



Article Single-Step Modification of Brewer's Spent Grains Using Phosphoric Acid and Application in Cheese Whey Remediation via Liquid-Phase Adsorption

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Abstract: Brewer's spent grains (BSG) are a significant by-product of beer production, and its improper disposal poses environmental challenges. This study investigated the use of BSG for activated carbon production with phosphoric acid as a chemical activator and its application in cheese whey remediation through liquid-phase adsorption. The adsorbent was thoroughly characterized through using techniques such as FTIR, SEM, N₂ isotherms, and surface charge distribution. The adsorbent exhibited substantial pores, a high surface area ($605.1 \text{ m}^2 \text{ g}^{-1}$), good porosity, and positive surface charges that facilitated favorable interactions with cheese whey compounds. Equilibrium was achieved in 330 min for lactose, BOD5, and COD. The maximum adsorption capacities were 12.77 g g⁻¹ for lactose, 3940.99 mg O₂ g⁻¹ for BOD₅, and 12,857.92 mg O₂ g⁻¹ for COD at 318 K. Removing these adsorbates from cheese whey effluent reduces its organic load, enabling water reuse in the manufacturing unit, depending on its intended use. The adsorption process was spontaneous and endothermic, with $\Delta H^{\circ} \geq 265.72$ kJ mol⁻¹. Additionally, the activated carbon produced demonstrated impressive regeneration capability with sodium hydroxide, maintaining 75% of its adsorption capacity. These results emphasize the potential of activated carbon as an effective adsorbent for cheese whey remediation, providing a sustainable solution for waste management in the dairy industry and water reuse.

Keywords: sustainable waste conversion; dairy industry wastewater; activated carbon; brewer's spent grains; adsorbent

1. Introduction

Lignocellulosic resources, obtained from either natural origins or through chemical and biotechnological methods, represent sustainable source materials. There is an increasing enthusiasm for employing these resources as alternatives to fossil-based carbon in the production of various chemicals and premium biomaterials [1]. The major constituents of lignocellulosic materials include cellulose, hemicellulose, holocellulose, and lignin, and their makeup can differ depending on factors such as the source material, harvesting methods, and growth conditions [2].

Brewer's spent grains (BSG) are a good example of lignocellulosic material. Their composition of lignin, cellulose, and hemicellulose can vary between 11 and 13%, 19 and 21%, and 34 and 48%, respectively [3–5]. The most significative by-product generated from brewing is BSG, estimated to be approximately 3 million tons per year [6,7]. The large amount of by-products generated can become a significant problem if not disposed



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of correctly. While a considerable amount is used for animal manufacturing, the quantity generated still exceeds consumption [8].

Therefore, it is necessary to find alternatives uses for BSG, such as in a biorefinery context in the production of sugars and amino acids [9], bioenergy [10], and ethanol [11]. Additionally, research indicates that BSG is a very promising material for producing activated carbon for use in adsorption processes [12–15]. BSG possesses great characteristics for use as an adsorbent due to its high concentration of carbon, silicon, and aluminum, as well as its high volatile content, which facilitates pore formation [16].

Several methods can be used to activate carbonaceous materials, with the majority of used methods being chemical methods involving phosphoric acid (H_3PO_4) and potassium hydroxide (KOH) [3]. As previously mentioned, various studies have employed phosphoric acid (H_3PO_4) as an activating agent. For instance, from banana peel, Romero-Ayana et al. [17] obtained activated carbon with a surface area over 2000 m² g⁻¹ and a yield higher than 35%. Highlighting the significance of method selection, it is crucial to consider factors such as the time required for synthesis, the nature and potential harm of the reagents, the properties of the resulting material, and, most importantly, the level of complexity and the equipment needed [18–20].

Cheese whey (CW) is the primary wastewater from cheese manufacturing, constituting a residue containing fats, proteins, and carbohydrates, resulting in a high organic load [21,22]. This effluent exhibits high resistance in terms of COD (700–78,000 mg L⁻¹) and BOD (500–17,000 mg L⁻¹) [22–24]. Numerous methods and strategies have been explored for managing the wastewater produced by the cheese manufacturing industry. These encompass a range of approaches, such as physical–chemical and biological methods, electrochemical solutions, constructed wetlands, advanced oxidation processes, and hybrid systems, among others [25–27].

Nguyen et al. [28] demonstrated that activated carbon possesses the capability to eliminate stubborn organic compounds. The utilization of waste in the form of activated carbon as part of the adsorption process has emerged as an alternative to conventional waste treatment procedures. This approach has demonstrated effectiveness, is cost-effective, eliminates the need for chemical processes, produces no sludge, and proves highly efficient in both discoloration and degradation processes [29]. Adsorption using activated carbon has become an emerging technology that the industry can explore for the treatment of liquid waste, and several studies have shown that the use of adsorption with activated carbon in industrial effluents yields better results when compared to conventional methods [30,31]. Wastewater treatment contributes to water savings by purifying polluted water for reuse in various industrial and commercial applications. This not only reduces the need for fresh water but also helps companies comply with stringent regulations, save on operational costs, preserve natural water resources, prevent environmental pollution, and promote sustainable water management [32,33].

The objective of this work was to evaluate the use of BSG to produce activated carbon using H_3PO_4 as a chemical activator and apply it in the remediation of cheese whey via liquid-phase adsorption.

2. Materials and Methods

2.1. Materials

The BSG samples were provided by craft beer producers in the northern region of Paraná State, Brazil. Before use, the BSG were quartered, and opposite quarters were used for analysis, while the others were separated. Subsequently, the samples were washed to remove any physical contaminants, such as leaves and sticks. Additionally, some of the BSG were dried in a forced circulation oven (Lucadema, model 82/480) at 60 °C for 24 h to remove all moisture from the samples. The CW was provided by a cheese factory in the northern region of Paraná State, Brazil, and the CW was obtained from the production of "Minas Frescal" cheese on site. The CW was extracted during the curd cutting stage of

producing coagulated milk. After the collection, the CW was filtered with a cheesecloth to remove any particulate matter from the production process.

2.2. Preparation of Adsorbent

This study employed a one-step acid activation procedure using H₃PO₄ [18]. In this process, 20 g BSG were combined with 20 g H₃PO₄ solution (85% w/v). The resulting mixture was stirred for 5 min and allowed to sit undisturbed for 8 h. Afterward, the material was rinsed with distilled water to eliminate any excess acid and subsequently dried at 105 °C overnight. Following the drying step, the sample underwent carbonization at 400 °C for 4 h, with a temperature increase rate of 10 °C min⁻¹ within a muffle furnace (Solidsteel, model SSFM 16L). The sample was then subjected to washing with a NaHCO₃ solution (2% w/v) until it reached a pH of 7. Finally, the sample was dried for approximately 4 h at 120 °C and coded as AC_{PO4}. In order to gauge the effectiveness of the synthesized adsorbent, a commercial activated carbon ($\emptyset_{\text{particle}} = 5 \text{ mm}$) was employed as a reference sample in all tests.

2.3. Adsorbent Characterization

The samples were characterized using scanning electron microscopy (SEM) with energy dispersive spectroscopy (VEGA3—TESCAN) to obtain micrographs and determine their elemental composition. N₂ adsorption/desorption isotherm measurements were carried out using a sorption analyzer (NOVA 2000e—Quantachrome Instruments). Fouriertransform infrared spectroscopy (FTIR, Spectrum Two—Perkin Elmer) was also used. The point of zero charges (PZC) or surface charge distribution was determined by mixing 50 mg adsorbent with 50 mL aqueous solution at different initial pH conditions (2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12), adjusting the solutions with HCl or NaOH 0.1 mol L⁻¹, and measuring the pH after 24 h of equilibrium [30].

2.4. Cheese Whey Adsorption Assays

To evaluate the capacity of the adsorbent in real effluent decontamination processes, adsorption tests with cheese whey were carried out. The parameters evaluated during the adsorption tests included the reduction in lactose content, reduction in biochemical oxygen demand (BOD₅), and reduction in chemical oxygen demand (COD). These parameters were evaluated to determine the level of decontamination of the actual effluent. Lactose content was determined via titration using the adapted Lane–Eynon method [34], while the BOD₅ and COD contents were determined using the American Public Health Association method [35].

The acid modification of the BSG was evaluated through a test comparing the biomass and the synthesized material to commercial activated carbon to estimate the impact of the activation method on the adsorbent's adsorptive capacity. The cheese whey volume was 50 mL at pH = 6.5, the adsorbent concentration was 10 g L⁻¹ (m = 0.05 g), the temperature was 25 °C, and the reaction time was 24 h. The initial experiments were conducted by altering the activated carbon concentration to identify the ideal quantity of adsorbent. This allowed for subsequent tests to be performed with the minimal amount of material required, thus optimizing its utilization. The concentration of the AC_{PO4} activated carbon was varied from 0.5 g L⁻¹ to 10 g L⁻¹ (m = 0.025–0.5 g), and we used 50 mL of cheese whey at pH = 6.5, 25 °C, under agitation in a shaker (TE-424 Tecnal) for 12 h.

The equations for calculating the percentage removal of lactose, BOD₅, and COD (R, %) (Equation (1)), adsorption capacity at any time for the lactose (q_L , $g g^{-1}$) (Equation (2)), and adsorption capacity for the BOD₅ and COD (q_B , q_C , mg g^{-1}) (Equation (3)) are presented below:

$$\mathbf{R} = \left(\frac{\mathbf{C}_0 - \mathbf{C}}{\mathbf{C}_0}\right) \mathbf{100} \tag{1}$$

$$q_{\rm L} = \left(\frac{(x_0 - x_t) \rho}{m}\right) V \tag{2}$$

$$q_{\rm B} = q_{\rm C} = \left(\frac{y_0 - y_t}{m}\right) V \tag{3}$$

where R (%) is the percentage of reduction of the analyzed parameter, C_0 (g of lactose 100 g⁻¹ of cheese whey or mg of $O_2 L^{-1}$ of cheese whey) is the initial concentration of the parameters lactose, BOD₅, and COD, respectively, C (g of lactose 100 g⁻¹ of cheese whey or mg of $O_2 L^{-1}$ of cheese whey) is the final concentration of the parameters lactose, BOD₅, and COD, q_L (g of lactose g^{-1} of adsorbent) is the quantity of lactose adsorbed at time t, x_0 (g of lactose g^{-1} of cheese whey) is the initial concentration of lactose, x_t (g of lactose g^{-1} of cheese whey) is the initial concentration of lactose, x_t (g of lactose g^{-1} of cheese whey) is the time t concentration of lactose, ρ (1023.2 g of cheese whey L^{-1} of cheese whey) is the specific mass of cheese whey, m (g) is the mass of the adsorbent, V (L) is the volume of the solution of cheese whey, q_B and q_C (mg of $O_2 g^{-1}$ of adsorbent) represent the quantity of biological/chemical oxygen dissolved in the CW at time t, y_0 (mg of $O_2 g^{-1}$ of cheese whey) is the initial quantity of biological/chemical oxygen dissolved in the CW, and y_t (mg of $O_2 g^{-1}$ of cheese whey) is the time t quantity of biological/chemical oxygen dissolved in the CW.

2.4.1. Kinetic Modeling

To determine the equilibrium time (t_e) for the adsorption assays with the CW, a kinetic study was performed using the same parameters as the preliminary tests. Aliquots were collected every 15 min for the first 2 h and then every hour until equilibrium.

The theoretical amount of lactose, BOD₅, and COD adsorbed at equilibrium (q_e) was determined using four kinetic models: pseudo-first-order (PFO), pseudo-second-order (PSO), and Avrami fractional-order (AFO) [18,36–38]. These values were then compared with the experimental values obtained for the parameters adsorbed at equilibrium (q_{eExp}). The pseudo-first-order (Equation (4)), pseudo-second-order (Equation (5)), and Avrami fractional-order (Equation (6)) models are represented below:

$$q_t = q_e (1 - e^{-k_1 t}) \tag{4}$$

$$q_{t} = \frac{k_{2}q_{e}^{2} t}{1 + (k_{2}q_{e}t)}$$
(5)

$$q_t = q_e (1 - e^{\left(-k_A t\right)^{n_A}})$$
(6)

where $q_e (mg g^{-1})$ is the quantity of the parameters adsorbed at equilibrium, $k_1 (min^{-1})$ represents the pseudo-first-order kinetic constant, t (min) represents the reaction time, $k_2 (g mg^{-1} min^{-1})$ represents the pseudo-second-order kinetic constant, $k_A (min^{-1})$ represents the Avrami kinetic constant, and n_A (dimensionless) is the exponent Avrami of time.

2.4.2. Equilibrium Modeling

The present study involved delving into the adsorption equilibrium process and specifically examining the relationship between the concentration of parameters (C_e) in the liquid phase (solution) and the concentration of parameters (q_e) on the surface of the solid phase (adsorbent). This investigation involved analyzing adsorption isotherms and assessing how temperature impacts the maximum adsorbent capacity of the materials. Experimental isotherm data were collected at temperatures of 288, 298, 308, and 318 K and then adjusted using four models: Langmuir (Equation (7)), Freundlich (Equation (8)), Dubinin–Radushkevich (Equation (9, 10 and 11)), and Hill (Equation (12)) [39–41].

$$q_e = q_L \frac{K_L C_e}{1 + K_L C_e} \tag{7}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{8}$$

$$q_{e} = q_{mDR} \exp\left(-\beta \varepsilon^{2}\right) \tag{9}$$

$$\varepsilon = \operatorname{RTln}\left(\frac{C_{\rm S}}{C_{\rm e}}\right) \tag{10}$$

$$E_s = \left(\frac{1}{\sqrt{2\beta}}\right) \tag{11}$$

$$q_{e} = \frac{n_{H}q_{mH}}{1 + \left(\frac{C_{1/2}}{C_{e}}\right)^{n_{H}}}$$
(12)

where q_L (mg g⁻¹) is the maximum biosorption capacity of the Langmuir model, K_L (L mg⁻¹) is the Langmuir constant, K_F ((mg g⁻¹) (mg L⁻¹)^{-1/n}) is the Freundlich constant, 1/n (dimensionless) is the heterogeneity factor, β (mol² kJ⁻²) is the Dubinin–Radushkevich constant, ϵ is the Polanyi potential, R (8314 J mol⁻¹ K⁻¹) is the universal gas constant, C_S (mg L⁻¹) is the solubility, $C_{1/2}$ (mg L⁻¹) is the concentration at half saturation, n_H (dimensionless) is the number of molecules per site, and q_{mH} (mg g⁻¹) is the density of receptor sites.

2.4.3. Thermodynamic Modeling

A thermodynamic study was carried out to improve our understanding of the energetic changes involved during the adsorption process at different temperatures. Enthalpy (ΔH°) , entropy (ΔS°) , the free energy of adsorption (ΔG°) , and activation energy (E_a) were calculated for a better understanding of the effects of the parameters under the interaction mechanism between the adsorbent and adsorbate involved in the adsorption process. The equations of Van 't Hoff, Gibbs–Helmholtz, and Arrhenius [42,43] were used to determine the parameters mentioned above. The standard Gibbs free energy change (ΔG° , kJ mol⁻¹), enthalpy change (ΔH° , kJ mol⁻¹), entropy change (ΔS° , kJ mol⁻¹ K⁻¹), and activation energy (E_a, kJ mol⁻¹) were calculated using the following Equations:

$$K_{e} = \frac{KM_{W}\gamma^{CW}}{\Gamma}$$
(13)

$$\Delta G^{\circ} = -RTln(K_e) \tag{14}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$
⁽¹⁵⁾

$$\ln(K_e) = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(16)

$$\mathbf{k}' = \mathbf{A} \, \mathbf{e}^{-\frac{\mathbf{E}_a}{\mathbf{R}\mathbf{I}}} \tag{17}$$

$$\ln (\mathbf{k}') = \ln \mathbf{A} - \frac{\mathbf{E}_{\mathsf{a}}}{\mathbf{R}\mathbf{T}}$$
(18)

where K_e (dimensionless) is the equilibrium constant, K (L mg⁻¹) is the constant parameter from the most suitable isotherm fit, M_W (26,600 g mol⁻¹) is the molecular weight of the solid constituents in cheese whey, γ (dimensionless, assuming $\gamma^{CW} = 1$) is the activity coefficient of cheese whey, Γ (1 mol L⁻¹) is the unitary activity coefficient of cheese whey, T (K) is the temperature, R (8.314 × 10⁻³ kJ mol⁻¹ K⁻¹) is the universal gas constant, ΔS° (kJ mol⁻¹ K⁻¹) represents adsorption entropy, ΔH° (kJ mol⁻¹) represents adsorption enthalpy, ΔG° (kJ mol⁻¹) represents the free energy of adsorption, k'(min⁻¹) is the constant parameter from the most suitable kinetic fit, A (dimensionless) is a pre-exponential factor, and E_a (kJ mol⁻¹) represents the activation energy.

2.5. Desorption and Regeneration Experiments

After the adsorption of CW was carried out under the optimal conditions (see conditions in Section 3.4), desorption experiments of CW from AC_{PO4} were carried out using HCl (0.1 mol L⁻¹) and NaOH (0.1 mol L⁻¹) solutions as eluents [44–46]. A total of 500 mg of AC_{PO4} loaded with CW were in contact with 50 mL of the eluent (HCl or NaOH) and agitated for 2 h at 200 rpm for desorption. The concentration of lactose, BOD₅, and COD in the liquid phase were determined as in Section 2.4. The regeneration assays were carried out 5 times.

2.6. Statistical Analysis

Nonlinear techniques were applied to assess the compatibility of the kinetic and equilibrium data through the utilization of the Simplex method and the Levenberg–Marquardt algorithm. These methods were employed within the fitting capabilities of the Microcal Origin 2021 software. To gauge the appropriateness of the kinetic and equilibrium models, various metrics were employed, including the residual sum of squares (RSS), determination coefficient (R²), adjusted determination coefficient (R²_{adj}), standard deviation of residues (SD), and the Bayesian information criterion (BIC). Mathematical representations for these metrics are presented in Equations (19)–(23).

$$RSS = \sum_{i}^{n} \left(q_{i, exp} - q_{i, model} \right)^{2}$$
(19)

$$R^{2} = \left(\frac{\sum_{i}^{n} (q_{i,exp} - q_{exp})^{2} - \sum_{i}^{n} (q_{i,exp} - q_{i,model})^{2}}{\sum_{i}^{n} (q_{i,exp} - q_{exp})^{2}}\right)$$
(20)

$$R_{adj}^{2} = 1 - \left(1 - R^{2}\right) \cdot \left(\frac{n - 1}{n - p - 1}\right)$$
(21)

$$SD = \sqrt{\left(\frac{1}{n-p}\right) \cdot \sum_{i}^{n} \left(q_{i, exp} - q_{i, model}\right)^{2}}$$
(22)

$$BIC = nLn\left(\frac{RSS}{n}\right) + pLn(n)$$
(23)

In the equations provided above, each $q_{i, model}$ represents the predicted theoretical q value for a specific individual as per the model's prediction. Correspondingly, $q_{i, exp}$ stands for the individual experimental q value obtained through actual experimentation. The symbol q_{exp} denotes the mean of all the measured experimental q values. The variable n signifies the total count of experiments conducted, while p represents the count of parameters in the fitting model.

Our analysis included the presentation of R^2_{adj} , SD, and BIC values to facilitate a comparison between the various kinetics and equilibrium models outlined in this study. The ideal model exhibited R^2_{adj} values nearing 1.000, lower SD values, and minimized BIC values. However, selecting the optimal kinetic and equilibrium model involves a more nuanced assessment beyond relying solely on R^2 values, especially when these models encompass differing parameter quantities. Hence, it becomes imperative to ascertain whether enhancements in R^2 values stem from an increase in parameters or if, in a physical sense, the model featuring a greater number of parameters more effectively elucidates the underlying process.

Nevertheless, the disparity in BIC values among models could be decisive when the discrepancy in BIC values is \leq 2.0, indicating the absence of a significant distinction between the two models. Within the range of BIC value differences spanning 2 to 6, a favorable trend arises toward the model possessing the lower BIC value, signifying its enhanced suitability. In instances where the range of BIC value differences stretches from 6 to 10, a robust likelihood emerges that the model with the lower BIC value constitutes the most fitting choice. However, if the contrast in BIC values attains \geq 10.0, a confident prediction can be made that the model endowed with the lower BIC value is unequivocally the superior fit.

3. Results and Discussion

3.1. Adsorbents Characterization

Figure 1 shows the SEM micrographs obtained for the materials used in this study. All the materials presented a rugged surface with laminar and granular particles, which are characteristic of biomass and activated carbons obtained from biomass [47–49]. The AC_{PO4} (Figure 1e,f) displayed a great distribution of pores on the surface, characteristic of materials with excellent adsorptive capacity and high surface area, as shown in previous publications [50,51]. These favorable characteristics can allow for the favorable penetration of cheese whey molecules into the pores of the particles [52].



Figure 1. SEM micrographs: BSG (**a**) $500 \times$ magnification and (**b**) $5000 \times$ magnification; commercial activated carbon (5 mm) (**c**) $500 \times$ magnification and (**d**) $5000 \times$ magnification; ACPO₄ (**e**) $500 \times$ magnification and (**f**) $5000 \times$ magnification.

The elemental composition of the materials was determined via EDS analysis, as shown in Table 1. Overall, the primary element in all materials was carbon, indicating that the materials were carbonized throughout the synthesis process, as was the case for AC_{PO4} and the commercial activated carbon. This high carbon content might also be a sign of the adsorptive capacity of the adsorbents, as shown in the literature [18,53]. Because the materials were carbonized in the presence of air, oxygen was also expected. Silicon, magnesium, potassium, and calcium emanated from the inherent composition of the barley that generated the BSG during beer production [16,54]. The presence of phosphorus in the AC_{PO4} comes from the reagent used during synthesis (H₃PO₄).

Table 1. EDS analysis of the adsorbents.

Adsorbent				Composition	(%)		
Ausorbent	С	0	Si	Mg	К	Ca	Р
BSG	86.35	13.23	0.42	0.26	0.11	0.74	
Commercial 5 mm	86.35	13.23	0.42				-
PO ₄	54.47	30.72	1.74		-		13.07



Figure 2 shows the N_2 adsorption–desorption isotherms for the adsorbents obtained.

Figure 2. N₂ measurements: (**a**) adsorption and desorption isotherm for BSG; (**b**) adsorption and desorption isotherm for the commercial activated carbon (5 mm); (**c**) adsorption and desorption isotherm for AC_{PO4} ; (**d**) pore size distribution.

In Figure 2a,b, the isotherms are like Type I isotherms, typical of microporous materials, while the isotherms in Figure 2c resemble Type II isotherms, characteristic of microporous and mesoporous materials [55,56]. This shift in the isotherm format occurred for the chemically activated material, where the volume of N_2 adsorbed decreased, probably due to the interaction between the base material and chemical/thermal reactions that occurred during the activation process, modifying the surface structure of the materials, especially the shape and depth of the pores. Other publications in the literature have reported similar behavior regarding the shift in isotherm format and adsorptive volume [57,58]. The distribution of the pores in the materials can be seen in Figure 2d. The range of the pore size distribution was concentrated around 1.8 nm, which is regarded as a micropore range and is frequently observed in works that use activated carbon as an adsorbent [59–61].

Table 2 shows the BET's surface area (S_0), mean pore diameter (d_p), and pore volumes (V_p) of the different materials analyzed in this study. It was possible to observe that after the BSG was activated with H_3PO_4 , the surface area value increased almost six-fold. This is possible because chemical activation with this acid is dehydrating. In this mechanism, the acid attacks the porous structure of the material and, due to its high affinity with water, it removes the hydrogen and oxygen atoms from the base material, dehydrating it, causing the porous structure to improve and, consequently, its surface area and pore volume to increase. This increase in surface area after activation shows that this method managed to improve the surface characteristics of the base material. It is also worth noting that the AC_{PO4} had a higher surface area than the commercial activated carbon that was used as our control, demonstrating that this synthesis is efficient and can produce highquality adsorbent materials. By observing the pore diameter values, it was possible to see that the activated carbons had pore diameters characteristic of micropore materials (dp < 2 nm), while the BSG had a slightly higher value, falling in the mesoporous material range ($2 \le dp \le 50$ nm). These findings align with the outcomes observed in the isotherm graphs depicted in Figure 2 and are consistent with data from previous research studies, as shown in Table 3.

Table 2. Textura	l properties of the adsorbents.	
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Adsorbent	So $(m^2 g^{-1})$	Vp (cm 3 g $^{-1}$)	dp (nm)
BSG	104.3	0.11	2.03
Commercial 5 mm	377.5	0.33	1.10
ACPO4	605.1	0.41	2.01

Table 3. Results from the literature comparing	; activated carbons from biomass with H ₃ PO ₄
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Precursor	BET Surface Area (m ² g ⁻¹)	Activation Temperature (°C)	Reference
BSG	605.1	400	This study
Spent coffee grounds	614.8	800	[62]
Peanut shells	590.7	400	[63]
BSG	768.4	500	[8]
Rice husk residue	585.0	400	[63]

The acquired FTIR spectra for the adsorbents are shown in Figure 3. Two major regions were detected in the BSG spectrum (Figure 3a), with bands between 7500 and 7000 cm⁻¹ in the first region that are characteristic vibration signals of the CH₃, CH₂, and CH bonds in the second overtone region, which may indicate the possible presence of lignocellulosic compounds such as cellulose, hemicellulose, and lignin [64,65]. The bands between 5400 and 4500 cm⁻¹ in the second region made it possible to identify the vibration characteristics between the C-C and H₂O bonds in the combination region [8,66]. For the commercial activated carbon sample (Figure 3b), the same band regions of the BSG were found, indicating the presence of carbonaceous structures in the material.



Figure 3. FTIR spectra for (a) the BSG, (b) the commercial activated carbon (5 mm), and (c) AC_{PO4}.

In Figure 3c, the spectrum is divided into three regions. The first and second regions are like those in Figure 3a,b; however, the third region with bands between 4710 and 4210 cm⁻¹ with a maximum at approximately 4333 cm⁻¹ is characteristic of the combination between the C-H + C-H groups (methyl, methylene, or methine), which also indicates that the material contains a carbon structure [67].

Figure 4 displays the outcomes of the PZC analysis performed on the materials. The PZC assesses the surface characteristics of the adsorbent, providing insights into whether the material tends to be more acidic or basic in nature. When the pH_{PZC} exceeds the pH of the solution, it suggests a negative charge on the material's surface, whereas when the pH_{PZC} is lower than the pH of the solution, it indicates a positive surface charge [18]. The pH of the cheese whey used during the adsorption tests was pH = 6.5.



Figure 4. Point of zero charge for the adsorbents.

Our analysis revealed a variety of pH_{PZC} values for the adsorbents. Specifically, for both the commercial activated carbon and BSG, their pH_{PZC} values exceeded the pH of the cheese whey, indicating a negatively charged surface on these materials. In contrast, AC_{PO4} exhibited a pH_{PZC} lower than the pH of the cheese whey, signifying a positively charged surface [68,69]. It is known that the electrical charges of cheese whey proteins have a negative charge, so the physisorption process of whey molecules will be favored onto materials with a positive surface charge, such as AC_{PO4} [70–72].

3.2. Cheese Whey Characterization

Before the adsorption assays, the complete characterization of the cheese whey was carried out to determine the initial parameters of the effluent, and the results for lactose, BOD5, and COD were 4.79 g of lactose 100 g^{-1} of cheese whey, 4329.60 mg of $O_2 \text{ L}^{-1}$ of cheese whey, and 72,578.30 mg of $O_2 \text{ L}^{-1}$ of cheese whey, respectively. It was possible to observe that the COD/BOD₅ ratio was approximately 17, which indicates that this effluent (COD/BOD₅ > 4) has a very low level of biodegradability, meaning that the use of physicochemical methods would be required for the degradation of this pollutant, such as adsorption [73,74]. Furthermore, it is known that due to its natural composition, cheese whey is a highly recalcitrant pollutant, especially due to its solid content (mostly lactose) and its high turbidity, which prevents the passage of light and hinders the oxygenation of water bodies.

Thus, it is necessary to monitor these parameters as indicators of the degradation of this pollutant [75,76].

3.3. Adsorption Experiment of Cheese Whey onto Activated Carbons3.3.1. Acid Modification Effect

Figure 5 shows the results of the acid modification test on the BSG. It was evident that acid modification had a positive impact on the removal of lactose, increasing from 17.9% when using 40.6% of BSG when using the commercial adsorbent. Similarly, BOD5 removal improved from 12.5% with BSG to 29.7% with the commercial adsorbent, and COD removal increased from 21.5% with BSG to 59.4% with the commercial adsorbent. This outcome was anticipated because biomass (BSG) naturally possesses a low adsorption capacity due to its lack of surface porosity and limited interaction with the adsorbate [77]. This differs from other materials (e.g., commercial 5 mm activated carbon and AC_{PO4}) that have undergone activation through physical or chemical means [78]. Such modifications aim to enhance their structural, morphological, and surface characteristics, allowing the adsorbents to acquire adsorption capacity either through increased surface area, increased porosity, or more favorable surface interactions [79].



Figure 5. Effect of acid modification in cheese whey adsorption.

 AC_{PO4} exhibited the highest removal percentages for lactose (67.6%), BOD₅ (47.3%), and COD (88.5%) when compared to biomass (BSG) and the commercial adsorbent (Commercial 5 mm). This superior performance can be attributed to the intrinsic characteristics of the material (outlined in Section 3.1), such as its higher specific surface area (S_o) (605.1 m² g⁻¹) and positive surface charge distribution (pH_{PCZ}). These characteristics enhanced the adsorption of molecules found in the CW, particularly in conjunction with the extensive pore distribution observed on the surface of the adsorbent, as revealed via SEM analysis. As a result, AC_{PO4} was chosen as the preferred adsorbent for the subsequent adsorption experiments involving CW in this study.

3.3.2. AC_{PO4} Dosage Effect

The impact of AC_{PO4} dosage on CW adsorption is depicted in Figure 6. The removal of lactose (R, %) increased as the AC_{PO4} dosage changed from 0.5 to 10 g L⁻¹ (Figure 6a), rising from 25.2% to 63.3%. Similarly, for BOD_5 (Figure 6b), it increased from 20.7% to 45.9%, and for COD (Figure 6c), it increased from 72.2% to 91.1%. This phenomenon can be explained by the higher amount of adsorbent added to the reaction mixture. When there is a greater mass of adsorbent present on the material's surface, it leads to an increased number of active sites becoming accessible, consequently causing a natural increase in the removal of adsorbates from the CW [80,81]. Table 4 presents a comparison between the results obtained by the adsorption technique (in this study) in the removal of lactose, BOD₅, and COD from cheese whey with other studies in the literature using various techniques for wastewater treatment. It becomes clear that the adsorption technique is as effective for removing organic content from cheese whey as the different techniques used in other studies in the literature. Thus, the use of liquid-phase adsorption is a viable alternative for treating effluents from dairy facilities, reducing their organic load and allowing this waste to be used as residual water for cleaning the external areas of dairy facilities, as feedwater in boiler systems for steam and electricity generation, or for irrigating various crops.



Figure 6. Effect of AC_{PO4} dosage in cheese whey adsorption: (a) lactose; (b) BOD₅; (c) COD.

Technique		Reference		
	Lactose	BOD ₅	COD	
Adsorption with activated carbon	63	46	91	This study
Upflow anaerobic sludge blanket	-	-	90	[82]
Vertically moving biofilm system	_	_	89	[83]
Activated sludge	-	-	90	[23]
Coagulation-flocculation with FeCl ₃	54	23	32	[94]
Coagulation–flocculation with $Al_2(SO_4)_3$	49	35	36	[84]
Ozone	40	43	63	[24]
Precipitation with lime	56	45	55	
Precipitation with NaOH	34	44	50	[00]

Table 4. Comparison between different techniques described in the literature for cheese whey wastewater treatment.

In addition, it is essential to note that the adsorption capacity is inversely proportional to the mass of the adsorbent present in the medium. Consequently, the adsorption capacity, in the case of lactose uptake, decreased from 41.34 g lactose g-1 adsorbent with a dosage of 0.5 g L-1 to 5.20 g lactose g-1 adsorbent with 10 g L-1 of ACPO4. Similarly, for

BOD5 uptake, it decreased from 400.93 mg O_2 g-1 adsorbent using 0.5 g L-1 of ACPO4 to 35.96 mg O_2 g-1 using 10 g L-1, and for COD uptake, it decreased from 5252.04 mg O_2 g-1 adsorbent using 0.5 g L-1 of ACPO4 to 400.41 mg O_2 g-1 using 10 g L-1. Consequently, the subsequent experimental procedures for obtaining kinetic profiles and the equilibrium studies were conducted using a dosage of 2 g L-1. This dosage was chosen as it represents the intersection of the curves obtained in the dosage experiments [86,87].

3.3.3. AC_{PO4} Adsorption Kinetics

The kinetics of lactose, BOD_5 , and COD uptake onto AC_{PO4} were investigated using three different models: PFO, PSO, and AFO models (Table 5).

Table 5. Kinetic parameters for the uptake of CW onto AC_{PO4}. Conditions: adsorbent dosage of 2 g L^{-1} , temperature of 25 °C, initial pH of 6.5.

	Description	Absorbate						
Model	Parameter	Lactose	BOD ₅	COD				
	q _e	3.44 g lactose g^{-1} adsorbent	$482.24 \text{ mg O}_2 \text{ g}^{-1} \text{ adsorbent}$	5234.06 mg O_2 g ⁻¹ adsorbent				
	k ₁	$8.37 \times 10^{-3} \mathrm{min}^{-1}$	$24.93 \times 10^{-3} \mathrm{min}^{-1}$	$10.98 \times 10^{-3} \mathrm{min}^{-1}$				
	t _{1/2}	87.10 min	28.02 min	62.68 min				
PFO	t _{0.95}	359.32 min	121.25 min	279.52 min				
	R ² _{adj}	0.95	0.95	0.97				
	SD	0.27 g lactose g^{-1} adsorbent	$31.15 \text{ mg O}_2 \text{ g}^{-1} \text{ adsorbent}$	252.03 mg O_2 g ⁻¹ adsorbent				
	BIC	-28.54	94.54	148.90				
	q _e	3.52 g lactose g^{-1} adsorbent	518.40 mg O_2 g ⁻¹ adsorbent	5315.40 mg $O_2 g^{-1}$ adsorbent				
	k ₂	$1.16 imes 10^{-3}~{ m g}~{ m lactose}~{ m g}^{-1}$ adsorbent min $^{-1}$	$\begin{array}{c} 0.06\times 10^{-3}~\text{mg}~\text{O}_2~\text{g}^{-1}\\ \text{adsorbent}~\text{min}^{-1} \end{array}$	$\begin{array}{c} 0.02\times 10^{-3}~\text{mg}~\text{O}_2~\text{g}^{-1}\\ \text{adsorbent}~\text{min}^{-1} \end{array}$				
PSO	t _{1/2}	136.93 min	27.09 min	61.93 min				
	t _{0.95}	382.95 min	308.90 min	333.04 min				
	R ² _{adj}	0.94	0.96	0.98				
	SD	0.30 g lactose g^{-1} adsorbent	18.43 mg $O_2 g^{-1}$ adsorbent	171.17 mg O_2 g ⁻¹ adsorbent				
	BIC	-25.97	70.89	168.74				
	q _e	3.18 g lactose g^{-1} adsorbent	506.44 mg O_2 g ⁻¹ adsorbent	5303.37 mg $O_2 g^{-1}$ adsorbent				
	k _{AV}	$19.56 \times 10^{-3} \mathrm{min}^{-1}$	$10.69 \times 10^{-3} \mathrm{min}^{-1}$	$5.22 \times 10^{-3} \mathrm{min}^{-1}$				
	n _{AV}	2.57	0.47	0.59				
AFO	t _{1/2}	73.88 min	24.86 min	61.18 min				
	t _{0.95}	200.34 min	217.30 min	315.99 min				
	R ² _{adj}	0.97	0.97	0.99				
	SD	0.21 g lactose g^{-1} adsorbent	23.41 mg $O_2 g^{-1}$ adsorbent	$107.93 \text{ mg O}_2 \text{ g}^{-1} \text{ adsorbent}$				
	BIC	-40.38	83.13	119.81				

The statistical evaluation of the kinetic models considered R^2_{adj} , SD, and BIC values (Section 2.6). The model with the highest R^2_{adj} (close to 1), lowest SD, and lowest BIC values for all the studied adsorbates was the AFO model, indicating that this model was the most suitable for fitting the dispersion of the kinetic data. The Bayesian information criterion becomes more significant when $\Delta BIC \ge 2$ [88,89]. When $\Delta BIC \ge 10$, the model with the lowest BIC score is undoubtedly the best statistically fitted model [90]. For lactose, the ΔBIC value between PFO and AFO was 11.84, and between PSO and AFO, it was 14.41. For BOD₅, the ΔBIC value between PFO and AFO was 11.41, and between PSO and AFO,

it was 12.24. Finally, for COD, the Δ BIC value between PFO and AFO was 29.09, and between PSO and AFO, it was 48.93. Hence, based on the BIC values presented in Table 4, it is evident that AFO is the most suitable kinetic model for characterizing the adsorption kinetics of lactose, BOD₅, and COD onto AC_{PO4}.

Because different kinetic adsorption models utilize different units for the kinetic rate constant (k), making direct comparisons regarding the time needed to reach equilibrium becomes challenging. Therefore, alternative measures like $t_{1/2}$ (the time to achieve 50% saturation of the adsorbent) and $t_{0.95}$ (the time to achieve 95% saturation of the adsorbent) were employed. These values were determined by interpolation from the adjusted curve (as shown in Table 5). For the AFO kinetic model, the $t_{1/2}$ values ranged from 24.86 to 73.88 min, while the $t_{0.95}$ values ranged from 200.34 to 315.99 min. Since the AFO model was deemed the most suitable for describing the kinetics, these values offer a more accurate representation of the time-related parameter. To ensure that the system reached equilibrium, it was necessary for the contact time to exceed $t_{0.95}$. Consequently, the decision was made to use contact times of 330 min to ensure equilibrium attainment.

Figure 7 illustrates the AFO model for all the adsorbates studied in the uptake of CW onto AC_{PO4} .



Figure 7. AFO kinetic curves of cheese whey uptake. Conditions: adsorbent dosage of 2 g L^{-1} , temperature of 25 °C, initial pH of 6.5.

3.3.4. AC_{PO4} Adsorption Equilibrium

The adsorption isotherms for lactose, BOD_5 , and COD onto AC_{PO4} were determined under optimized conditions using Langmuir, Freundlich, Dubinin–Radushkevich, and Hill models at temperatures of 288 K, 298 K, 308 K, and 318 K. The isotherm parameters are shown in Table 6.

							Т	(K)					
Model	-		288			298			308			318	
Widdei	Tarameter	Adsorbate											
		Lactose	BOD ₅	COD	Lactose	BOD ₅	COD	Lactose	BOD ₅	COD	Lactose	BOD ₅	COD
	q _{mL} *	4.55	713.50	7378.63	5.41	988.04	9050.27	6.86	1115.78	10,657.12	7.44	1349.31	12,220.00
11r	k_L (L mg ⁻¹)	0.0001	0.0004	0.00002	0.0005	0.0004	0.00004	0.40	0.77	0.11	0.54	1.02	0.16
gmı	R ² _{adj}	0.995	0.999	0.995	0.998	0.998	0.981	0.996	0.997	0.973	0.998	0.993	0.998
Lan	SD	0.09	4.75	165.35	0.06	8.87	432.10	0.10	17.84	577.46	0.77	32.43	171.29
	BIC	-20.60	18.80	54.30	-24.84	25.05	63.90	-19.93	32.03	66.80	-22.40	38.00	54.65
	k_F^+	1.07	4.27	11.71	1.88	6.05	29.75	2.16	29.92	322.26	2.84	57.06	853.09
lich	n _F	1.46	1.80	1.78	2.29	1.77	1.99	2.13	2.47	3.27	2.47	2.81	4.29
pun	R ² _{adj}	0.989	0.991	0.975	0.988	0.989	0.973	0.985	0.988	0.948	0.997	0.998	0.978
Fre	SD	0.15	16.48	381.15	0.15	27.05	511.61	0.20	36.14	848.75	0.11	18.59	601.47
	BIC	-15.83	31.24	62.65	-15.62	36.18	65.56	-12.55	39.09	70.65	-19.63	32.44	67.21
rich	q _{mDR} *	4.25	496.32	6219.23	4.27	911.62	8286.64	5.17	1016.97	9794.23	8.06	1726.89	11,237.52
Jkev	β (mol ² kJ ⁻²)	31.23	25.66	31.19	20.27	17.00	20.80	21.32	12.92	11.88	8.07	5.35	10.59
dush	Es (kJ mol $^{-1}$)	0.13	0.14	0.13	0.16	0.17	0.16	0.15	0.20	0.21	0.25	0.31	0.22
–Ra	R ² _{adj}	0.997	0.996	0.985	0.998	0.998	0.928	0.997	0.996	0.977	0.999	0.999	0.999
inin	SD	0.06	10.50	296.43	0.06	10.52	833.99	0.09	18.19	532.19	0.04	10.35	127.37
Dub	BIC	-24.07	22.97	49.69	-18.04	22.98	57.97	-14.67	27.37	54.37	-21.79	22.85	42.93

Table 6. Equilibrium parameters for the uptake of CW onto AC_{PO4}. Conditions: adsorbent dosage of 2 g L^{-1} , initial pH 6.5, and contact time of 330 min.

		T (K)											
Madal	Parameter		288			298			308			318	
Widdei		Adsorbate											
		Lactose	BOD ₅	COD	Lactose	BOD ₅	COD	Lactose	BOD ₅	COD	Lactose	BOD ₅	COD
	q _{mH} *	3.69	719.89	6721.23	4.22	1043.76	8229.11	4.72	1371.13	12,759.16	12.77	3940.99	12,857.92
	$C_{1/2} (mg L^{-1})$	3.17	2697.27	27,607.02	1.77	2591.11	21,454.73	1.83	1549.59	11,212.78	3.45	4526.72	6488.04
III	n _H	1.36	0.99	1.19	1.16	1.03	1.18	1.25	0.90	0.89	0.75	0.58	0.96
Щ	R ² _{adj}	0.998	0.999	0.996	0.999	0.999	0.998	0.998	0.998	0.999	0.999	0.999	0.999
	SD	0.07	5.31	146.99	0.06	9.75	124.25	0.09	18.57	95.62	0.04	9.63	188.63
	BIC	-27.50	17.51	44.08	-28.66	22.38	42.74	-25.35	27.53	40.64	-28.69	22.28	46.07

Table 6. Cont.

Note(s): * The unit of q_{mL} , q_{mDF} , and q_{mH} for lactose is (g lactose g^{-1} adsorbent), and for BOD₅ and COD, it is (mg O₂ g^{-1} adsorbent). + The unit of k_F is ((mg g^{-1}) (mg L^{-1})^{-1/n}).

The equilibrium models were assessed based on the R^2_{adj} , SD, and BIC values. As mentioned earlier, Δ BIC values between Langmuir, Freundlich, Dubinin–Radushkevich, and Hill models were all ≤ 10 at temperatures ranging from 288 K to 318 K (Table 5). This suggests a strong likelihood that the model with the lowest BIC value is the most appropriate choice. In this case, the Hill model proved to be the most suitable for describing the adsorption of lactose, BOD5, and COD onto AC_{PO4} [91,92].

It is also worth noting that the Hill isotherms obtained through data fitting are favorable (Figure 8), indicating a high adsorption capacity while utilizing a minimal quantity of AC_{PO4} material [85,86]. With an increase in Ce, the adsorption capacity also increased significantly, reaching values of approximately 5.7 g g⁻¹ for lactose, 1150 mg O₂ g⁻¹ for BOD₅, and 11,000 mg O₂ g⁻¹ for COD (experimental values). It is evident that the adsorption capacity benefitted from higher temperatures, with the highest values observed at 318 K. This phenomenon can be attributed to the thermal agitation effect, where an increase in agitation rate reduces the film resistance to mass transfer around the adsorbent particles, enhancing the adsorption of molecules present in the cheese whey onto the active sites of AC_{PO4} [93,94]. In summary, these results confirm that AC_{PO4} can effectively be employed for the treatment of cheese whey through the adsorption process. This reduces its organic load and facilitates the remediation of this pollutant, allowing for potential reuse as treated water or its safe return to the aquatic environment.



Figure 8. Adsorption isotherms of cheese whey on AC_{PO4} at different temperatures: (a) lactose; (b) BOD_5 ; (c) COD. Conditions: adsorbent dosage of 2 g L⁻¹, initial pH of 6.5, and contact time of 330 min.

3.3.5. AC_{PO4} Thermodynamic Parameters

The thermodynamic equilibrium parameters were evaluated using the Van 't Hoff equation, where the Langmuir parameter (K_L , expressed in L mg⁻¹) was utilized to estimate the thermodynamic equilibrium constant (K_e) [43,95,96]. The thermodynamic data are presented in Table 7.

At first, the decline in ΔG° with an increase in temperature implies that the adsorption of lactose, BOD₅, and COD onto AC_{PO4} became increasingly favorable at elevated temperatures. Additionally, the consistently negative ΔG° values at all temperature levels indicate that the adsorption process is spontaneous and favorable. ΔG° values between -20 and 0 kJ mol⁻¹ indicate a predominance of the physisorption phenomenon, as observed at the lower temperatures in this study (288–298 K), ranging from -1.51 to -6.26 kJ mol⁻¹. However, at higher temperatures (308–318 K), the ΔG° values are ≤ -20 kJ mol⁻¹, ranging from -20.44 to -26.99 kJ mol⁻¹, indicating a shift in the predominant adsorption equilibrium mechanism [97,98]. Additionally, positive ΔS° values for all adsorbates imply some structural adjustments at the interface during the adsorption process.

Adsorbate	T (K)	$\Delta { m G}^\circ$ (kJ mol $^{-1}$)	$\Delta \mathrm{H}^\circ$ (kJ mol $^{-1}$)	ΔS° (J mol $^{-1}$ K $^{-1}$)	E_a (kJ mol ⁻¹)	
	288	-3.31				
Lactose	298	-6.26	238.26	830 12	29.24	
Lactose	308	-23.74	200.20	000.12	27.24	
	318	-25.31	-			
	288	-5.66		829.87		
BOD5	298	-5.86	237 16		21 71	
2023	308	-25.42	237.10		21.7 1	
	318	-26.99	-			
	288	1.51				
COD	298	-0.15	265 72	910.37	39.25	
	308	-20.44	200.72		07.20	
	318	-22.09	-			

Table 7. Thermodynamic parameters for the uptake of CW onto AC_{PO4}.

Moreover, the positive ΔH° values provide confirmation that the adsorption of these adsorbates is an endothermic process. This observation aligns with the fact that as temperature rises, the adsorption of lactose, BOD₅, and COD onto AC_{PO4} increases in line with Le Chatelier's principle, which pertains to perturbing chemical equilibrium [99]. Moreover, the ΔH° values exceeding 40 kJ mol⁻¹ for all adsorbates suggest that the process is not solely driven by physisorption. In the case of lactose, BOD₅, and COD adsorption, it may involve a combination of physisorption and ion exchange or chemisorption onto the surface of the AC_{PO4} adsorbent [42,100].

Finally, it is worth noting that the activation energy (E_a) values associated with the adsorption of lactose, BOD₅, and COD onto AC_{PO4} exhibited remarkable similarity, differing by only about 6 kJ mol⁻¹. This slight variation in activation energy could indicate a subtle difference in the affinity between the adsorbate and the adsorbent's surface. However, the closely matched activation energy values suggest that the adherence process for lactose, BOD₅, and COD is quite similar. The magnitude of the activation energy provides valuable insights into the fundamental mechanism of the adsorption process. Usually, physisorption, which is based on physical attraction, is associated with activation energies below 40 kJ mol $^{-1}$. On the other hand, chemisorption, a chemical process, requires higher energy levels, typically those exceeding 40 kJ mol⁻¹. The activation energy (E_a) values we determined for the adsorption of lactose, BOD₅, and COD indicate that physisorption is the prevailing mechanism governing the adsorption of these substances on the AC_{PO4} surface [101–103]. This fact is also supported by the results listed in Table 6. When observing the value of Es obtained through the Dubinin-Radushkevich model, one can infer about the adsorption mechanism. For Es < 8 (kJ mol⁻¹), the process is mainly based on physical adsorption, which can be observed for all the values obtained for the adsorption of lactose, BOD₅, and COD. This reaffirms that indeed a physisorption process was the governing mechanism in this study [104].

3.4. Proposal of the Adsorption Mechanism

The proposed adsorption mechanism was based on findings from the characterization results of AC_{PO4} , including FTIR and pH_{PZC} , as well as insights from thermodynamic modeling. The adsorbent was anticipated to be a lignocellulosic substance primarily composed of cellulose and lignin, featuring functional groups like CO, CC, and OH-[105,106]. The pH level of the CW's operation was 6.5, resulting in a positive charge on the material's surface at this pH. Regarding the molecules found in the CW, it was established that proteins presented in the CW carry a negative charge, which promotes

the bonding between the adsorbate and adsorbent. Finally, thermodynamic information revealed that the primary adsorption mechanism for CW on AC_{PO4} is physisorption, driven by physical interactions such as hydrogen bonding, π – π interactions, anion– π interactions, and electrostatic interactions, as depicted in Figure 9 [89,100,107].



Figure 9. Proposed adsorption mechanism for the adsorption of cheese whey onto AC_{PO4}.

3.5. Regeneration and Reuse of the AC_{PO4} Adsorbent

Firstly, adsorption experiments were conducted under specific conditions, including a 2 g L⁻¹ dosage of the adsorbent, an initial pH of 6.5, a temperature of 318 K, and a contact time of 330 min. Consequently, the adsorption capacity for lactose reached approximately 3.50 g lactose g⁻¹ adsorbent; for BOD₅, it was around 500.00 mg O₂ g⁻¹ adsorbent, and for COD, it was approximately 5300.00 mg O₂ g⁻¹ adsorbent. Following this, HCl and NaOH were evaluated as eluents, with 0.1 mol L⁻¹ NaOH proving to be the most effective eluent, releasing all adsorbates into the liquid phase within 75 min. These adsorption–desorption cycles were repeated five times, and the outcomes are illustrated in Figure 10.



Figure 10. Recycle test for the adsorption of cheese whey onto AC_{PO4} : (a) lactose; (b) BOD_5 ; (c) COD.

4. Conclusions

The remediation of cheese whey using activated carbon synthesized through singlestep acid modification with H_3PO_4 (AC_{PO4}) via liquid-phase adsorption has proven to be an efficient method for treating and recovering this residue from the dairy industry. ACPO4 exhibits physical and chemical characteristics favorable for the adsorption process, including a high surface area of 605.1 m² g⁻¹, well-developed pores with high volume and diameter, and positive surface charges that facilitate favorable electrostatic interactions with the molecules present in cheese whey. The kinetic data confirm that equilibrium was reached after 330 min for the parameters evaluated in the adsorption process (lactose, BOD₅, and COD). The isothermal curves follow the Hill isotherm model, with a maximum adsorption capacity of 12.77 g g⁻¹ for lactose, 3940.99 mg O_2 g⁻¹ for BOD₅, and 12,857.92 mg O_2 g⁻¹ for COD at the highest temperature (318 K). The thermodynamic results indicate that adsorption ($\Delta H^{\circ} \ge 265.72 \text{ kJ mol}^{-1}$) for all the adsorbates was spontaneous, favorable, and endothermic. AC_{PO4} can be regenerated with NaOH and reused up to four times, with only a 25% reduction in its adsorption capacity. In conclusion, based on these findings, it can be stated that using AC_{PO4} as an adsorbent for cheese whey remediation is promising and offers an alternative for managing dairy industry residues and reusing water resources. By allowing the water recovered after adsorptive processes to be used within the industrial environment for various purposes, significant water savings are generated.

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