Article

Efficient Sulfate Adsorption on Modified Adsorbents Prepared from *Zea mays* Stems

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Abstract: The effect of temperature on the sulfate adsorption capacity of adsorbents prepared from corn stalks (*Zea mays*) was evaluated. Two bioadsorbents were prepared from biomass: a biochar modified with H₂SO₄ with mass: volume ratio 1:1 (B 1:1), and cellulose modified with cetyl trimethyl ammonium chloride (CTAC). There were also determined thermodynamic parameters (ΔG° , ΔS° and ΔH°) and it was studied the adsorption kinetics and isotherm. At 25 °C was obtained the highest adsorption capacity of 16.4 and 7.4 mg/g with mass/volume ratio B 1:1 and modified corn (MC) respectively; it was observed an adverse effect of temperature increase on bioadsorbents' performance. The thermodynamic parameters showed that the adsorption process is exothermic, not spontaneous, and it was given by chemisorption. Adsorption kinetics showed that equilibrium was reached at 420 min and that the pseudo-second-order model adjusted the experimental data with $R^2 > 0.98$ and q_e of 16.64 and 7.48 mg/g for B 1:1 as well as MC. The adsorption isotherm showed a good fit to Freundlich's model when using B 1:1, whereas using MC as adsorbents the data was adjusted by Dubinin-Radushkevich's model. *Zea mays* stems are an abundant agricultural residue and are a good source for the preparation of biochar type bioadsorbents as well as the extraction of cellulose, its use is recommended in the removal of sulfates in solution.

Keywords: biochar; adsorption kinetics; sulphate ions; corn; cellulose modification

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1. Introduction

Sulfate ions appear in surface and ground water. The main sources of sulfate in natural water are chemical weathering and the oxidation processes of sulfur-containing minerals [1]. However, their concentration in water bodies has been increasing over time, due to the discharge of industrial effluents such as those from acid mine drainage, pharmaceutical wastewater, printing and dyeing [2]. Although the sulfate ion is often considered nontoxic, high concentrations of sulfate ions in water can cause an imbalance in the natural sulfur cycle in the ecosystem and endanger human health with prolonged ingestion, causing a laxative effect, dehydration and gastrointestinal irritation [3]. Therefore, the sulfate ion needs to be removed from any wastewater before it is discharged into the surrounding environment.

Several physical, biological and chemical processes have been investigated for the removal of sulfates dissolved in water and wastewater. These processes include adsorption [4], electrocoagulation [5], ion exchange [6], chemical precipitation [7], coagulation, crystallization, membrane filtration and reverse osmosis [8]. Adsorption removal is widely used due to its capacity for fast and effective removal. The adsorbent plays an important role in determining the effectiveness of the adsorption technology. Ideally, the desired adsorbent should be of low cost, have high adsorption capacity and be renewable [9].

Adsorbents of lignocellulosic origin have been traditionally implemented in adsorption processes. However, a few adsorbents derived from cornstalks have been implemented in the removal of anions [10,11], and these adsorbents have been studied in terms of the kinetic and equilibrium study of adsorption, as well as thermodynamic analysis. The study of the adsorption rate also plays an important role in the implementation of adsorption technology for contaminant removal, since rapid adsorption is ideal, in order to reduce the cost of wastewater treatment and the consumption of time and energy entailed [12]. The adjustment to the kinetics models has contributed to the understanding of the process mechanism [13]. Isothermic study has helped to determine the affinity and interactions between the contaminants and adsorbent's active centers [14]. Numerical modelling based on thermodynamics provides an economical and accurate tool for studying the adsorption process, its costs and the effects of important parameters [15]. Therefore, this study focused on the evaluation of the effects of temperature on the adsorption capacity of sulfates in adsorbents prepared from cornstalks (*Zea mays*). Two bioadsorbents were prepared from biomass: a biochar modified with H_2SO_4 at a mass/volume ratio of 1:1 (B 1:1) and cellulose modified with cetyl trimethyl ammonium chloride (CTAC). Their thermodynamic parameters (ΔG° , ΔS° and ΔH°) were determined, and the corresponding adsorption kinetics and isotherms were studied. This study also examined the kinetics and equilibrium of sulfate anion adsorption on the prepared bioadsorbents.

2. Materials and Methods

2.1. Materials

To prepare the synthetic sulfate solution, analytical grade potassium sulfate (K_2SO_4), Merck Millipore brand with 95% purity, was used as a reagent. Cellulose modification was carried out with 25% methyl trimethyl ammonium chloride (MTAC), and the biocarbons were activated with 98% sulfuric acid (H_2SO_4). A Biobase UV/Vis spectrophotometer model BK-UV1900 was used to determine the final contaminant concentration.

2.2. Biomass Pretreatment

Raw cornstalks (RCSs) were collected as postharvest waste from a village in Bolivar, Colombia. Biomass in better condition was selected to guarantee its properties. The cornstalks were then washed with deionized water, dried in an oven for 12 h at 60 °C and then ground in an electric mill. Sizes between 1 and 2 mm were selected in a shaker-type sieve.

2.3. Preparation of Bioadsorbents

The pretreated cornstalks were impregnated with 50 g of pretreated biomass with 50% H_2SO_4 in a 1:1 weight-to-volume ratio (B 1:1) for 24 h at room temperature (30 °C). Subsequently, the mixture was carbonized in a muffle oven at 520 °C for 30 min with a 10 °C/min ramp. The biochar obtained was washed with abundant distilled water up to neutral pH, dried at 100 °C for 8 h and stored in airtight containers until its use in the adsorption tests [16]. At the end of the process, a yield of 70% was obtained, with 15 g of B 1:1.

For the preparation of the modified cellulose, sizes smaller than 0.14 mm were initially selected. Then, the cellulose was extracted by placing 20 g of the cornstalks in contact with distilled water with mechanical agitation for 10 min. The mixture was filtered, the supernatant was discarded and 500 mL of 4% NaOH solution was added and agitated at 200 rpm at 80 °C for 2 h. The solid sample obtained was washed, treated with NaOH and washed again until the washing water was clear. The cellulose was dried to a constant mass at room temperature. A solution with 50 g of NaCl, 500 mL of distilled water and 50 mL of acid was then added. The mixture was stirred for 24 h at 30 °C and then decanted. The solid obtained was cellulose, which was dried for 3 h at 60 °C [17]. The cellulose was modified by adding 62.8 mL of cetyl trimethyl ammonium chloride (CTAC) at 100 mmol/L, using magnetic agitation at 250 rpm for 24 h at 27 °C [18]. The process is summarized in Figure 1.

Figure 1. Mechanism of biochar modified with H₂SO₄ at a mass/volume ratio of 1:1 (B 1:1) and modified corn (MC) bioadsorbent preparation process.

2.4. Adsorption Tests

The sulfate solution was prepared by dissolving 0.1479 g of dehydrated Na₂SO₄ in 1 L of distilled water according to the ASTM D 560-60 [19]. The experiments were conducted by placing 5 mL of contaminated solution in contact with 0.01 g of adsorbent at 200 rpm in an orbital shaker at different temperatures (25, 30, 35, 40 and 45 °C). Sulfate anion detection was performed by UV/Vis spectrometry at 420 nm. The adsorption capacity (q_e) was determined using Equation (1):

$$q_e \left(\frac{\text{mg}}{\text{g}} \right) = \frac{(C_0 - C_e) * V}{m} \quad (1)$$

where C_0 and C_e represent the initial concentration of anions in the solutions and the concentration in equilibrium after the adsorption process, both expressed in mg/L. V is the volume of the solution in L, and m the amount of adsorbent in g.

2.5. Thermodynamic Parameters

The thermodynamic parameters, namely Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°), were determined by Van't Hoff's graphical method (Equations (2) and (3)) and used to examine the nature of the adsorption and its thermodynamic behavior [20].

$$\Delta G^\circ = -RT \ln(K_c) \quad (2)$$

$$\ln K_C = \frac{-\Delta H^\circ}{R T} + \frac{\Delta S^\circ}{R} \quad (3)$$

where R is the ideal gas constant and has a value of 8314 J/mol K, T is the temperature expressed in kelvin and K_c is the adsorption equilibrium constant.

2.6. Kinetics and Isotherms of Adsorption

Kinetics was studied to determine the saturation time of the adsorbent and the mechanisms that control the adsorption process [21]. Kinetic experiments were carried out at the best temperature condition at 100 mg/L using adsorbent doses of 2 g/L in 100 mL solution, pH 4, at 200 rpm agitation. Samples were taken at 5, 10, 20, 30, 60, 180, 300, 420 and 1440 min for each assay. The pseudo-first-order (Equation (4)), pseudo-second-order

(Equation (5)) and Elovich (Equation (6)) models were adjusted to analyze the experimental kinetic data; their equations and parameters are summarized in Table 1.

Table 1. Kinetic adsorption models [22].

Model	Equation	Parameters
Pseudo-first order	$q_t = q_e \left(1 - e^{-k_1 t}\right)$ (4)	k_1 (min^{-1}): Lagergren's constant q_e (mg/g): amount of contaminant adsorbed per unit mass in the equilibrium q_t (mg/g): amount of contaminant adsorbed per unit of mass at any time t t (min): time
Pseudo-second order	$q_t = \frac{t}{\frac{1}{k_2 * q_e^2} + \frac{t}{q_e}}$ (5)	k_2 ($\text{g mmol}^{-1} \text{min}^{-1}$): second-order reaction speed coefficient q_e (mg/g): amount of contaminant adsorbed per unit mass in the equilibrium q_t (mg/g): amount of contaminant adsorbed per unit of mass at any time t t (min): time
Elovich	$q_t = \frac{1}{\beta} * \ln(\alpha\beta) + \frac{1}{\beta} * \ln(t)$ (6)	α ($\text{mg g}^{-1} \text{min}^{-1}$): initial adsorption rate β (g mg^{-1}): desorption constant related to surface range and activation energy for chemisorption q_t (mg/g) representing the amount of chemisorption gas in a time t t (min): time

The isotherms were studied to describe the phenomena responsible for the process and to represent the amount of solute adsorbed per unit mass in the equilibrium as the initial concentration varies [23]. The experiments were carried out by placing 2 g/L of adsorbent in contact with 100 mL of the solution of the anions at different concentrations, namely 20, 40, 60, 80 and 100 mg/L, for 24 h. The models of Langmuir (Equation (7)), Freundlich (Equation (8)) and Dubinin–Radushkevich (Equation (10)), were adjusted to the experimental data by nonlinear regression in the OriginPro8 software. The equations and parameters are summarized in Table 2.

Table 2. Isothermal models [10].

Model	Equation	Parameters
Langmuir	$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$ (7)	C_e (mg/L): concentration of adsorbate in the equilibrium q_e (mg/g) amount of adsorbate adsorbed per gram of adsorbent at equilibrium $Q_{\max}$ (mg/g): coverage capacity in the monolayer K_L : Langmuir isothermal constant
Freundlich	$q_e = K_F C_e^{1/2}$ (8)	q_e (mg/g): amount of adsorbate adsorbed per gram of adsorbent at equilibrium K_F (L/g): Freundlich's isothermal constant, C_e (mg/L): equilibrium adsorbate concentration
Dubinin–Radushkevich	$q_e = q_{DR} * e^{-K_{DR} \varepsilon^2}$ (9)	ε^2 : potential of Polanyi, which is based on temperature K_{DR} (mol ² /kJ ²): Dubinin–Radushkevich's constant related to adsorption energy
	$\varepsilon = RT * \ln\left(1 + \frac{1}{C_e}\right)$ (10)	E (KJ/mol): the average adsorption energy per molecule of adsorbate required to transfer one mole of the ion from the solution to the surface of the adsorbent
	$E = \frac{1}{\sqrt{2K_{DR}}}$ (11)	

3. Results

3.1. Characterization of RCSs and MC

The elemental content variations of raw and modified corn (RCSs and MC, respectively) are shown in Table 3. In the RCS sample, the contents of nitrogen, carbon and hydrogen were 1.35%, 41.38% and 6.34%, respectively. After the treatment with CTAC, the contents of three elements in MC increased significantly. In particular, the nitrogen content reached 6.34%, confirming that related functional groups (amine groups) were successfully loaded onto the cellulose molecules in the modification process. These results are similar to those reported by Fan and Zhang [24] in their modification of cellulose from cornstalks with epichlorohydrin, N, N-dimethylformamide, pyridine and diethylamine.

Table 3. Elemental content of raw cornstalk (RCS) and modified corn (MC) samples.

	RCS	MC
N (%)	1.35	6.34
C (%)	41.38	52.17
H (%)	6.27	6.93

3.2. Effect of Temperature

The zero pH loading point (pH_{PZC}) was established to determine the ideal pH for anion adsorption, as the exposed surface of a bioadsorbent is protonated at pH values below the pH_{PZC} [21]. The pH_{PZC} of the B 1:1 was 5.17 and that of the MC was 6. Therefore, to guarantee the protonation of the surface of the biomaterial, the working pH of 4 was selected for use in the adsorption tests using the B 1:1 and the MC.

The bioadsorption tests were performed at pH 4, initial concentration of 100 mg/L and adsorbent dose of 2 g/L, varying the temperature between 25 and 45 °C. Figure 2 shows the effects of temperature on sulfate adsorption capacity of B 1:1 and MC. The results showed that a temperature of 25 °C resulted in the best behavior of the adsorbents in the removal of the anion, and B 1:1 presented the best performance. Consequently, as the temperature increased, the adsorption capacity of the adsorbents decreased, which could be due to the exothermic nature of the process, as similarly reported for the removal of sulfates on quaternized cellulose [25].

Figure 2. Effect of temperature on sulfate adsorption capacity using B 1:1 and MC.

The thermodynamic parameters, namely ΔH° , ΔS° and ΔG° , were calculated using Van't Hoff's method, and the results are summarized in Table 4. The negative values of ΔH° indicate that the process is exothermic, as shown by the results presented in Figure 1, which demonstrates that the application of energy to the system is not required for the reactions to occur [26]. The value of ΔH° was higher for B 1:1, which explains the greater exothermic character of the reactions on the biochar. This would explain the decrease of the capacity of adsorption of B 1:1 as the temperature increased up to 45 °C. The decrease of the adsorption capacity as the temperature increased could result from the weakening of the interaction of forces between the adsorbate and the adsorbent due to the increase in the energy of the system [27].

Table 4. Thermodynamic parameters of sulfate adsorption.

Adsorbent	T (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol·K)	ΔS° (KJ/mol)
B 1:1	298	9.197	−57.359	−0.223
	303	10.313	-	
	308	11.429	-	
	313	12.546		
	318	13.662		
MC	298	11.8795	−25.5705	−0.1256
	303	12.5075		
	308	13.1355		
	313	13.7636		
	318	14.3916		

The positive value of ΔG° shows that the system is not spontaneous, and the increase in its value indicates that the system loses spontaneity as the temperature increases, indicating that agitation is necessary [16]. The negative entropy value indicates the associative process of sulfate adsorption over B 1:1 and MC, which shows that the existing particles in the solution were smaller after the adsorption process, demonstrating that the process takes place by chemisorption [28].

3.3. Adsorption Kinetics

The effect of time on the adsorbent removal capacity (Figure 3) was assessed to determine the possible mechanisms involved in the adsorption process [29]. It was found

that anion uptake happened quickly in the first few minutes of the process and gradually decreased until equilibrium was reached. This phenomenon occurred due to the availability of free active sites of adsorption for sulfate retention, which are occupied as the contact time passes [1]. Equilibrium was reached at about 420 min for the two adsorbents, with better performance of B 1:1, which could be due to surface protonation as a result of its modification with sulfuric acid [30].

Figure 3. Sulfate adsorption kinetics for (a) B 1:1 and (b) MC.

The experimental data were fitted to the pseudo-first-order, pseudo-second-order and Elovich models by nonlinear regression, and the fitting parameters are summarized in Table 5.

Table 5. Adjustment parameters of sulfate adsorption kinetics.

Model	Parameters	MC	B 1:1
Pseudo-first order	q_e (mg/g)	6.8739	14.801
	k_1 (min^{-1})	0.0258	0.018
	SE	0.19820	0.5168
	R^2	0.9730	0.966
Pseudo-second order	q_e (mg/g)	7.4891	16.646
	k_2 (g/mg·min)	0.0045	0.0013
	SE	0.0764	0.4291
	R^2	0.9975	0.988
Elovich	α (mg/g·min)	0.7856	0.976
	β (g/mg)	0.9199	0.976
	SE	0.2935	0.2113
	R^2	0.9455	0.959

The kinetics of sulfate adsorption over B 1:1 and MC is described by the pseudo-second-order model, whose correlation coefficient (R^2) is closer to 1.0, and the equilibrium adsorption quantities calculated are much closer to the experimental values. This suggests that the mechanism by which adsorption occurs is chemical, in which the speed of adsorption is limited by valence forces given by the exchange of electrons between the adsorbate and the adsorbent [24], and that the limiting step is chemisorption due to physicochemical interactions between the two phases [31], as evidenced by the thermodynamic parameters (Table 2). A previous study also showed that sulfate adsorption follows the pseudo-second-order model [9].

3.4. Adsorption Equilibrium

The sulfate adsorption isotherms over B 1:1 and MC are represented in Figure 4, and the experimental data were adjusted with the Langmuir, Freundlich and Dubinin–

Radushkevich equations (Table 6). The sulfate adsorption isotherm over B 1:1 rose very rapidly as concentrations increased (Figure 3a), indicating a high affinity of part of the bioadsorbent for the anion. When using MC, the adsorption capacity increased at lower sulfate concentrations. However, as the sulfate concentration in solution increased, the amount of sulfate adsorbed reached a limit value and decreased. The behavior of MC suggested that there is a strong affinity between sulfate ions and adsorbent, although it showed worse performance than B 1:1 [4].

Figure 4. Isothermal sulfate adsorption on (a) B 1:1 and (b) MC.

Table 6. Adjustment parameters of sulfate adsorption isotherms.

Model	Parameter	B 1:1	MC
Langmuir	$q_{\max}$ (mg/g)	29.514	19.779
	K_L (L/mg)	9.06×10^{-5}	5.16×10^{-5}
	SE	0.2937	0.5165
	R^2	0.945	0.7014
Freundlich	K_f (mg/g)	0.221	0.0627
	n	0.965	0.9041
	SE	1.139	2.9381
	R^2	0.946	0.7081
Dubinin–Radushkevich	q_{DR} (mg/g)	20.247	10.7359
	K_{DR} (mol ² /kJ ²)	1.29×10^{-4}	2.4493×10^{-4}
	E (KJ/mol)	62.257	45.1819
	SE	2.4117	2.1699
	R^2	0.919	0.8465

According to the standard error (SE) and R^2 values, Dubinin–Radushkevich’s model fits the data better when using MC. Since the E value is higher than 8 KJ/mol, it can be concluded that the process is controlled by chemisorption with strong interactions between the active centers and the anion [32], as evidenced by the calculation of thermodynamic parameters (Table 3). Based on the fit to Dubinin–Radushkevich’s model, it can be assumed that the bioadsorbent presents a heterogeneous structure [33]. Using B 1:1, it was found that Freundlich’s model describes the adsorption equilibrium, indicating that the process occurs in multilayers on the surface of the bioadsorbent due to its heterogeneity [10].

4. Conclusions

The conclusions of this study are as follows: (i) *Zea mays* stems are a good source for the preparation of bioadsorbent-type biochar as well as the extraction of cellulose. (ii) An evaluation of the effects of temperature showed that the highest adsorption capacity (16.4 mg/g and 7.3 mg/g for B 1:1 and MC, respectively) was obtained at 25 °C, and the increase in temperature had an adverse effect on the performance of the bioadsorbents. (iii) The thermodynamic parameters showed that the adsorption process is exothermic and not spontaneous and that it occurs by chemisorption. (iv) A better performance of B 1:1 was indicated, which could be due to the protonation of the bioadsorbent and the bivalent nature of the anion. (v) Adsorption kinetics showed that equilibrium was reached at 420 min and that the pseudo-second-order model adjusted the experimental data. (vi) The adsorption equilibrium determined that Freundlich's model adjusted the removal data for B 1:1, indicating that the process is multilayered. However, Dubinin–Radushkevich's model adjusted the adsorption data for MC, establishing that the mechanism that controls the process is chemisorption with strong interactions between the active centers and the anion.

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