination methods to produce mesoporous activated carbon for Pb(II) adsorption from aqueous solution," *Environmental Technology & Innovation*, vol. 24, Article ID 101997, 2021.

[36] C. C. Luhrs, M. Moberg, A. Maxson, L. Brewer, and S. &Menon, "IF-WS2/nanostructured carbon hybrids generation and their characterization," *Inorga*, vol. 2, no. 2, pp. 211–232, 2014.

[37] I. Okman, S. Karagöz, T. Tay, and M. &Erdem, "Activated carbons from grape seeds by chemical activation with potassium carbonate and potassium hydroxide," *Applied Surface Science*, vol. 293, pp. 138–142, 2014.

[38] H. Laksaci, A. Khelifi, B. Belhamdi, and M. &Trari, "The use of prepared activated carbon as adsorbent for the removal of orange G from aqueous solution," *Microchemical Journal*, vol. 145, pp. 908–913, 2019.

[39] P. Senthil Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi, and S. &Sivanesan, "Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions," *Desalination*, vol. 261, no. 1-2, pp. 52–60, 2010.

[40] M. Choudhary, R. Kumar, and S. &Neogi, "Activated biochar derived from Opuntiaficus-indica for the efficient adsorption of malachite green dye, Cu^{+2} and Ni^{+2} from water," *Journal of Hazardous Materials*, vol. 392, Article ID 122441, 2020.

[41] C. Tien, *Fundamentals of Adsorption Process*, Gulf Publishing Company, Houston, TX, USA, 1989.

[42] Y. A. Neolaka, A. A. Riwu, U. O. Aigbe et al., "Potential of activated carbon from various sources as a low-cost adsorbent to remove heavy metals and synthetic dyes," *Results in Chemistry*, vol. 5, Article ID 100711, 2023.

[43] K. J. Cronje, K. Chetty, M. Carsky, J. N. Sahu, and B. C. Meikap, "Optimization of chromium (VI) sorption potential using developed activated carbon from sugarcane bagasse with chemical activation by zinc chloride," *Desalination*, vol. 275, no. 1–3, pp. 276–284, 2011.

[44] Z. Wang, E. Nie, J. Li, Y. Zhao, X. Luo, and Z. Zheng, "Carbons prepared from Spartina alterniflora and its anaerobically digested residue by H_3PO_4 activation: characterization and adsorption of cadmium from aqueous solutions," *Journal of Hazardous Materials*, vol. 188, no. 1-3, pp. 29–36, 2011.

[45] A. K. Giri, R. Patel, and S. Mandal, "Removal of Cr (VI) from aqueous solution by *Eichhornia crassipes* root biomass-derived activated carbon," *Chemical Engineering Journal*, vol. 185-186, pp. 71–81, 2012.

[46] K. Mohanty, M. Jha, B. C. Meikap, and M. N. Biswas, "Removal of chromium (VI) from dilute aqueous solutions by activated carbon developed from Terminalia arjuna nuts activated with zinc chloride," *Chemical Engineering Science*, vol. 60, no. 11, pp. 3049–3059, 2005.

[47] F. Sardella, M. Gimenez, C. Navas, C. Morandi, C. Deiana, and K. Sapag, "Conversion of viticultural industry wastes into activated carbons for removal of lead and cadmium," *Journal of Environmental Chemical Engineering*, vol. 3, no. 1, pp. 253–260, 2015.

[48] J. Anandkumar and B. Mandal, "Removal of Cr(VI) from aqueous solution using Bael fruit (Aegle marmelos correa) shell as an adsorbent," *Journal of Hazardous Materials*, vol. 168, no. 2-3, pp. 633–640, 2009.

[49] S. Sugashini and K. M. M. S. Begum, "Preparation of activated carbon from carbonized rice husk by ozone activation for Cr (VI) removal," *New Carbon Materials*, vol. 30, no. 3, pp. 252–261, 2015.

[50] A. El Nemr, A. El-Sikaily, A. Khaled, and O. Abdelwahab, "Removal of toxic chromium from aqueous solution, wastewater and saline water by marine red alga Pterocladia capillacea and its activated carbon," *Arabian Journal of Chemistry*, vol. 8, no. 1, pp. 105–117, 2015.

[51] F. Cao, C. Lian, J. Yu, H. Yang, and S. Lin, "Study on the adsorption performance and competitive mechanism for heavy metal contaminants removal using novel multi-pore activated carbons derived from recyclable long-root *Eichhornia crassipes*," *Bioresource Technology*, vol. 276, pp. 211–218, 2019.

[52] A. Kumar and H. M. Jena, "Adsorption of Cr (VI) from aqueous solution by prepared high surface area activated carbon from Fox nutshell by chemical activation with H_3PO_4," *Journal of Environmental Chemical Engineering*, vol. 5, no. 2, pp. 2032–2041, 2017.

[53] A. K. Prajapati, S. Das, and M. K. Mondal, "Exhaustive studies on toxic Cr (VI) removal mechanism from aqueous solution using activated carbon of Aloe vera waste leaves," *Journal of Molecular Liquids*, vol. 307, Article ID 112956, 2020.

[54] S. Shamohammadi, M. Khajeh, R. Fattahi, and M. Kadkhodahosseini, "Introducing the new model of chemical adsorption for heavy metals by Jacobi activated carbon adsorbents, Iranian activated carbon and blowy sand," *Case Studies in Chemical and Environmental Engineering*, vol. 6, Article ID 100220, 2022.