



Resorcinol elimination through adsorption onto synthetic calcium phosphates: investigations into kinetics and thermodynamics

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Abstract

The characteristics and suitability of hydroxyapatite (HAp), which possesses attributes similar to an ideal adsorbent, were investigated to determine its effectiveness in removing resorcinol. The aim of this paper is to assess the adsorption behavior of resorcinol on hydroxyapatite powder synthesized using the co-precipitation method at ambient temperature. Additionally, the impact of starting resorcinol amounts and thermal conditions on the adsorption process was explored. X-ray diffraction analysis revealed the formation of the hydroxyapatite (HAp) structure under ambient temperature conditions. The FTIR spectroscopy analysis affirms the presence of functional groups and validates the sample's purity. Furthermore, the chemical analysis reveals a molar ratio of Ca/P = 0.6. The synthesized powder exhibits an adsorption capacity of 2.9 mg/g and reaches equilibrium within 80 minutes. The results indicate that the experimental data is appropriately represented by Langmuir and Freundlich equations of adsorption, as well as Pseudo-second-order adsorption kinetics. Thermodynamic assessments, including calculations of Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), The findings indicated that the adsorption processes exhibited physical characteristics, were endothermic, and occurred spontaneously.

Keywords: Hydroxyapatite (HAp); Adsorption equilibrium; Reaction rate; Thermodynamics; 1,3-Benzenediol.

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1. Introduction

The prominence of challenges associated with water resources and pollution is steadily increasing, primarily driven by escalating water demand and the influence of climate change on precipitation patterns. Consequently, water scarcity has become a pressing concern. This underscores the necessity of water depollution to address the escalating water demands. Consequently, the eradication of organic pollutants from groundwater and the extraction of contaminants from contaminated water have emerged as significant areas of research and policy discussion. Even in minimal quantities, the presence of these compounds can hinder the reutilization of water [1–3].

Resorcinol is one of these compounds. It is categorized as a typical phenolic compound and its chemical name is 1,3-dihydroxybenzene. Resorcinol is commonly encountered in effluents from various industries, including textile, dyes, paper and pulp, cosmetics, rubber, petrochemicals, petroleum refining, plastics, pharmaceuticals, steel, and other sectors [4]. This compound has a strong toxicity, high oxygen demand and a low degradability [5].

Numerous treatment methods are available for the elimination of phenolic compounds, including ion exchange, adsorption, reverse osmosis, precipitation, distillation, chemical oxidation, solvent extraction, complexation, gas stripping, bioremediation [6], and electrocoagulation [7], ultrasound treatment [8] and liquid/liquid extraction [9]. Among the various methods employed in water treatment, the adsorption technique is widely recognized as the most commonly utilized approach. It is considered an attractive and beneficial option for the treatment of phenolic substances from wastewater effluent. Activated carbon is the most commonly used adsorption support material in this regard [4,6,10,11], clay [12], cellulose functionalized with magnetic poly (dopamine) [13], surfactant modified NaOH treated fly ash [14], synthetic mesoporous silicas (SBA-15) [15], and hydroxyapatite [16–19]. It is crucial to emphasize the process of adsorption entails the adherence or accumulation of atoms, ions, or molecules from a substance onto the surface of a solid or liquid, leading to a concentration increase at the surface interface. Properties characterizing these materials include adsorption capacity, which can be linked with surface area-to-volume ratio, interaction energy determining the reversible nature of adsorption, adsorption kinetics, pressure resistance,

temperature sensitivity, attrition resistance, adsorbent morphology, as well as financial and environmental cost considerations. In this work, it is crucial to highlight the unsolved scientific problems related to the adsorbent under study. These unresolved issues serve as the motivation for conducting the research and contribute to the scientific significance of the study. By addressing these gaps in knowledge, the research aims to provide novel insights and potential solutions to these challenges. When discussing the unsolved scientific problems, it is important to offer a distinct comprehension of the current state of knowledge in the field. This can involve summarizing the existing literature and highlighting the limitations or gaps in previous studies concerning the adsorbent in question. Emphasize the specific aspects or aspects of the adsorbent that have not been adequately addressed or require further investigation.

The application of adsorbents in various industries and the importance of comparing them cannot be overstated. Adsorbents play a crucial role in addressing environmental challenges, water and air purification, and industrial processes worldwide. By comparing different adsorbents, such as activated carbon, zeolite, and hydroxyapatite, researchers and engineers can identify the most suitable adsorbent for specific applications based on factors like adsorption capacity, cost-effectiveness, regeneration potential, and environmental impact. This comparative analysis ensures that the chosen adsorbent meets the desired performance requirements and aligns with sustainable practices. Moreover, comparing adsorbents fosters innovation and drives advancements in the field, leading to the development of more efficient and tailored solutions to tackle emerging contaminants and address evolving environmental concerns. In Morocco, apatite phosphate is abundant and for this our laboratory uses hydroxyapatite (HAp), apatitic tricalcium phosphate (PTCa) as an adsorbent in research on the depollution of polluted water, namely the dyes reactive yellow 4 [20,21] and reactive direct yellow 28 [22], fluoride [16]. HAp offers numerous advantages as an adsorbent, including high adsorption capacity and selectivity for various pollutants and contaminants in water and solutions. However, it's important to note that other adsorbents are also used worldwide, such as zeolite and cellulose. Zeolite is appreciated for its unique porous structure and its ability to adsorb a wide range of undesired substances [23]. Cellulose [13], on the other hand, is widely utilized due to its abundance, biodegradability, and capacity to adsorb certain organic pollutants. Overall, these diverse adsorbents provide varied and complementary solutions for the treatment of contaminated water and solutions, contributing to the global efforts of environmental preservation.

The principal target of this research is to comprehensively analyze the adsorption potential of resorcinol from aqueous solutions using synthetic hydroxyapatite (HAp). Various experimental factors, including initial adsorbent concentration, contact time, and temperature, were examined to determine their impact on the adsorption process. The outcomes were evaluated using kinetic and isotherm models, and thermodynamic parameters such as the determination and analysis of enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG) were performed.

2. Materials and methods

2.1) Adsorbents

Hydroxyapatite synthesis involves a gradual precipitation process in an alkaline environment. It is achieved through a double decomposition reaction between a calcium nitrate solution and an ammonium phosphate solution. To initiate the reaction, Solution A, consisting of 26 g of diammonium hydrogen phosphate ((NH₄)₂HPO₄) dissolved in 1300 ml of decarbonated distilled water, along with 1500 ml of ammonia, is simultaneously pumped using a peristaltic pump into Solution B. Solution B comprises 47 g of calcium nitrate Ca(NO₃)₂ · 4H₂O dissolved in 550 ml of distilled water and is brought to a boil with a constant stirring speed of 150 rpm. The presence of excess ammonia is crucial to maintain an alkaline pH of 9. After the complete addition of solution A, the mixture is continuously boiled and stirred for approximately 30 minutes. The resulting precipitate is then hot-filtered using a Buchner funnel and subsequently rinsed with a solution composed of one liter of distilled water and 30 ml of ammonia. Finally, the precipitate is dried at 80°C for 24 hours [16,24].

The specific surface area was determined through the application of the BET method, where N₂ adsorption at 77 K was employed. Infrared spectroscopy (IR) was conducted by dispersing the anhydrous KBr with approximately 2 mg of the product for every 200 mg of KBr, using a spectrometer of BRUKER type. The X-ray powder diffraction (XRD) pattern was acquired employing a Panalytical X Pert 3 Powder diffractometer equipped with copper Ka radiation ($K\alpha_1 = 1.5405980 \text{ \AA}$).

2.2) Adsorption experiments

2.2.1) Adsorbate

To create a stock solution of resorcinol, pure samples of the solute were dissolved in distilled water. Batch adsorption studies for a single solute system were conducted in a test tube. In these studies, 10 ml of a known concentration solution of resorcinol was used to investigate equilibrium isotherms and the impact of varied factors including kinetics, pH, initial concentration, and adsorbent dose on the adsorption of resorcinol onto HAP. The concentration of resorcinol (figure 1) was determined using a UV spectrophotometer (UV-2005, Selecta, Spain) employing the method involving 4-aminoantipyrine [25,26] was employed to evaluate the quantity of resorcinol adsorbed. This method forms colored complexes with certain phenolic compounds. The batch process involved combining 5 ml of the NH₄Cl-NH₄OH buffer solution with 50 ml of the resorcinol solution to be analyzed. The solution's pH was adjusted to 9.5 using the NH₄Cl-NH₄OH buffer solution. Subsequently, 1.0 ml of the 4-aminoantipyrine solution was added to 2.0 ml of K₃[Fe(CN)₆] solution. The resulting mixture was carefully subjected to agitation and subsequently allowed to reach equilibrium at ambient temperature for 5 minutes [27,28]. The absorbance of the resulting solution was then assessed by employing the spectrophotometer at 500 nm.

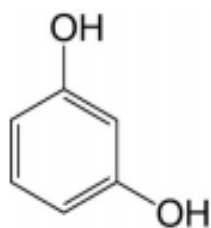


Figure 1: Chemical structure of resorcinol molecule

2.2.2) Experimental protocol

The study of resorcinol adsorption by synthetic hydroxyapatite (Hap) was conducted in a static mode (batch). For each experiment, the solid was brought into contact with a resorcinol solution. The blend was agitated consistently at a fixed rate of 500 rpm for a duration of one minute before being transferred to a temperature-regulated water bath set at 25°C. The solid is subsequently isolated from the colloid via separation utilizing a fritted glass apparatus. The concentration of resorcinol is assessed employing a UV-visible spectrophotometer. The amount of resorcinol adsorbed by the adsorbent is quantified by the subsequent equation [29–31]:

$$Qt = \frac{(C_0 - C_t)V}{m} \quad (1)$$

In which :

Q_t : amount of resorcinol in mg/g of adsorbent.

C_0 : represents the initial concentration, while C_t signifies the concentration of resorcinol at time t (in mg/l).

V : volume of the solution (in l).

m : quantity of adsorbent employed (in g).

The simplicity in their application makes the classical Langmuir [32] (eq. 2) and Freundlich [33] (eq. 3 and 4) models, which describe monolayer formation, valuable. So, by utilizing the linearized Langmuir equation [32], we were able to ascertain the key adsorption parameters: the saturation adsorption capacity represented by Q_∞ , and the constant interaction between the adsorbate and adsorbent denoted as b .

$$1/Q_{ad} = 1/(bQ_\infty)C_{eq} + 1/Q_\infty \quad (2)$$

$$Y = aX^m \quad \text{with } m \leq 1 \quad (3)$$

Assume Y represents the adsorbed substance per unit surface area or mass of the adsorbent, and X denotes the equilibrium concentration of the adsorbate in the solution. The parameters a and m define the relationship between the adsorbent and adsorbate. When the equation is linearly converted, we obtain:

$$\log(Y) = \log(a) + m\log(X) \quad (4)$$

The relationship between the logarithm of Y and the logarithm of X helps to determine m and a . It's important to note that at very low levels of adsorption, the Freundlich's law typically describes the adsorption mode. Conversely, when there's a high recovery rate, the Langmuir's law accurately describes this process.

2.3 pH study

In a 10 ml test tube containing a resorcinol solution, HAp was introduced. The initial concentration of resorcinol was uniformly set to 100 mg/L for all experimental

conditions. In order to manipulate the pH, HCl (0.1 M) and NaOH (0.1 M) were employed. The resulting mixture was stirred for two minutes and subsequently placed in a thermostatic bath held at a constant temperature of 25°C. After a 5-hour contact period, the particulate phase was separated from the solution via filtration using a porous glass, and the solution's pH was measured.

2.3) Adsorbent Comparisons

Although hydroxyapatite (HAp), zeolite [23], and cellulose [13] serve as alternative adsorbents, activated carbon remains a widely accepted reference point due to its remarkable adsorption capabilities and versatility. However, it is important to acknowledge that adsorbents have their limitations and face criticisms. Among these limitations, one common issue is the lack of selectivity, where adsorbents may inadvertently adsorb both target pollutants and desirable components found in the solution being treated. This can lead to a loss of valuable substances or a need for additional purification steps. Saturation and Regeneration: Adsorbents have a limited adsorption capacity, and once they reach saturation, their efficiency decreases. Regeneration processes to restore adsorbent capacity can be energy-intensive and costly. Kinetics: Adsorption kinetics can be relatively slow, especially for large-sized molecules or in cases where mass transfer limitations exist, which can impact the efficiency of the adsorption process. Cost: Some adsorbents, such as activated carbon, can be expensive, particularly when considering large-scale applications. The cost-effectiveness of adsorbents is an important consideration in determining their practical viability. Disposal of Spent Adsorbents: Proper disposal of spent adsorbents, especially those contaminated with hazardous substances, can pose environmental challenges and require careful handling and treatment. Environmental Impact: The manufacturing and disposal of designated adsorbents, like activated carbon, may have environmental implications due to the energy-intensive manufacturing process or potential release of contaminants during regeneration or disposal.

Specificity: Adsorbents may have limited effectiveness against certain types of pollutants or contaminants. Different adsorbents may be required for specific classes of pollutants, leading to a need for tailored solutions.

3. Results and Discussions

3.1) Adsorbent

The hydroxyapatite sample displays a specific surface area of approximately 137 m²/g, indicating a deficiency in its structure. The infrared absorption spectrum (Figure 2) demonstrates the presence of characteristic absorption bands associated with hydroxyapatite. The prominent feature in the IR spectrum of hydroxyapatite is the band observed at approximately 1020 cm⁻¹, corresponding to the vibrational mode of ν_3 . Bands at 864, 599 and 559 cm⁻¹ aligns with the ν_1 and ν_4 vibration modes of PO₄ groups. The characteristic band of HPO₄²⁻ ions (864,45 cm⁻¹) is also manifests within the spectrum. Additionally, bands attributed to hydroxide ions (OH) in hydroxyapatite are observed at 3567.94 and 674.66 cm⁻¹.

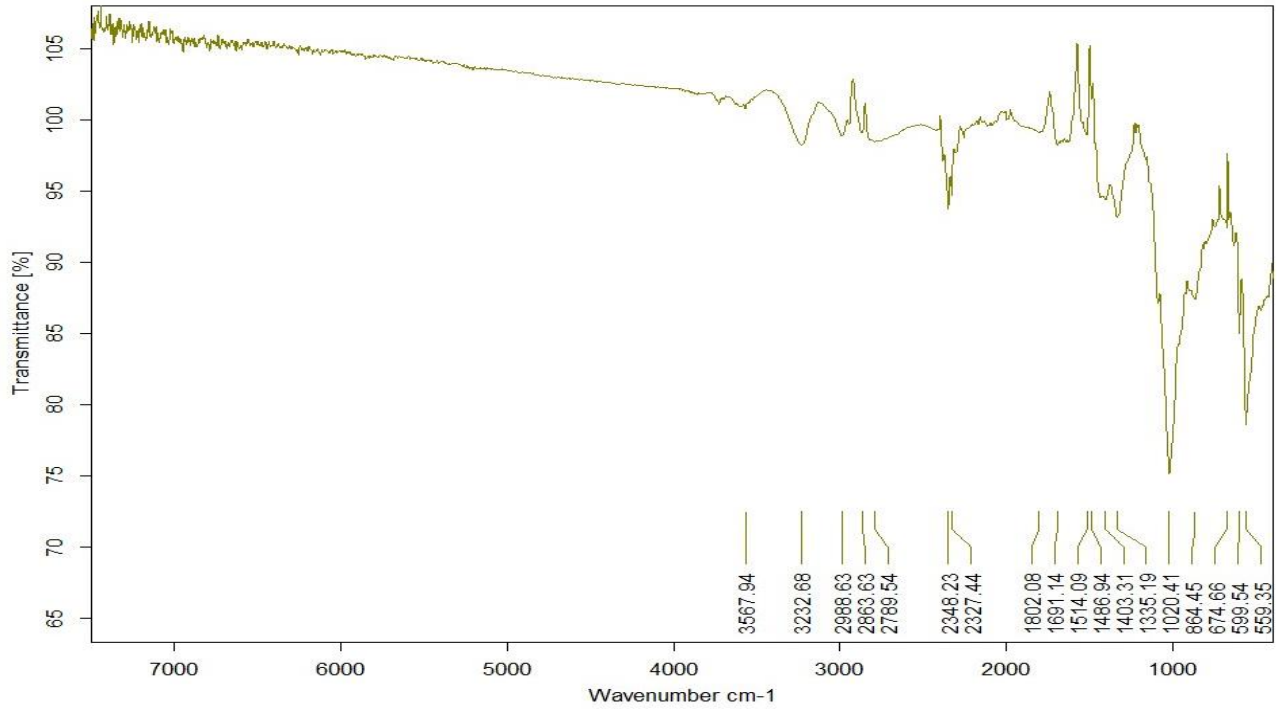


Figure 2: infrared spectrum of Hap

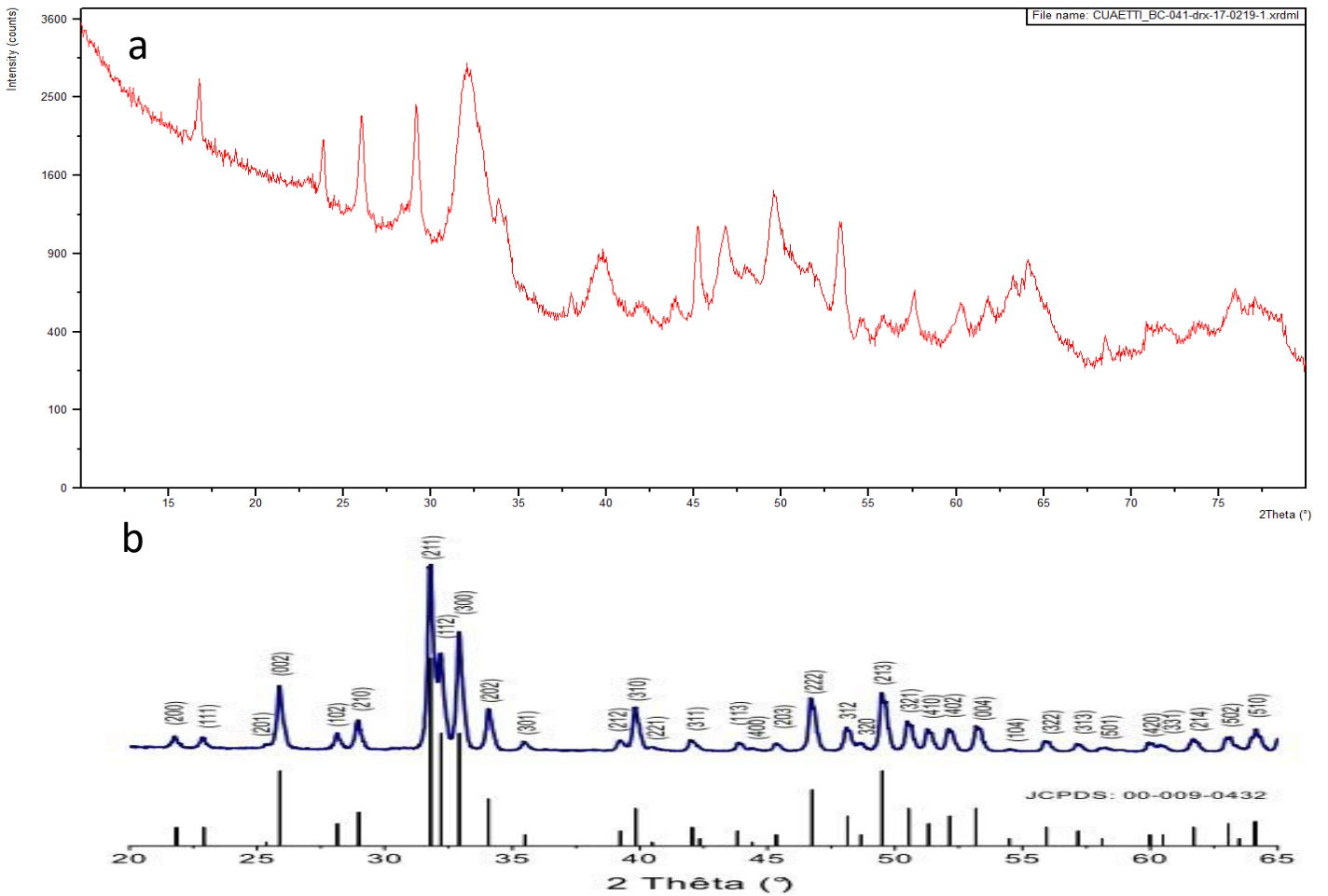


Figure 3: XRD patterns of (Figure 3 a) synthesized HAP and (Figure 3 b) pure HAP (JCPDS no. 09-0432)

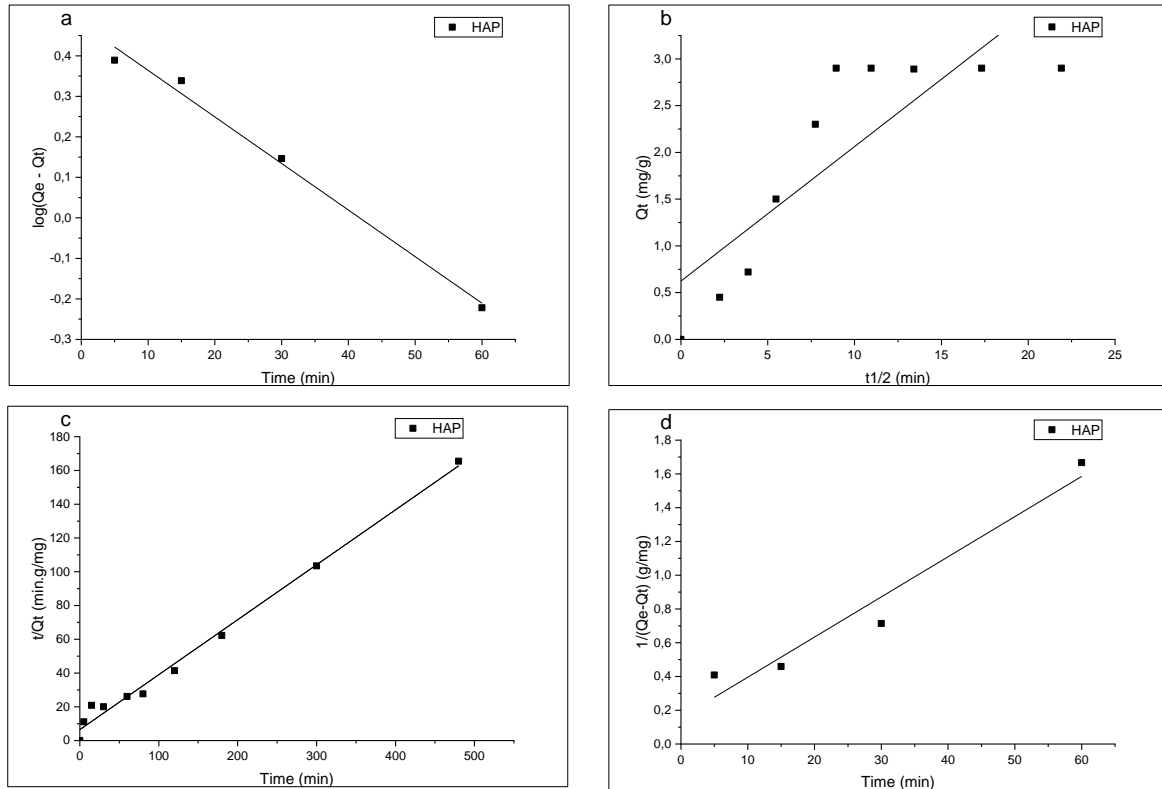


Figure 4: Adsorption kinetics of Resorcinol on hydroxyapatite conducted at 25°C (initial Resorcinol concentration: 100 mg/l, 200 mg of solid, pH: 6.66, stirring duration: 1 minute)

Table 1: Kinetic parameters associated with the adsorption of resorcinol onto HAp.

Pseudo-first order				Pseudo-second order			Second order			Intra-particle diffusion		
$Q_{e,exp}$ (mg/g)	$Q_{e,cal}$ (mg/g)	k_1 (min ⁻¹)	R^2	$Q_{e,cal}$ (mg/g)	k_1 (g/mg.min-1)	R^2	$Q_{e,cal}$ (mg/g)	k_1 (min- 1.g/mg)	R^2	k_p (g.mg- 1.min ^{0.5})	C (mg/g)	R^2
2,90	3,01	-0,0115	0,989	3,07	0,008	0,991	6,34	0,02379	0,950	0,14452	0,50828	0,751

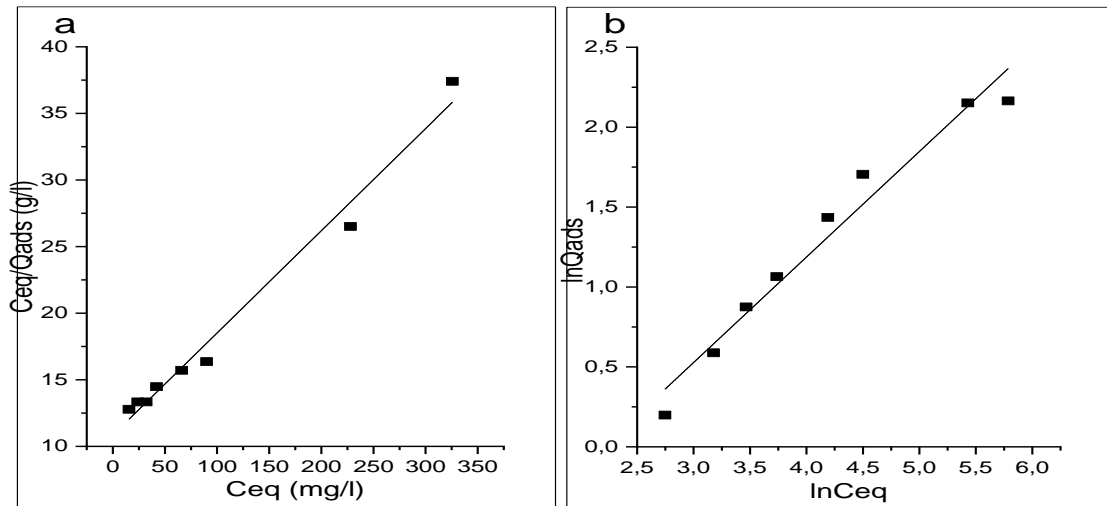


Figure 5: Modelling the adsorption isotherm of resorcinol onto HAp phosphate using (Figure 5 a) the Langmuir model and (Figure 5 b) the Freundlich model.

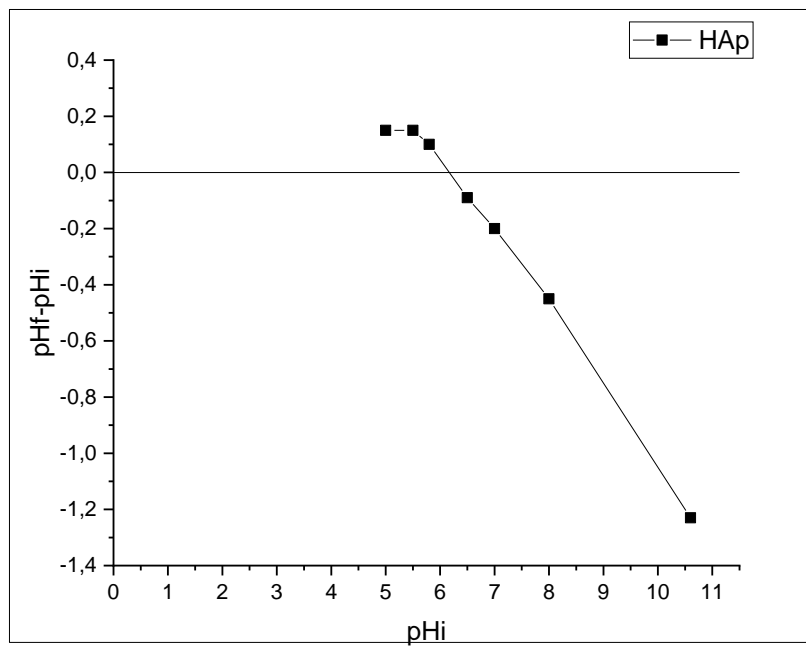


Figure 6: Identification of the zero point of charge of HAp.

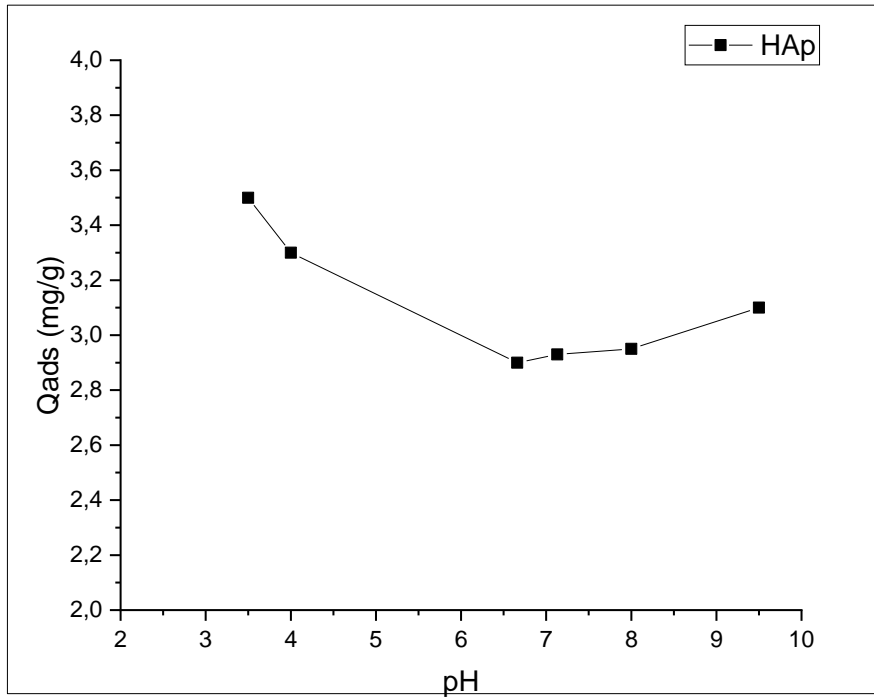


Figure 7: Effect of pH on the equilibrium adsorption resorcinol onto HAp

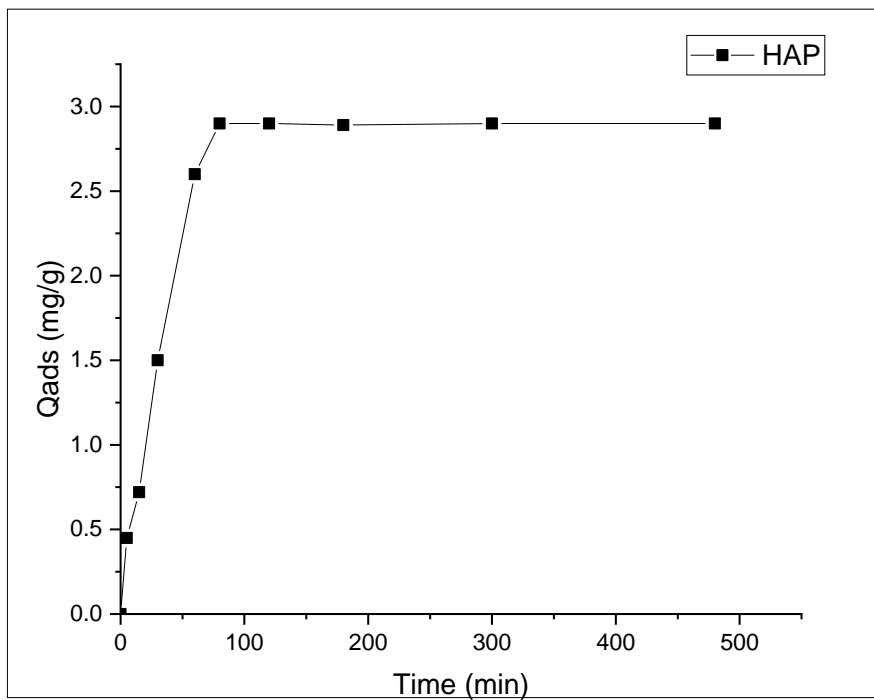


Figure 8: Adsorption kinetics of resorcinol onto HAp (200 mg of solid, an initial resorcinol concentration of 100 ml/l, starting pH, at 298 K, stirred for 1 minute)

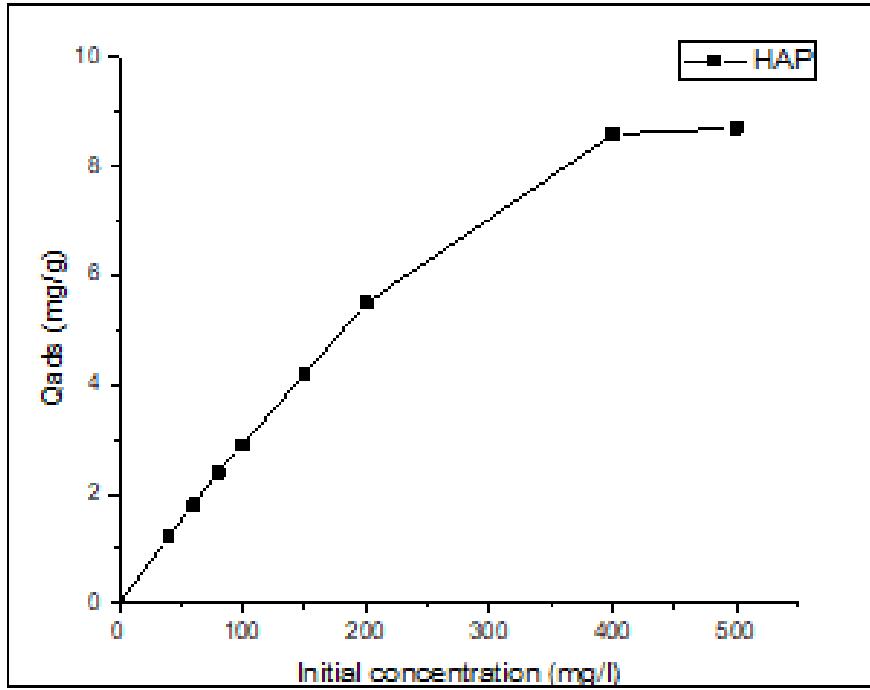


Figure 9: Isotherms depicting the adsorption of Resorcinol on Hydroxyapatite. (Solid mass: 200 mg, agitation time: 1 minute, Temperature: 298 K).

Table 2: Parameter values for the fitting of Freundlich and Langmuir models

Freundlich		Langmuir			
m	a (l/g)	R ²	b (l/g)	Q _∞ (mg/g)	R ²
0,6601	-0,45283	0,99	0,0071	13,03	0,99

Table 3: Thermodynamic parameters for resorcinol adsorption on HAp powder

T (K)	K _c	ΔG (KJ/mol)	ΔS (J/mol K)	ΔH (KJ/mol)	R ²
293	1.17	-0.38	45.476	12.829	0.966
298	1.38	-0.80			
308	1.66	-1.30			
318	1.79	-1.54			
323	1.99	-1.85			

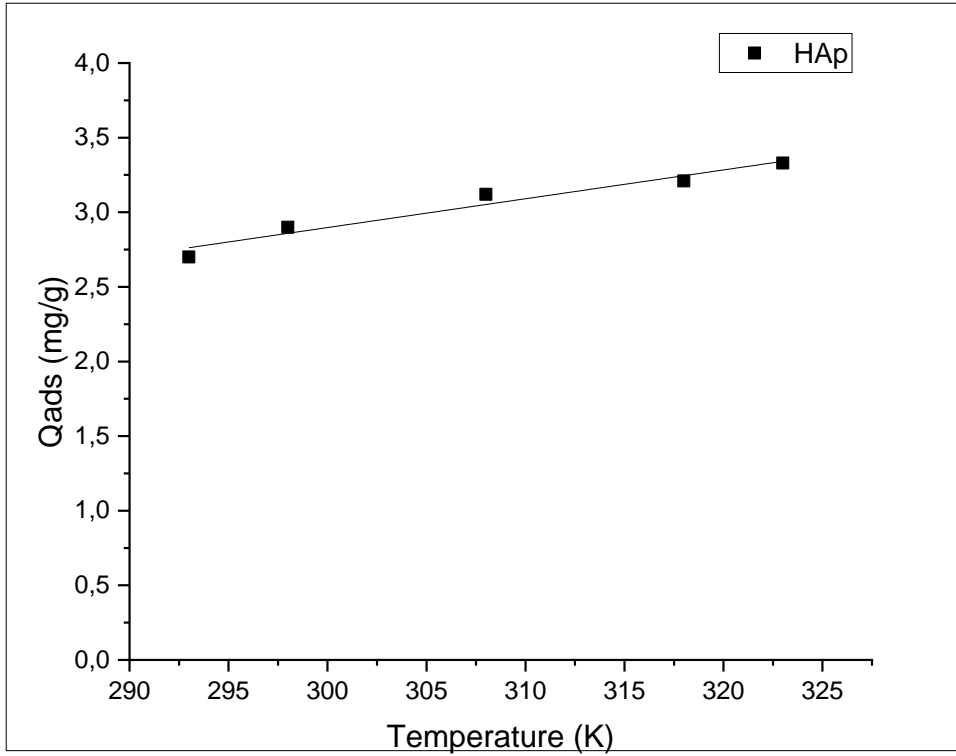


Figure 10: Impact of temperature on the adsorption of Resorcinol onto HAp (with a solid quantity of 200 mg, initial Resorcinol concentration of 100 mg/l, initial pH, stirring time of 1 minute, and contact time of 4 hours)

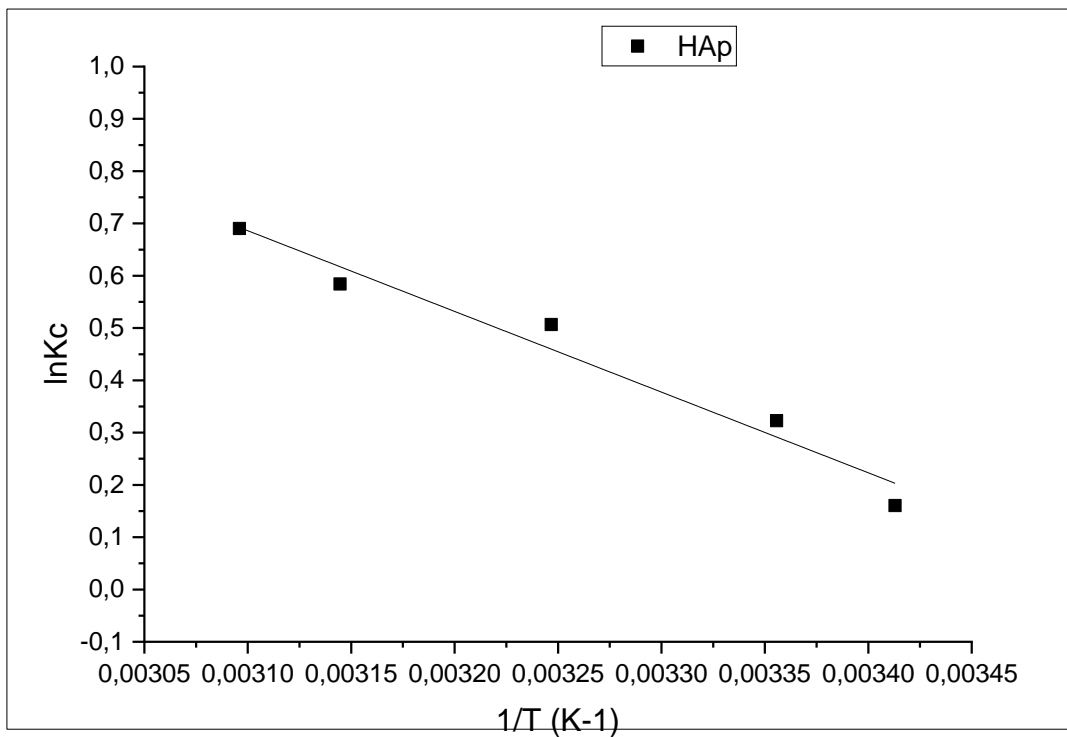
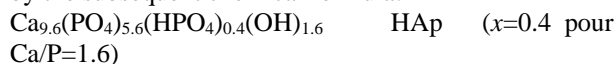


Figure 11: Van't Hoff plot for estimation of thermodynamic parameters

The chemical analysis given a Ca/P atomic ratio of 1.60. This ratio is lower compared to stoichiometric hydroxyapatite (1.67). This result aligns with the presence of hydrogen phosphate ions (HPO_4^{2-}) as observed in the infrared absorption spectrum. It is a calcium-deficient hydroxyapatite that can be expressed by the subsequent chemical formula:



The X-ray diffraction pattern (Figure 3 a) closely aligns with the reference pattern of pure hydroxyapatite (Figure 3 b) (JCPDS no. 09-0432). No additional phase is observed. The apparent dimensions of the crystallites were determined using the Scherrer equation. The values obtained for the two examined peaks (002) and (310) are 41.5 and 17.5 nm, respectively. These values indicate that the HAP crystals are elongated along the c-axis ($L(002) > L(310)$).

The pH evolution (pH (final) - pH (initial)) as a function of adjusted initial pH (Figure 6) yields a pH PZC of hydroxyapatite at 6.25, indicating that for higher pH values, the surface is negatively charged, whereas for pH values below 6.25, the surface exhibits a positive charge.

3.2) Effect of pH on the equilibrium adsorption resorcinol onto HAp

The following figure (Figure 7) exemplifies the impact of pH on the adsorption of resorcinol by HAp. The results clearly demonstrate a substantial effect of pH on the adsorption process. The adsorption capacity of resorcinol exhibits a decreasing trend as the pH rises, reaching its lowest point at a pH value of 7.13. Beyond this pH value, the adsorption capacity increases slightly. The maximum adsorption is recorded at pH 3.5 with a value of 3.5 mg/g. This observation can be rationalized by considering the point of zero charge (pHz) of hydroxyapatite, ascertained to be 6.25. Once the pH of the solution surpasses the pHz threshold, the surface of hydroxyapatite particles acquires a negative charge. Conversely, when the pH is below the pHz, the surface becomes positively charged. As a result, the adsorbent-adsorbate interactions for resorcinol with negatively charged HAp particles gradually become significant for pH values smaller than pHz. On the other hand, in pH environments higher than pHz and under strongly basic conditions, where resorcinol exists in its deprotonated and ionized form, the ionic strength is altered accordingly, leading to a relatively improved adsorption, Lin et al. observed a comparable trend in the adsorption behavior of phenol, corroborating our findings.

3.2) Adsorption Kinetics

Equilibrium was swiftly established, with the resorcinol reaching its maximum adsorption within the 80 minutes of contact (figure 8). This fixation can be credited to the plentiful presence of active sites during the initial phase, despite a decrease in relative adsorption sites over time. In Figure 8, the resorcinol adsorption kinetics of the HAP is depicted at a specific organic concentration (100 mg/l). Based on this information, the approximate equilibrium state time for the resorcinol apatite adsorption system can be determined to be around 80 minutes under the specified test conditions. The

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kinetics of adsorption were assessed using the Lagergren [34] quasi-first-order (eq. 5) kinetic model, the quasi-second-order model (eq. 6), second order (eq. 7) and the intraparticle diffusion (eq. 8) (Figure 4) model on the kinetic data.

$$\log(Q_e - Q_t) = \log(Q_e) - K_1/2.3t \quad (5)$$

The model proposed by Ho and McKay in 1999 and 2000 [35,36], known as the pseudo second order model, has been investigated to understand the adsorption mechanism.

$$t/Q_t = 1/2K_2Q_e^2 + t/Q_e \quad (6)$$

$$1/(Q_e - Q_t) = 1/Q_e + K_3t \quad (7)$$

In this equation, Q_e represents the equilibrium adsorbate quantity (mg/g), while t denotes the contact time. K_1 , K_2 , and K_3 correspond to the adsorption rate constants for the pseudo-first-order (min^{-1}), pseudo-second-order (g/mg minute), and second-order ($\text{min}^{-1} \text{g/mg}$), respectively. The factor that establishes the rate of intraparticle diffusion, as stipulated by Weber and Morris in 1963, entails computing the initial intra-particle transport rate through the graph of Q_t against $t^{1/2}$:

$$q_t = k_p t^{1/2} + C \quad (8)$$

In this context, q_t represents the amount of solute adsorbed on the sorbent surface at time t (mg/g), k_p represents the intra-particle rate coefficient (mg g⁻¹ min^{0.5}), t signifies the time (minute), and C (mg/g) is a constant indicating the boundary layer thickness. The intra-particle diffusion model was utilized to determine the dominant stage in the adsorption process. Based on Weber and Morris' theory, a linear regression of Q_t against $t^{1/2}$ passing through the origin would indicate sole control by intraparticle diffusion. However, as depicted in Figure 4 b, the regression was not linear and the plot didn't originate from the origin, indicating that intraparticle diffusion did not solely govern the adsorption process.

The adsorption rate constants of resorcinol on hydroxyapatite for pseudo first order, pseudo second order and second order were determined graphically (Figures 5 a, 5 c and 5 d).

The determination of the different rate constants (Table 1) shows that the pseudo-second order model with a good correlation coefficient ($R^2=0.991$) is the most reliable.

3.3) Adsorption isotherms studies

The study examined the adsorption characteristics of resorcinol on phosphate by exposing 200 mg of adsorbent to 10 ml of different solutions with resorcinol concentrations spanning from 40 to 500 mg/l and a duration of 4 hours. Figure 9 displays the correlation between the quantity of adsorbate and its concentration at equilibrium within the medium. It's evident that the absorbed amount of resorcinol increases notably with varying medium concentrations in solution before reaching a plateau, suggesting a form of monolayer adsorption. Representation of the adsorption isotherms using the Freundlich and Langmuir models is

illustrated in Figure 5. Based on the correlation coefficients' values (see Table 2), both the Freundlich (Figure 5 b) and Langmuir models (Figure 5 a) are suitable for describing the adsorption isotherms on hydroxyapatite phosphate. The determined adsorption capacity Q_1 , which represents the maximum adsorption capacity at complete monolayer coverage, is 13.03 mg/g.

3.4) Thermodynamics

In Figure 10, we depicted the change in the adsorbed quantity as a function of temperature. As temperature rises, there's a corresponding elevation in the adsorption capacity of resorcinol at equilibrium. This temperature upsurge within the range of 293–323 K is attributable due to the heat-absorbing characteristic of the adsorption process.

According to literature, the thermodynamic factors associated with the adsorption process, such as enthalpy change (ΔH), the standard free energy change (ΔG) and entropy change (ΔS), can be computed by utilizing the subsequent equations [29,38–40] :

$$\Delta G = -RT \ln K_c \quad (9)$$

$$\Delta G = \Delta H - T \Delta S \quad (10)$$

$$\ln K_c = \Delta S/R - \Delta H/RT \quad (11)$$

$$K_c = \frac{(C_0 - C_{eq})}{C_{eq}} \quad (12)$$

Here, K_c represents the equilibrium constant, ΔG stands for Gibbs free energy (J/mole), ΔH denotes Enthalpy (J/mole), ΔS signifies Entropy (J/mol K), T represents the absolute temperature (K), R (8.314 J/mol K) signifies the gas constant and C_0 indicates the initial concentration of the adsorbate while C_{eq} denotes the concentration at equilibrium. A linear relationship between $\ln K_c$ and $1/T$ was observed for an initial resorcinol concentration of 100 mg/l, as depicted in Figure 11. Using the slope and intercept obtained from this plot, the values for ΔH and ΔS were derived and are elaborated upon in Table 3. The positive ΔS value indicates an increase in randomness during the process [41,42]. Additionally, the positive change in ΔH (less than 40 kJ/mol) suggests that the adsorption of resorcinol onto HAP primarily involves physisorption processes. At each temperature, the existence of negative values for the free energy (ΔG) indicates the possibility and inherent character of the ongoing adsorption process [43]. The range of variation in free energy for physisorption and chemisorption lies within the interval of -20 to 0 KJ/mol and -80 to -400 KJ/mol [41]. The ΔG values reported in Table 3 fall within the range of -20 to 0 KJ/mol, suggesting that physisorption is the dominant mechanism. Additionally, the obtained adsorption values (ΔH) in this investigation (-20 KJ/mol) correspond to the forces of hydrogen bonding and dipole bonding for the adsorbent [44]. The positive values of ΔS indicate that the adsorption process of resorcinol onto HAP was thermally favored. Moreover, these positive ΔS values suggest an augmentation in the degrees of freedom at the solid-liquid interface during the adsorption of resorcinol onto HAP. The positive ΔH° value confirms the endothermic nature of the adsorption process [45,46].

3.5) Comparative Analysis with Previously Reported Adsorbents

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Over the past decade, significant progress has been made in the field of adsorbents and their adsorption capabilities, resulting in the development of innovative technologies and materials that offer enhanced performance in removing resorcinol contaminant. The purpose of the comparative study involving six adsorbents (Hap, $Q_{ads}= 8,71$ mg/g (this study); OMC ($Q_{ads}= 36,3$ mg/g) [47]; OMC-NH₃H₂O ($Q_{ads}= 40,6$ mg/g) [48]; GAC ($Q_{ads}=36$ mg/g) [49]; CTAB/NaOH/fly ash composite ($Q_{ads}=83, 28$ mg/g) [3]; and OMC-B ($Q_{ads}=43.9$ mg/g) [50]) is to evaluate the advancements made and identify the most effective adsorbents. The obtained results highlight notable differences among these adsorbents. Firstly, the CTAB/NaOH/fly ash composite adsorbent demonstrated exceptional adsorption capacity, effectively capturing contaminants. This remarkable efficiency can be linked to its substantial specific surface area and strong affinity for targeted substances. Conversely, the OMC adsorbent exhibited slightly lower adsorption capacity but remained effective for resorcinol removal. The OMC-B adsorbent, however, displayed moderate adsorption capacity and comparatively lower efficiency. Both the GAC and HAP adsorbents exhibited relatively low adsorption capacities, placing them at the lower end of our comparative ranking. These findings underscore the importance of selecting an appropriate adsorbent based on specific application requirements, considering the necessary adsorption capacity for successful contaminant removal.

4. Prospective research

In the field of adsorption, scientific research continues to explore and reveal new horizons. An important area is the study of novel phosphate-based adsorbents and their effectiveness in removing phenolic contaminants from various media, particularly in aqueous environments. Understanding the underlying mechanisms governing adsorption processes, such as exploring surface interactions, molecular arrangements, and the role of factors such as temperature, pH and ionic strength, remains an essential task. Additionally, there is an increasing emphasis on optimizing adsorption capacity and selectivity, to tailor materials to specific pollutants or complex mixtures commonly found in industrial wastewater. This involves examining synergistic effects between multiple adsorption mechanisms, such as electrostatic interactions, Van der Waals forces, and surface functional groups, to improve adsorption efficiency. Furthermore, advanced characterization techniques, and computational modeling offer promising avenues for designing new materials. Also, the exploration of the dynamic behavior of adsorbate adsorbent systems under various conditions and the development of predictive models to elucidate the adsorption behavior constitute a burgeoning frontier. The quest for sustainable and environmentally friendly adsorption processes is also attracting interest, driving research toward renewable and inexpensive adsorbents, as well as exploring ways to regenerate or reuse adsorbents to minimize waste. environmental impact and maximize efficiency. In view of the above, adsorption by phosphate materials is a dynamic field that continually

advances our understanding, technologies and applications to address environmental challenges through the efficient removal of pollutants, including compounds phenolics and the recovery of these resources.

5. Conclusions

In conclusion, this study demonstrates the efficacy of environmentally friendly materials, such as HAp, in the removal of resorcinol from water. The adsorption process on HAp conforms well to the Freundlich and Langmuir models, indicating a favorable adsorption behavior. The kinetics study reveals a relatively rapid attainment of equilibrium, following a pseudo-second order mechanism. Furthermore, increasing the temperature enhances the maximum adsorption capacity, illustrating the correlation of thermodynamic factors with the adsorption process. Thermodynamic examination suggests that the adsorption of resorcinol onto hydroxyapatite is both physisorption-based and endothermic. Looking ahead, there are several perspectives to consider. Firstly, further investigations could focus on optimizing the adsorption conditions, for example adsorbent dosage, pH and contact time, to enhance the efficiency of resorcinol removal. Additionally, exploring the regeneration and reusability of HAp as an adsorbent would contribute to its sustainability and cost-effectiveness. Furthermore, the potential application of HAp in the removal of other organic pollutants from water could be explored. Finally, considering the environmental impact and scalability of using HAp as an adsorbent on a larger scale would be valuable for practical implementation. These perspectives offer avenues for future research and application of HAp in water treatment and pollution mitigation.

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