EEET ECOLOGICAL ENGINEERING & ENVIRONMENTAL TECHNOLOGY

Ecological Engineering & Environmental Technology, 2025, 26(1), 257–271 https://doi.org/10.12912/27197050/195952 ISSN 2719–7050, License CC-BY 4.0 Received: 2024.11.01 Accepted: 2024.11.28 Published: 2024.12.01

Adsorption of resorcinol onto synthetic calcium phosphate compounds: Kinetic, isotherm, and thermodynamic studies

Abdellatif El Bakri^{1*}, Nouhaila Ferraa¹, Abdelah Lachheb¹, Mounia Bennani-Ziatni¹

¹ Laboratory of Organic Chemistry, Catalysis, and Environment, Department of Chemistry, Faculty of Sciences, Ibn Tofail University, PB. 133-14050 Kenitra, Morocco

* Corresponding author's e-mail: abdellatif.elbakri@uit.ac.ma

ABSTRACT

Using batch adsorption methods, this work examines the adsorption behavior of resorcinol onto two artificial calcium phosphate compounds, tricalcium phosphate apatite (PTCa) and octocalcium phosphate apatite (OCPa). The study is to assess these materials' adsorption capacities and investigate the impacts of important parameters like pH, temperature, starting concentration, and adsorbent dosage. When both the Freundlich and Langmuir isotherm models were used, the Langmuir model fit the data better, suggesting monolayer adsorption. PTCa and OCPa were shown to have maximal adsorption capabilities of 13.27 mg/g and 5.05 mg/g, respectively. According to kinetic studies, the adsorption process exhibits pseudo-second-order kinetics, which points to chemisorption. The adsorption is exothermic and spontaneous, driven by physical interactions including van der Waals forces and hydrogen bonds, according to thermodynamic considerations. The study comes to the conclusion that PTCa and OCPa, with their high adsorption capacities and advantageous thermodynamic and kinetic properties, are attractive materials for the elimination of resorcinol from aqueous solutions.

Keywords: OCPa; PTCa; adsorption equilibrium; thermodynamics; resorcinol.

INTRODUCTION

Pollutant species are released into the environment as a result of numerous human activities. Treatments aiming at eliminating these contaminants are frequently required, whether to address an already contaminated resource or to control emissions at the source. A typical method for treating gaseous or aqueous effluents is adsorption (Sylvie et al., 2007). The problem of aqueous effluents tainted by organic micropollutants, especially resorcinol, will be our main focus in this context. At high quantities, phenol and its compounds give drinking water a disagreeable taste and odor. Industrial effluents frequently contain phenol and its compounds (Sun et al., 2019; Yan et al., 2021). Industries include petrochemicals, plastics, leather, pesticides, and resins are the main sources of their emission (Hejazi et al., 2019). Because phenolic chemicals, like resorcinol, are persistent and hazardous in

aquatic settings (Anku et al., 2017; Hanafi and Sapawe, 2020; Iftikhar et al., 2021), their growing industrial use in manufacturing processes presents a serious environmental risk (Suresh et al., 2012; Weber et al., 2015). Resorcinol is a dihydroxybenzene isomer that is frequently present in a variety of industrial effluents, such as dyes, plastics, and medicines (Mousa, 2009; Subramanyam and Mishra, 2013). When not adequately controlled, it can be a hazardous contaminant (Adam, 2016). Resorcinol's resistance to natural degradation prompts worries about possible health hazards, including harm to aquatic life and endocrine disruption, when it is found in water bodies (Järvik, 2011; Nawaz and Sengupta, 2019; Schrör and Moers, 2018). As a result, creating sustainable and efficient techniques to remove it from wastewater has emerged as a key area of environmental study.

These days, the process of adsorption has developed into a useful instrument for the separation and purification of unwanted materials. It is used in many different sectors, including petrochemical, chemical, and pharmaceutical ones, and it plays a major role in tackling environmental problems, especially in the water treatment sector (Aksu, 2005). Adsorption has become more wellknown among the different methods for eliminating organic pollutants from water because of its ease of use, effectiveness, and affordability (Thakur & Kandasubramanian, 2019). The success of adsorption, a flexible process that includes the buildup of solute molecules on the surface of a solid adsorbent, is mostly determined by the properties of the adsorbent material. The calcium phosphate compound hydroxyapatite (HAP) (El Rhilassi et al., 2012) has demonstrated potential as an adsorbent because of its large surface area, biocompatibility, and potent affinity for organic contaminants, such as phenolic chemicals (El Bakri et al., 2024; El Bakri et al., 2024). Phosphate-based materials are good candidates for additional research because prior studies have shown how effective they are at removing different organic contaminants from aqueous solutions (El Boujaady et al., 2011, 2014, 2017).

Adsorption enables one or more contaminants to build up on a solid material's surface. Significant porosity is frequently present in this material to significantly increase its adsorption capacity. As the loading (adsorbed fraction) of the adsorbent rises, the adsorption rate and capacity fall. The adsorbent is usually changed or regenerated after a certain amount of use (Salvador et al., 2015). For high-value adsorbents (such synthetic zeolites, monoliths, and activated carbon fabrics) (McQuillan et al., 2018; S. Wang et al., 2006), developing regeneration methods that are affordable, efficient, and straightforward to use is a major problem.

Using batch adsorption techniques, this work examines the adsorption behavior of resorcinol onto two synthetic calcium phosphate compounds: octocalcium phosphate apatite (OCPa) and tricalcium phosphate apatite (PTCa). The main goal is to examine these materials' adsorption capacity as well as the effects of important variables on the adsorption process, including pH, temperature, starting concentration, and adsorbent dose. Classical isotherm models, such as Freundlich and Langmuir were utilized to examine and comprehend the adsorption mechanism. The behavior of monolayer adsorption and the interaction between resorcinol and the adsorbents are clarified by these models. These models help clarify the behavior of monolayer adsorption and the interaction between resorcinol and the adsorbents.

The significance of resorcinol as a contaminant in various industrial applications necessitates an effective removal strategy. Resorcinol is known for its toxicity and potential environmental impact, making the development of efficient adsorbents crucial. Calcium phosphate compounds have gained attention due to their biocompatibility and high adsorption capacity, which make them suitable candidates for environmental remediation. This study aims to provide insights into the effectiveness of OCPa and PTCa in capturing resorcinol from aqueous solutions, thereby addressing both environmental and health concerns.

To achieve a comprehensive understanding of the adsorption process, various experimental conditions were systematically varied. The pH of the solution plays a critical role in influencing the ionization state of resorcinol and the surface charge of the adsorbents, affecting their interaction. Similarly, temperature variations can alter the kinetic energy of molecules, thereby impacting the adsorption rate and capacity. By optimizing these parameters, the study aims to identify the most favorable conditions for maximum resorcinol adsorption.

Furthermore, the application of isotherm models provides a deeper insight into the adsorption mechanisms at play. The Freundlich isotherm, indicative of heterogeneous adsorption, suggests that the adsorption sites on the adsorbents are not uniform. In contrast, on a surface with a limited number of identical sites, monolayer adsorption is assumed by the Langmuir isotherm, providing crucial information about the maximum adsorption capacity of OCPa and PTCa. By comparing these models, the study will elucidate the nature of the interactions between resorcinol and the synthetic calcium phosphate compounds, allowing for a more targeted approach in the design of effective adsorbents for similar contaminants.

This work's objective is to add to the expanding corpus of research on the use of phosphate-based materials to remove organic contaminants from water. The study aims to lay the groundwork for creating effective, long-lasting, and ecologically friendly water treatment solutions by investigating the adsorption capability of PTCa and OCPa for resorcinol.

MATERIALS AND METHODS

Adsorbents

PTCa: Using a technique created by Heughebaert, The solid tricalcium apatitic phosphate $(Ca_{o}(HPO_{4})(PO_{4})_{5}(OH))$ has a Ca/P atomic ratio of 1.5 and a high specific surface area (SSA). Solution A, which is made by dissolving 23.5 g of calcium nitrate tetrahydrate in 225 ml of distilled water with 40 ml of ammonia (pH \sim 11.2), and Solution B, which is made by dissolving 13 g of ammonium hydrogen phosphate in 650 ml of water with 20 ml of ammonia (pH ~9.9), are used in this co-precipitation process. A white precipitate is produced when Solution A is quickly added to Solution B at room temperature. After filtering and washing with an alkaline solution (1.5 liters of water and 7.5 ml of ammonia), the precipitate is dried for 24 hours at 80 °C in an oven hours (El Boujaady et al., 2011, 2014).

OCPa: According to Zahidi, OCPa is produced by the rapid double breakdown of octocalcium apatitic phosphate $(Ca_8(HPO_4)_{2,5}(PO_4)_{3,5}(OH)_{0,5})$, a calcium salt solution (solution A), and an ammoniacal orthophosphate solution in a water/ ethanol medium (solution B). By lowering the dielectric constant, ethanol stabilizes amorphous calcium phosphates and encourages the production of protonated species such as HPO_{4}^{2-} ions. 7.09 g of calcium nitrate tetrahydrate is dissolved in 100 mL of distilled water, and then 100 mL of ethanol is added to create Solution A. In Solution B, 3.96 g of $(NH_4)_2$ HPO₄ is dissolved in 250 mL of distilled water, and 2.95 mL of ethanol and 45 mL of ammonia are added. To create co-precipitation, solutions A and B are quickly swirled together at 37 °C. A basic solution (180 mL of degassed deionized water, 30 mL of ammonia, and 210 mL of ethanol) and an overnight drying process at 80 °C are then applied after the precipitate has been filtered using a Buchner funnel (El Boujaady et al., 2011).

Utilizing a Panalytical X Pert 3 Powder diffractometer, the X-ray powder diffraction (XRD) pattern was obtained using copper K α radiation (K α 1 = 1.5405980 Å). This technique is essential for determining the crystalline structure of the synthetic calcium phosphate compounds, as it allows for the identification of phase compositions and the assessment of crystallinity. The resulting diffraction patterns provide valuable insights into the structural properties of OCPa and PTCa, facilitating a deeper understanding of their interactions with resorcinol during the adsorption process.

To complement the XRD analysis, infrared spectroscopy (IR) was performed using a BRUKER spectrometer. For this, anhydrous KBr was mixed with roughly 2 mg of the product for each 200 mg of KBr. This method enables the characterization of functional groups present in the adsorbents and the adsorbate, shedding light on the chemical interactions that occur at the molecular level during adsorption. The IR spectra can reveal characteristic absorption bands associated with phosphate groups and any changes in the chemical structure of resorcinol upon adsorption, thereby enhancing our understanding of the adsorption mechanism.

Furthermore, the combination of XRD and IR analyses provides a comprehensive approach to characterizing the materials involved in this study. While XRD focuses on the long-range order and crystalline nature of the compounds, IR spectroscopy offers insights into the short-range molecular interactions and the presence of specific functional groups. Together, these techniques help elucidate the complex behavior of resorcinol adsorption onto calcium phosphate apatite, ultimately contributing to the development of effective adsorbent materials for environmental and industrial applications.

Adsorption tests

Adsorbate

Resolving pure samples in distilled water is the first step in creating a stock solution of resorcinol. The equilibrium isotherms and the effects of kinetics, pH, adsorbent dose and starting concentration on the adsorption of resorcinol onto synthetic phosphates (OCPa and PTCa) were investigated using batch adsorption tests. A UV spectrophotometer was used to measure the resorcinol concentration, employing a method that forms colored complexes using 4-aminoantipyrine (Fiamegos et al., 2002; Norwitz et al., 1981). The process involved adjusting the pH of the solution to 9.5, adding reagents, and allowing the mixture to reach equilibrium before measuring its absorbance at 500 nm (Tang et al., 2015; T. Wang et al., 2017).

Experimental protocol

OCPa and PTCa, two synthetic phosphates, were used to adsorb resorcinol in batch mode. The solid was exposed to a resorcinol solution for every experiment. After a minute of constant stirring at a fixed rate of 500 rpm, the mixture was transferred to a temperature-controlled water bath that was set at 25 °C. They then use a fritted glass apparatus to separate the solid from the colloid. The concentration of resorcinol is determined by means of a UV visible spectrophotometer. The following formula measures how much resorcinol the adsorbent has absorbed (Lian et al., 2019, 2020, 2021).

$$Qt = \frac{(C0 - Ct)V}{m} \tag{1}$$

where: Q_t – resorcinol content in mg/g of adsorbent; C_0 – The beginning concentration, while the resorcinol concentration at time t (in mg/l) is denoted by C_t ; V – the solution's volume (in l); m – the amount of adsorbent used (in g).

The simplicity of the Freundlich (1926) and conventional Langmuir (1916) Equation 2 models, which describe monolayer adsorption, is highly regarded. The continuous interaction between the adsorbent and the saturation adsorption capacity (Q_{∞}) and adsorbate (b) were identified as important adsorption characteristics applying the Langmuir equation that has been linearized (Langmuir., 1916).

$$1/Qad = 1/(bQ\infty)Ceq + 1/Q\infty \qquad (2)$$

$$Y = a X^m \text{ with } m \le 1 \tag{3}$$

where: X represents the equilibrium concentration of the adsorbate in the solution, and Y represents the amount of material adsorbed per unit mass or surface area of the adsorbent. The interaction between the adsorbent and adsorbate is defined by the parameters a and m. Following a linear conversion, we obtain:

$$log(Y) = log(a) + mlog(X)$$
(4)

Determining m and an is aided by the correlation between the logarithms of Y and X. It is noteworthy that the adsorption mode is usually described by Freundlich's law at very low levels of adsorption. On the other hand, the process is well described by Langmuir's law when the recovery rate is large.

pH study

Phosphate synthetics (PTCa and OCPa) were added to a 10-milliliter test tube that contained a resorcinol solution. For all experimental circumstances, the starting resorcinol concentration was consistently set at 100 mg/L. To alter the pH, 0.1 M HCl and 0.1 M NaOH were used. After two minutes of stirring, the resultant mixture was put in a thermostatic bath that was kept at a steady 25 °C. Following a 5-hour contact time, the pH of the solution was determined and the particle phase was filtered out using a porous glass. The difference between chemical and physical adsorption is shown in Figure 1.

RESULTS AND DISCUSSIONS

Effect of the amount of solid

To examine the impact of the amount of solid, we incorporated variable masses (ranging from 0.05 to 0.4 g) of PTCa and OCPa into volumes of 10 ml of resorcinol (100 mg/L).

The results regarding the impact of the quantity of phosphate adsorbents on the adsorption of resorcinol are illustrated in Figure 1. It is noted that the elimination of resorcinol intensifies as the



Figure 1. Distinction between physical adsorption and chemical adsorption (Nouacer, 2015)

quantity of phosphates increases, up to 0.2 g. This increase in the elimination rate may be attributed to the growth of the specific surface area and the increased availability of active sites (Lin et al., 2009). However, after more than 200 mg of PTCa and OCPa, there was no notable change in the percentage of resorcinol elimination (Figure 2). This situation may result from the overlap of active sites at higher quantities of resorcinol, due to the aggregation of particles. Lin et al. (2009) and El Asri et al. (2009) observed similar results, which could be attributed to the fact that resorcinol was distributed over a wide area of the surface, leading to a decrease in the adsorption volume. Therefore, in the context of our future research, 200 mg will be regarded as the ideal quantity of phosphate adsorbent that we will use.

Resorcinol's equilibrium adsorption onto OCPa and PTCa as a function of pH

One crucial factor in the adsorption process is the solution's pH (Guo et al., 2013). It is important for resorcinol adsorption. Generally, the amount adsorbed increases as the pH decreases. Few studies have been conducted on the effect of pH on the adsorption of resorcinol by phosphates. Lin et al. (2009) demonstrated that the optimal pH for the adsorption of phenol onto poorly crystallized hydroxyapatite is in the acidic range. Using either hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M), we examined the impact of pH on the adsorption of resorcinol at an initial concentration of 100 mg/L and 200 mg of synthetic phosphate. Figure 3 shows the results that were achieved.



Figure 2. Elimination of resorcinol based on the quantity of phosphates



Figure 3. The effect of pH on resorcinol's ability to adhere to the used phosphates

The amount adsorbed on both supports decreases with increasing pH. The maximum adsorption for resorcinol was recorded in an acidic medium. This can be explained by the fact that in an acidic medium at pH < pH PZC of the phosphates (El Bakri, et al., 2024a; El Bakri, et al., 2024b), the surface of the phosphates is positively charged, which favors donor-acceptor interactions between the positive charge of the phosphate and the delocalized electrons of the aromatic ring of resorcinol. In a strongly basic medium (pH > 8), the surface is negatively charged, and resorcinol can be found in both its ionized and deprotonated forms, consequently, it changes the ionic strength., and adsorption is improved. Similar results have been observed by Lin et al. (2009), Bouyarmane et al. (2014) and El Asri et al. (2009) in the case of phenol.

Adsorption kinetics

Resorcinol reached its maximal adsorption capacity within 80 minutes of contact, demonstrating the rapid establishment of equilibrium (Figure 4). Even though there are fewer relative adsorption sites over time, this adsorption can be ascribed to the early phase's extensive active site presence. The adsorption kinetics of resorcinol at a particular organic concentration (100 mg/l) on synthetic phosphates (PTCa and OCPa) are depicted in Figure 4. This data suggests that, under the given test conditions, the resorcinol adsorption system's approximate equilibrium period on these synthetic phosphates would be about 80 minutes. To assess the adsorption kinetics, the quasi-first-order Equation 5 kinetic model, the quasi-second-order Equation 6, second-order Equation 7, and intraparticle diffusion Equation 8 models were employed (Figure 5) (Lagergren et al., 1898) :

$$log(Qe - Qt) = log(Qe) - K1/2.3t$$
 (5)

$$t/Qt = 1/2 K2 Qe^2 + t/Qe$$
 (6)

$$1/(Qe - Qt) = 1/Qe + K3t$$
(7)

where: t stands for the contact period and Qefor the equilibrium adsorbate quantity (mg/g). K_1 represents the pseudo-firstorder (min⁻¹), K_2 represents the pseudosecond-order (g/mg minute), and K_3 represents the second-order (min⁻¹ g/mg) adsorption rate constants. According to Weber et al. (2015), the graph of Q_t against $t^{1/2}$, the parameter that determines the rate of intraparticle diffusion, is used to compute the initial intra-particle transport rate:

$$qt = Kpt^{1/2} + C$$
 (8)

where: t is the time (minute), The intra-particle rate coefficient is denoted by k_p (mg g⁻¹ min^{0.5}), the quantity of solute absorbed by q_t (mg/g) on the sorbent surface at time t, and the thickness of the boundary layer is represented by a constant, C (mg/g). The principal adsorption stage was identified using the intra-particle diffusion model. A linear regression of Q_t against t^{1/2} traveling through the origin would suggest sole



Figure 4. Resorcinol's adsorption kinetics onto synthetic phosphate (200 mg of solid, initial pH, at 298 K, agitated for 1 minute)



Figure 5. Resorcinol's phosphate synthetic adsorption kinetics were studied at 25 °C with 200 mg of solid, a pH of 6.66, and a stirring time of one minute

control by intraparticle diffusion, in accordance with the theories of Weber and Morris. However, as Figure 5 shows, the regression was not linear and the plot did not start at the origin, suggesting that the adsorption process was governed by more than just intraparticle diffusion.

Figure 5 shows the graphic computation of the pseudo first order, second order and pseudo second order adsorption rate constants of resorcinol on OCPa and PTCa.

In addition to the second order for the OCPa support, the pseudo-second order and pseudo-first order models are the most dependable for both supports, according to the determination of the various rate constants (Figure 6), having a good correlation value of almost ($R^2 = 0.99$).

Analysis of adsorption isotherms

Over the course of four hours, to examine the adsorption characteristics of resorcinol on phosphate, 0.200 g of adsorbent was subjected to 10 ml of different solutions with resorcinol concentrations varying (40–500 mg/l). Figure 6 shows the

connection between the amount of adsorbate and its concentration in the medium at equilibrium. varying the solution's concentrations. It is evident that the quantity of adsorbed resorcinol increases significantly before plateauing, indicating a type of monolayer adsorption. The representation of the adsorption isotherms using the Freundlich and Langmuir models is shown in Figure 7. The correlation coefficient values (see Table 1) appear to indicate the adsorption isotherms on PTCa may be effectively described by both the Freundlich and Langmuir models (Figure 7), while the Langmuir model is most suited for resorcinol adsorption on octocalcium phosphate. The greatest adsorption capacity at complete monolayer coverage, indicated by the computed adsorption capacity Q1, is 5.05 mg/g for OCPa and 13.27 mg/g for PTCa.

Thermodynamics

Both the adsorption process and the adsorbent's equilibrium capacity are significantly impacted by temperature. Temperature variations can affect the adsorbent's overall effectiveness in collecting target molecules as well as the pace of adsorption. In addition to altering the interaction



Figure 6. Kinetic factors related to resorcinol's adsorption onto synthetic phosphate



Figure 7. Resorcinol's adsorption isotherm on PTCa and OCPa is being modeled

Table 1. Setting parameters to meet the Freundlich and Langmuir models

Model		Adsorbent	
		PTCa	OCPa
Freundlich	m	0.6700	0.4797
	a (l/g)	0.02877	0.06153
	R ²	0.973	0.689
Langmuir	Q _∞ (mg/g)	13.27	5.05
	b (l/g)	0.0064	0.0133
	R ²	0.982	0.954

between adsorbates and the adsorbent's active sites, higher temperatures may increase the molecules' kinetic energy and hence the rate of adsorption. On the other hand, high temperatures can also cause desorption, which lowers the total adsorption capacity. Therefore, maximizing adsorbent performance in a variety of applications requires an understanding of the thermodynamic behavior of adsorption in response to temperature (Agarwal and Rani, 2017). For this study, we used resorcinol solutions at a concentration of 100 mg/L. We added 0.2 g of adsorbent to 10 mL of solution and stirred at a speed of 500 rpm for one minute. The mixture was then placed in a thermostatic bath. The temperature range considered was between 20 and 50 °C. The evolution of the adsorbed amount as a function of temperature (Figure 8) shows that the amount of resorcinol adsorbed decreases on the PTCa and OCPa supports as the temperature rises from 20 to 50 °C. These observations may be attributed to the nature of the interactions between the apatite and resorcinol. Thus, the increase in temperature destabilizes the physical forces involved between the phosphates and resorcinol.

In general, a heat exchange that can be either endothermic or exothermic occurs in tandem with the adsorption process. (Li et al., 2014). The measurement of the adsorption heat is the primary criterion that allows differentiation between chemisorption and physisorption. The equations have been used to calculate the thermodynamic parameters, including entropy (ΔS), enthalpy (ΔH), and Gibbs free energy (ΔG) (Demirbas et al., 2006; Rodríguez et al., 2008):

$$\Delta G = -R T LnKc \tag{9}$$

$$\Delta G = \Delta H - T \,\Delta S \tag{10}$$

$$LnKc = \Delta S/R - \Delta H/RT$$
(11)

$$Kc = \frac{(C0 - Ceq)}{Ceq} \tag{12}$$

where: ΔG -Gibbs free energy change (Joules/mol); ΔS – entropy change (Joules/mol·K) ; ΔH – enthalpy change (Joules/mol); K_c – equilibrium constant ; T – temperature absolute (K); R – ideal gas constant; C_0 – the adsorbate's initial concentration; C_{eq} – the adsorbate's equilibrium concentration.

 ΔH and ΔS , the thermodynamic parameters of adsorption for the resorcinol onto the apatite are determined from the plots (Figure 9) of LnK_c versus the inverse of the temperature in Kelvin.

The exothermic nature of resorcinol's adsorption onto PTC and OCPa is confirmed by the negative values of ΔH shown in Table 2. This suggests stronger connections between the resorcinol molecules and the adsorbent surfaces since it shows that the adsorption releases energy. Additionally, the system experiences a reduction in randomness during adsorption, as indicated by the negative values of entropy (ΔS). In particular, structured interactions between adsorbates and the adsorbent surface are characterized by the resorcinol molecules at the solid-liquid interface being more ordered when adsorbed onto the PTCa and OCPa supports. Additionally, Table 3's negative values of Gibbs free energy (ΔG) at each temperature suggest that the resorcinol adsorption process onto the apatite is spontaneous and thermodynamically beneficial. This further supports the effective binding of resorcinol to the apatite surface by indicating that, under the specified experimental conditions, the adsorption takes place without the requirement for external energy input. The exothermic and spontaneous nature of the adsorption process is supported by the combined thermodynamic parameters, such as ΔH , ΔS , and ΔG , which offer important insights into its nature.



Figure 8. Temperature's impact on resorcinol adsorption onto phosphates



Figure 9. Entropy and enthalpy of resorcinol adsorption onto the studied phosphates

Table 2. Resorcinol adsorption's thermodynamic properties on the phosphates under study

	Adsorbents		
	PTCa	OCPa	
∆H (KJ/mol)	-7.477	-8.623	
∆S (J/mol K)	-23.239	-28.048	
R ²	0.870	0.980	

Table 3. Resorcinol's Gibbs free energy of adsorption onto the phosphates under study

Adsorbents	Т (К)	K _c	∆G (KJ/mol)
PTCa	293	1.28	-0.61
	298	1.23	-0.52
	308	1.21	-0.49
	318	1.06	-0.15
	323	0.94	0.17
ОСРа	293	1.18	-0.41
	298	1.09	-0.22
	308	1.02	-0.04
	318	0.91	0.25
	323	0.83	0.50

According to Table 3, the measured values of ΔG , which range from 0 to -20 kJ/mol, strongly imply that physisorption is the dominating mechanism in this instance, since the change in Gibbs free energy (ΔG) for chemisorption normally falls between -80 and -400 kJ/mol. Less negative ΔG values are generally linked to physisorption, which is defined by weaker van der Waals forces as compared to the stronger covalent or ionic interactions in chemisorption. The very small value of ΔG in this investigation aligns with the features of physisorption,

in which the adsorbent-adsorbate interaction is more physical than chemical. This observation is in line with preceding studies by Mahmoodi et al. (2011), who emphasized that processes controlled by physical adsorption mechanisms are indicated by such ΔG values. The predominance of physisorption implies that resorcinol and the surfaces of PTCa and OCPa, the adsorbents, have mostly weak and reversible contacts, which may permit desorption under some circumstances. As a result, this research confirms that physisorption is crucial to the adsorption of resorcinol onto these supports and emphasizes the significance of taking the thermodynamic data into account when figuring out the nature of the adsorption process.

Furthermore, The Gibbs free energy of adsorption for a variety of interactions was calculated by Yon Oepen (1991). For Van der Waals forces, the Gibbs free energy ΔG is between 4 and 10 kJ/mol, for hydrogen bonding, it is between 2 and 40 kJ/mol, and for chemical bonding, it is less than 60 kJ/mol (Agarwal and Rani, 2017). The adsorption processes of resorcinol onto the investigated phosphates are probably due to hydrogen bonding and dipolar interactions between resorcinol and water molecules, according to the values observed (Table 2).

Characterization of adsorbents after adsorption

Study by infrared (IR) absorption spectroscopy

The FT-IR absorption spectrum of PTCa-Resorcinol is shown in Figure 10. Following adsorption, the band at 876.7 cm⁻¹ that corresponds to HPO_{4}^{2-} ions emerge at 874.7 cm⁻¹. This shift can be attributed to the chemical interaction of resorcinol with the HPO_{4}^{2-} ions of PTCa. The OH- bands observed at 631.23 and 3368.77 cm⁻¹ after adsorption have shifted, indicating the chemical interaction of resorcinol with the O-H groups of PTCa. Similarly, the transmittances at wavenumbers 560.87, 600.50, 962.28, and 1023.35 cm⁻¹ related to $PO4^{3-}$ ions have been shifted to 560.73, 600.39, 962.21, and 1023.26 cm⁻¹, respectively, after the adsorption of resorcinol. In this case, a chemical interaction of resorcinol with the $PO4^{3-}$ groups of PTCa is assumed. Thus, it may be said that the interaction between PTCa and resorcinol involves the OH⁻, HPO4²⁻, and PO4³⁻ groups. The infrared absorption spectra of dried OCPa after resorcinol adsorption are shown in Figure 11.

Figure 10 shows that following the adsorption of resorcinol on OCPa, the band assigned to $HPO_{4^{2^{-}}}$ ions at 877.24 cm⁻¹ occurs at about 874.65 cm⁻¹. It is also noted that the bands attributable to $PO_{4^{3^{-}}}$ ions (560.66, 600.44, 961.80, 1023.22, and 1336.62 cm⁻¹) have shifted to (560.28, 600.23, 961.90, 1023.22, and 1338.45 cm⁻¹), respectively.

Therefore, we can say that the interaction between octocalcium phosphate and resorcinol involves both the $HPO_{4^{2-}}$ and $PO_{4^{3-}}$ groups.

Study by X-ray diffraction

The X-ray diffraction patterns of apatite tricalcium phosphate (PTCa) and apatite octocalcium phosphate (OCPa) both prior to and following adsorption with resorcinol are shown in Figure 12.



Figure 10. FT-IR absorption spectra of PTCa before and after adsorption of Resorcinol



Figure 11. FT-IR absorption spectra of OCPa before and after adsorption of Resorcinol



Figure 12. X-ray diffraction of synthesized phosphates prior to and following resorcinol adsorption

No modifications were detected following the interaction of the substrates (PTCa and OCPa) with resorcinol. However, the intensity of the diffraction peaks after adsorption is apparently lower than that of the initial phosphate (PTCa and OCPa) peaks, indicating a decrease in crystallinity following resorcinol adsorption. These reductions in crystallinity may be attributed to the incorporation of phenols into the micropores and macropores of the studied phosphates.

CONCLUSIONS

The adsorption behavior of resorcinol onto artificial calcium phosphate compounds more especially, PTCa and OCPa was the main focus of this investigation. The results show that both materials have notable resorcinol adsorption capabilities, and that variables like pH, temperature, adsorbent dosage, and the adsorption process is affected by the initial resorcinol concentration. Both the Freundlich and Langmuir models provided a good description of the resorcinol adsorption isotherms. However, the Langmuir model fit the data better, indicating that monolayer adsorption takes place on the adsorbents' surface. PTCa has a greater capacity for removing resorcinol, as evidenced by the highest adsorption capacities of 13.27 mg/g for PTCa and 5.05 mg/g for OCPa.

Kinetic investigations revealed that the adsorption of resorcinol onto PTCa and OCPa followed pseudo-second-order kinetics, indicating that chemisorption plays a significant role in the process. Additionally, thermodynamic simulations showed that the adsorption process is exothermic and spontaneous, with negative values for Gibbs free energy (ΔG) and enthalpy (ΔH). These results suggest that the physical factors governing adsorption, such as hydrogen bonds and van der Waals interactions, predominate, particularly at lower temperatures.

Based on the results of the investigation, PTCa and OCPa may be effective adsorbents for removing resorcinol from aqueous solutions. They are promising materials for use in water treatment technologies because of their high adsorption capabilities, advantageous kinetic and thermodynamic properties, and adaptability to different environmental situations. To further prove these adsorbents' practicality in environmental remediation initiatives, future studies should examine their regeneration and reuse as well as their utilization in actual wastewater systems.

REFERENCES

- Adam, O. (2016). Removal of resorcinol from aqueous solution by activated carbon: Isotherms, thermodynamics and kinetics. *American Chemical Science Journal, 16*(1), 1–13. https://doi.org/10.9734/ acsj/2016/27637
- Agarwal, S., Rani, A. (2017). Adsorption of resorcinol from aqueous solution onto CTAB/NaOH/flyash composites: Equilibrium, kinetics and thermodynamics. *Journal of Environmental Chemical Engineering*, 5(1), 526–538. https://doi.org/10.1016/j. jece.2016.11.035
- Aksu, Z. (2005). Application of biosorption for the removal of organic pollutants: A review. In *Process Biochemistry* 40(3–4), 997–1026. https://doi. org/10.1016/j.procbio.2004.04.008
- 4. Anku, W. W., Mamo, M.A., Govender, P.P. 2017. Phenolic compounds in water: sources, reactivity,

toxicity and treatment methods. In Phenolic Compounds - Natural Sources, Importance and Applications. *InTech*. https://doi.org/10.5772/66927

- Bouyarmane et al. (2014). Etude des processus d'adsorption et de photodégradation des polluants organiques supportés sur les composites TiO2-Apatite (Thèse de Doctorat). Université Mohamed V, Rabat, Maroc.
- Demirbas, A., Sari, A., Isildak, O. (2006). Adsorption thermodynamics of stearic acid onto bentonite. *Journal of Hazardous Materials*, 135(1–3), 226–231. https://doi.org/10.1016/j.jhazmat.2005.11.056
- 7. El Asri. (2009). *Nouveaux matériaux de structure apatite préparés à partir du phosphate naturel marocain à applications environnementales* (Thèse de Doctorat). Université Mohamed V, Rabat, Maroc
- El Bakri, A., El Boujaady, H., Ferraa, N., Bennani-Ziatni, M. (2024a). The removal of phenol through adsorption onto synthetic calcium phosphates – a study encompassing analyses of kinetics and thermodynamics. *Ecological Engineering and Environmental Technology*, 25(4), 301–315. https://doi. org/10.12912/27197050/184155
- El Bakri, A., Ferraa, N., Rhilassi, A. El, Bennani-Ziatni, M. (2024b). Resorcinol elimination through adsorption onto synthetic calcium phosphates: investigations into kinetics and thermodynamics. In *International Journal of Chemical and Biochemical Sciences (IJCBS) 25*(13). www.iscientific.org/ Journal.html
- El Boujaady, H., El Rhilassi, A., Bennani-Ziatni, M., El Hamri, R., Taitai, A., Lacout, J. L. (2011). Removal of a textile dye by adsorption on synthetic calcium phosphates. In *Desalination* 275(1–3), 10–16. https://doi.org/10.1016/j.desal.2011.03.036
- 11. El Boujaady, H., Mourabet, M., Bennani-Ziatni, M., Taitai, A. (2014). Adsorption/desorption of Direct Yellow 28 on apatitic phosphate: Mechanism, kinetic and thermodynamic studies. *Journal of the Association of Arab Universities for Basic and Applied Sciences, 16*, 64–73. https://doi.org/10.1016/j. jaubas.2013.09.001
- 12. El Boujaady, H., Mourabet, M., El Rhilassi, A., Bennani-Ziatni, M., El Hamri, R., Taitai, A. (2017). Interaction of adsorption of reactive yellow 4 from aqueous solutions onto synthesized calcium phosphate. *Journal of Saudi Chemical Society*, 21, 94– 100. https://doi.org/10.1016/j.jscs.2013.10.009
- 13. El Rhilassi, A., Mourabet, M., El Boujaady, H., Bennani-Ziatni, M., Hamri, R. El, Taitai, A. (2012). Adsorption and release of amino acids mixture onto apatitic calcium phosphates analogous to bone mineral. *Applied Surface Science*, 259, 376–384. https:// doi.org/10.1016/j.apsusc.2012.07.055
- 14. Farhan Hanafi, M., Sapawe, N. (2020). A review on the water problem associate with organic pollutants

derived from phenol, methyl orange, and remazol brilliant blue dyes. *Materials Today: Proceedings*, *31*, A141–A150. https://doi.org/10.1016/j. matpr.2021.01.258

- 15. Fiamegos, Y., Stalikas, C., Pilidis, G. (2002). 4-Aminoantipyrine spectrophotometric method of phenol analysis Study of the reaction products via liquid chromatography with diode-array and mass spectrometric detection. In *Analytica Chimica Acta* 467.
- 16. Freundlich, H. (1926). *Colloid and Capillary Chem*¬*istry*, Methuen, London.
- 17. Guo, Y., Zhu, Z., Qiu, Y., Zhao, J. (2013). Enhanced adsorption of acid brown 14 dye on calcined Mg/ Fe layered double hydroxide with memory effect. *Chemical Engineering Journal*, 219, 69–77. https:// doi.org/10.1016/j.cej.2012.12.084
- 18. Hejazi, F., Ghoreyshi, A.A., Rahimnejad, M. (2019). Simultaneous phenol removal and electricity generation using a hybrid granular activated carbon adsorption-biodegradation process in a batch recycled tubular microbial fuel cell. *Biomass* and *Bioenergy*, 129. https://doi.org/10.1016/j. biombioe.2019.105336
- 19. Iftikhar, T., Asif, M., Aziz, A., Ashraf, G., Jun, S., Li, G., Liu, H. (2021). Topical advances in nanomaterials based electrochemical sensors for resorcinol detection. In *Trends in Environmental Analytical Chemistry 31*. Elsevier B.V. https://doi. org/10.1016/j.teac.2021.e00138
- Lagergren, S. (1898). About the theory of so called ad¬sorption of soluble substances, S. Vetenskapsakad, Hand. *Band*, 24(4), 1–39.
- 21. Langmuir, Irving, B. (1916). The evaporation, con¬densation and reflection of molecules and the mech¬anism of adsorption.
- 22. Li, Q., Yu, H., Song, J., Pan, X., Liu, J., Wang, Y., Tang, L. (2014). Synthesis of SBA-15/polyaniline mesoporous composite for removal of resorcinol from aqueous solution. *Applied Surface Science, 290*, 260–266. https://doi.org/10.1016/j. apsusc.2013.11.065
- 23. Lian, Q., Islam, F., Ahmad, Z. U., Lei, X., Depan, D., Zappi, M., Gang, D. D., Holmes, W., & Yan, H. (2021). Enhanced adsorption of resorcinol onto phosphate functionalized graphene oxide synthesized via Arbuzov Reaction: A proposed mechanism of hydrogen bonding and π-π interactions. *Chemosphere*, 280. https://doi.org/10.1016/j. chemosphere.2021.130730
- 24. Lian, Q., Konggidinata, M.I., Ahmad, Z.U., Gang, D.D., Yao, L., Subramaniam, R., Revellame, E., Holmes, W.B., Zappi, M. (2019). Combined effects of textural and surface properties of modified ordered mesoporous carbon (OMC) on BTEX adsorption. *Journal of Hazardous Materials*, 377, 381– 390. https://doi.org/10.1016/j.jhazmat.2019.05.079

- 25. Lian, Q., Yao, L., Uddin Ahmad, Z., Gang, D. D., Konggidinata, M. I., Gallo, A. A., & Zappi, M. E. (2020). Enhanced Pb(II) adsorption onto functionalized ordered mesoporous carbon (OMC) from aqueous solutions: the important role of surface property and adsorption mechanism. *Environmental Science and Pollution Research*, 27(19), 23616–23630. https://doi.org/10.1007/s11356-020-08487-9
- 26. Lin, K., Pan, J., Chen, Y., Cheng, R., Xu, X. (2009). Study the adsorption of phenol from aqueous solution on hydroxyapatite nanopowders. *Journal of Hazardous Materials*, 161(1), 231–240. https://doi. org/10.1016/j.jhazmat.2008.03.076
- Mahmoodi, N. M., Hayati, B., Arami, M., Lan, C. (2011). Adsorption of textile dyes on Pine Cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies. *Desalination*, 268(1–3), 117– 125. https://doi.org/10.1016/j.desal.2010.10.007
- McQuillan, R. V., Stevens, G. W., Mumford, K. A. (2018). The electrochemical regeneration of granular activated carbons: A review. In *Journal of Hazardous Materials* 355, 34–49. Elsevier B.V. https:// doi.org/10.1016/j.jhazmat.2018.04.079
- 29. Mousa, Mohammad. 2009. *Removal of various aromatic compounds from synthetic and refinery wastewater using soybean peroxidase*. Library and Archives Canada = Bibliothèque et Archives Canada.
- 30. Nawaz, T., Sengupta, S. (2019). Contaminants of Emerging Concern: Occurrence, Fate, and Remediation. In Advances in Water Purification Techniques: Meeting the Needs of Developed and Developing Countries, 67–114. Elsevier. https://doi. org/10.1016/B978-0-12-814790-0.00004-1
- 31. Norwitz, G., Bardsley, A.H., Keliher, P.N. (1981). Determination of Phenol in the Presence of Sulfite (Sulfur Dioxide) by the Aminoantipyrine Pectro¬photometric Method. *Analytica Chimica Acta*, 128, 251–256.
- 32. Nouacer, S. (2015). Application des tiges de dattes dans l'adsorption de métaux toxiques de l'eau (Thèse de Doctorat). Université Badi Mokhtar, Anaba, Algerie.
- 33. Oliver. (2011). Intensification of Activated Sludge Process – the Impact of Ozone and Activated Carbon (Thèse de Doctorat). Tallinn University of Technology, Ehitajate tee 5, Tallinn, Estonia
- 34. Rodríguez, E., Encinas, A., Masa, F.J., Beltrán, F.J. (2008). Influence of resorcinol chemical oxidation on the removal of resulting organic carbon by activated carbon adsorption. *Chemosphere*, 70(8), 1366–1374. https://doi.org/10.1016/j. chemosphere.2007.09.035
- Salvador, F., Martin-Sanchez, N., Sanchez-Hernandez, R., Sanchez-Montero, M.J., Izquierdo, C. (2015). Regeneration of carbonaceous adsorbents. Part I: Thermal Regeneration. In *Microporous and*

Mesoporous Materials 202, 259–276. Elsevier. https://doi.org/10.1016/j.micromeso.2014.02.045

- Schrör, J.-P., & Moers, A. (2018). The endophytic fungus Stemphylium globuliferum – secondary metabolites and biological activities.
- 37. Subramanyam, R., & Mishra, I. M. (2013). Critical Review of Anaerobic Biodegradation of Benzenediols: Catechol, Resorcinol, and Hydroquinone. https://doi.org/10.1061/(ASCE)HZ
- 38. Sun, J., Liu, X., Zhang, F., Zhou, J., Wu, J., Alsaedi, A., Hayat, T., & Li, J. (2019). Insight into the mechanism of adsorption of phenol and resorcinol on activated carbons with different oxidation degrees. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 563, 22–30. https://doi. org/10.1016/j.colsurfa.2018.11.042
- 39. Suresh, S., Srivastava, V. C., & Mishra, I. M. (2012). Adsorption of catechol, resorcinol, hydroquinone, and their derivatives: A review. In International Journal of Energy and Environmental Engineering (Vol. 3, Issue 1). Springer Verlag. https://doi. org/10.1186/2251-6832-3-32
- 40. Sylvie Lacombe et Thu-Hoa Tran-Thi 2007. La photocatalyse pour l'élimination des polluants. L'actualité chimique, n° 308-309 79.
- 41. Tang, W., Huang, H., Gao, Y., Liu, X., Yang, X., Ni, H., & Zhang, J. (2015). Preparation of a novel porous adsorption material from coal slag and its adsorption properties of phenol from aqueous solution. *Materials and Design*, 88, 1191–1200. https:// doi.org/10.1016/j.matdes.2015.09.079
- 42. Thakur, K., & Kandasubramanian, B. (2019). Graphene and graphene oxide-based composites for

removal of organic pollutants: a review. In *Journal of Chemical and Engineering Data 64*(3), 833–867. American Chemical Society. https://doi. org/10.1021/acs.jced.8b01057

- 43. Wang, S., Li, H., Xie, S., Liu, S., & Xu, L. (2006). Physical and chemical regeneration of zeolitic adsorbents for dye removal in wastewater treatment. *Chemosphere*, 65(1), 82–87. https://doi. org/10.1016/j.chemosphere.2006.02.043
- 44. Wang, T., Xu, Z. Y., Wu, L. G., Li, B. R., Chen, M. X., Xue, S. Y., Zhu, Y. C., & Cai, J. (2017). Enhanced photocatalytic activity for degrading phenol in seawater by TiO2-based catalysts under weak light irradiation. *RSC Advances*, 7(51), 31921–31929. https://doi.org/10.1039/c7ra04732k
- 45. Weber, B., Chavez, A., Morales-Mejia, J., Eichenauer, S., Stadlbauer, E. A., & Almanza, R. (2015). Wet air oxidation of resorcinol as a model treatment for refractory organics in wastewaters from the wood processing industry. *Journal of Environmental Management*, 161, 137–143. https://doi.org/10.1016/j.jenvman.2015.06.046
- 46. Yan, X., Li, Y., Hu, X., Feng, R., Zhou, M., & Han, D. (2021). Enhanced adsorption of phenol from aqueous solution by carbonized trace ZIF-8-decorated activated carbon pellets. *Chinese Journal of Chemical Engineering*, 33, 279–285. https://doi. org/10.1016/j.cjche.2020.06.027
- 47. Yon Oepen, B., K6rdel, W., & Klein, W. (1991). Sorption of Nonpolar and Polar Compounds to Soils: Processes, Measurements and Experience with the Applicability of the Modified OECD-Guideline 106, 22.