

Adsorption isotherm, kinetic and mechanism studies of 2-nitrophenol on sedimentary phosphate

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Abstract: Sedimentary phosphate (SP) was used as an adsorbent for the removal of 2-nitrophenol from aqueous solutions in an attempt to investigate (the feasibility of) its application (to) in wastewater purification. The adsorbent was characterized by X-ray diffraction (XRD), IR spectroscopy, Fluorescence X and BET. The results indicated that the SP (was) is francolite ($\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3\cdot 6\text{H}_2\text{O}$) and mesoporous. The effect of the adsorption time and the pH of the solution were studied. The pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to fit adsorption data in the kinetic studies. The equilibrium isotherms were determined using the Langmuir, Freundlich and Dubinin-Radushkevich models. The results show that the Dubinin-Radushkevich isotherm had better agreement with the 2-nitrophenol adsorption on SP with a correlation coefficient of 0.98, an equilibrium adsorption capacity of 633 mg. g⁻¹ and a corresponding contact time of 2 h. The results imply that intraparticle diffusion could be summarized as the basic rate-controlling mechanisms during 2-nitrophenol adsorption on SP.

Keywords: Sedimentary phosphate; Adsorption; Organic matter; 2-Nitrophenol; Environment.

Introduction

Phenolic compounds are typical pollutants in wastewater and are generated from various industries, such as petroleum refineries and steel foundries. Phenols are known to be moderately or highly toxic at low concentrations to plants, fish and many other organisms, and their presence in natural waters can lead to the formation of substituted compounds during disinfection and oxidation processes. These substances have been categorized as priority pollutants by the US Environmental Protection Agency (USEPA) and must be eliminated with a specific treatment; most importantly, they cannot be naturally degraded in the environment¹.

Various processes have been utilized for the removal of pollutants from wastewater including photocatalytic oxidation, sonochemical degradation, electrochemical degradation and adsorption. Among these methods adsorption is still the most widely used, since it can effectively remove many types of pollutants²⁻⁵. Sedimentary phosphate (SP) is an important natural resource in Morocco and must be valorized. SP includes more than two hundred mineralogical species that are used not only as fertilizers but also in laboratory, especially as

catalysts (either alone or conveniently modified) in a wide range of organic reactions⁶ and as adsorbent to remove metals (Pb^{2+} , Zn^{2+} , Cu^{2+} , and Cd^{2+}) from wastewater⁷⁻¹⁰. Others studies have shown the ability of natural or modified phosphate to adsorb those metals¹¹.

This study aims to evaluate the adsorption capacity of SP as an alternative adsorbent to remove 2-nitrophenol from the aqueous phase and to elucidate the mechanism of the proposed process.

The adsorption of 2-nitrophenol onto SP was systematically investigated. For example, we studied the effect of contact time, the initial concentration of 2-nitrophenol and the initial solution pH on 2-nitrophenol adsorption. The equilibrium and kinetics of the adsorption process were thoroughly studied.

Materials and Methods

Characterization of SP

The structure of SP was identified using X-ray powder diffraction (XRD) (Bruker D8 Focus diffractometer). Infrared spectra were recorded from 400 to 4000 cm⁻¹ on a Fourier transform spectrometer (Nicolet 380) using pellets of KBr and

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natural phosphate (NP). The nitrogen adsorption isotherm was measured using a Micromeritics ASAP 2020 volumetric adsorption analyzer. The specific surface area of SP was calculated according to the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption isotherm data in the relative pressure range from 0.05 to 0.25.

Adsorption Experiments

Batch adsorption experiments were conducted using 100 mL Erlenmeyer flasks with the addition of SP and a 2-nitrophenol solution at a shaking speed of 150 rpm while maintaining at a constant temperature. Kinetic experiments were performed by mixing 0.05 g of SP into 50 mL 2-nitrophenol solution with a known concentration 100, 150 and 200 mg L⁻¹ at 25 °C ± 1 for 3 h. Then, the suspension was filtered. The adsorbate concentrations were determined by a UV-Visible 2450 SHIMADZU spectrophotometer at 351 nm. The amount of 2-nitrophenol adsorbed per unit mass onto SP was calculated according to Eq (1):

$$q = V(C_0 - C_f)/m \quad (1)$$

Where C_0 and C_f are the initial and final (after adsorption) concentrations of the 2-nitrophenol solution (mg L⁻¹), respectively. V is the volume of the 2-nitrophenol solution (L), and m (g) represents the mass of SP.

To study the effect of initial solution pH, the various solution of 2-nitrophenol was adjusted to values over the range of 2 to 8 by dropwise addition

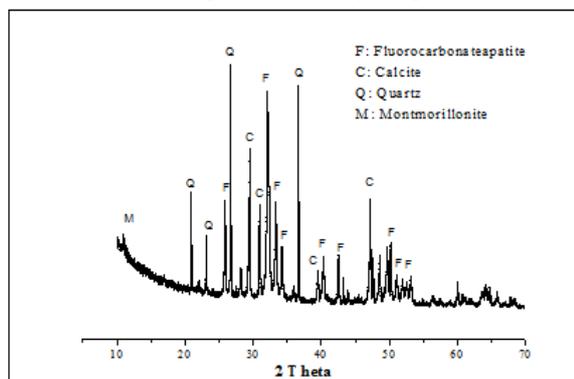


Figure 1. XRD patterns of the sedimentary phosphate.

The chemical composition of SP is P₂O₅ (27.8%), CaO (51.9%), SiO₂ (2.70), F (6.08%), Na₂O (0.47%), Fe₂O₃ (0.19), Al₂O₃ (0.35%), MgO (0.68%), SO₃ (1.67%) and K₂O (0.048%). It is worth noting that other metals (i.e., Zn, Cr) were detected in the range of ppm.

The specific surface area (13.69 m² g⁻¹) was calculated by the Brunauer-Emmett-Teller (BET) method using adsorption data. The isotherm plot is type IV according to Brunauer's classification with a

of 0.1 M HCl or 0.1 M of NaOH.

To study the adsorption isotherm, 0.05 g of SP was added to 50 mL of 2-nitrophenol solutions of different concentrations (62.5-1000 mg L⁻¹) under natural pH (close to 6) conditions and at 25 °C ± 1 for 2 h.

Results and Discussion

Natural phosphate characterization

The SP was extracted from a Gantour deposit (Morocco). After washing with water, the fraction of phosphate rock particles with the size between 100 and 400 μm was used. It was then dried overnight at 105 °C and crushed to obtain the phosphate support having sizes under 125 μm. The X-ray diffraction pattern (Fig. 1) showed that the mineralogy of SP is similar to that of francolite (Ca₁₀(PO₄CO₃)₆F₂), the most widely prevalent mineral belonging to the family of apatite. IR analysis was performed by preparing the pellet from the mixture of 0.01 g sample and 0.09 g KBr to gain information on the nature of the functional groups and the molecular bonds of the sample. The bands of the phosphate group are located at 1053, 624, and 574 cm⁻¹, whereas those of carbonate compounds are at 1432 and 864 cm⁻¹. The hydroxyl stretching vibration frequency is observed at 3417 cm⁻¹ and 3369 cm⁻¹ for SP before and after adsorption, respectively (Fig. 2). In SP, the oxygen atom bond acts as a hydrogen bond acceptor, which tends to form a bond with the OH portion of 2-nitrophenol.

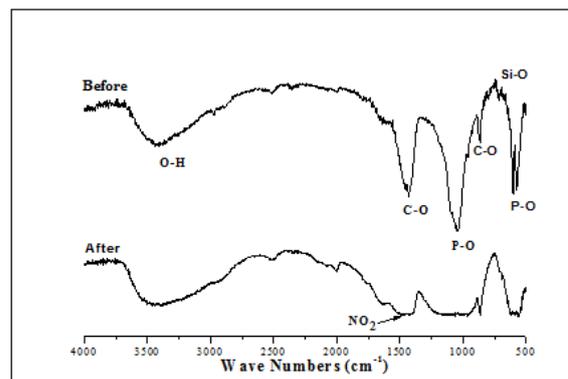


Figure 2. FTIR spectra of the sedimentary phosphate.

hysteresis loop (type H3) in the relative pressure range from 0.7 to 1, implying the presence of mesopore structures in the SP. Whereas the total pore volume (0.023 cm³.g⁻¹) and pore size distribution of SP centred at 1-2, 4-5 and 7-8 nm were estimated using the Barret-Joyner-Halenda (BJH) approximation.

As shown in Fig.3, MEB studies indicated that materials consist of irregular pores. The particles exhibit dimensions well below 20 μm.

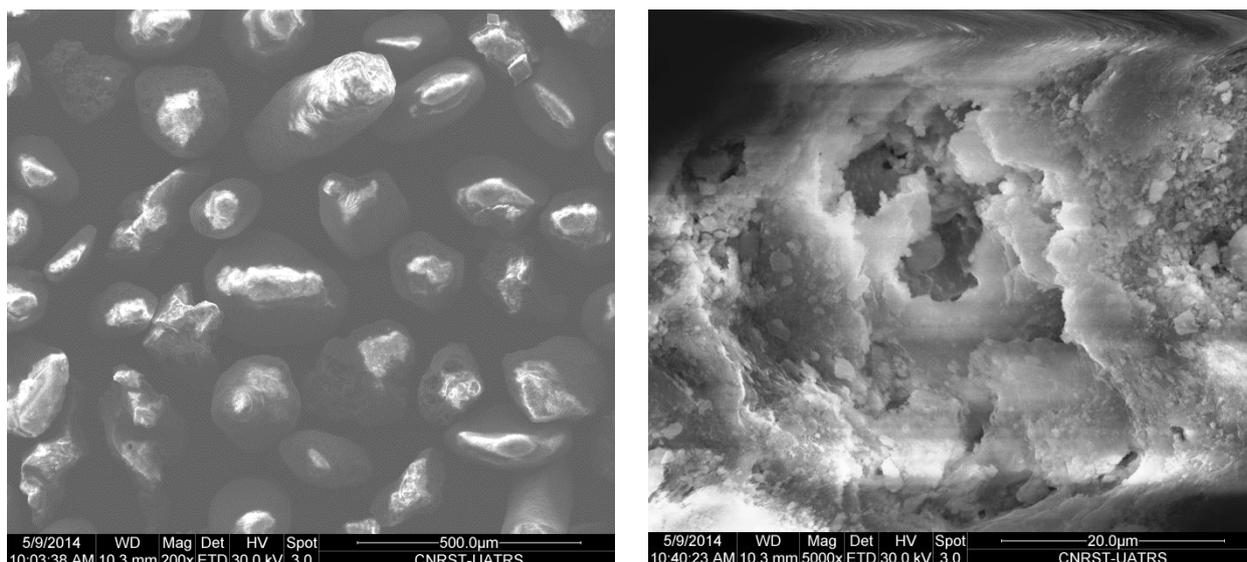


Figure 3. The MEB images of sedimentary phosphate.

Adsorption kinetics and isotherms

Effect of contact time, concentration and adsorption kinetics

The results of the adsorption of 2-nitrophenol onto SP at different concentrations are shown in Fig. 4.

For 200 mg L⁻¹, the uptake of 2-nitrophenol by SP reaches the adsorption equilibrium in approximately 6 min (109.95 mg g⁻¹).

For 150 mg L⁻¹ and 100 mg L⁻¹, the adsorption

capacity increased rapidly (80.55 and 25.02 mg g⁻¹ in 5 and 10 min, respectively). After this initial fast adsorption period, the uptake of 2-nitrophenol was much slower and became nearly constant without further changes within 2 h (93.62 and 35.37 mg g⁻¹, respectively).

It was observed that the amount of 2-nitrophenol adsorbed increased from 35.37 to 80.55 and 109.95 mg g⁻¹ with an increase in the initial adsorbate concentration from 100 to 200 mg L⁻¹.

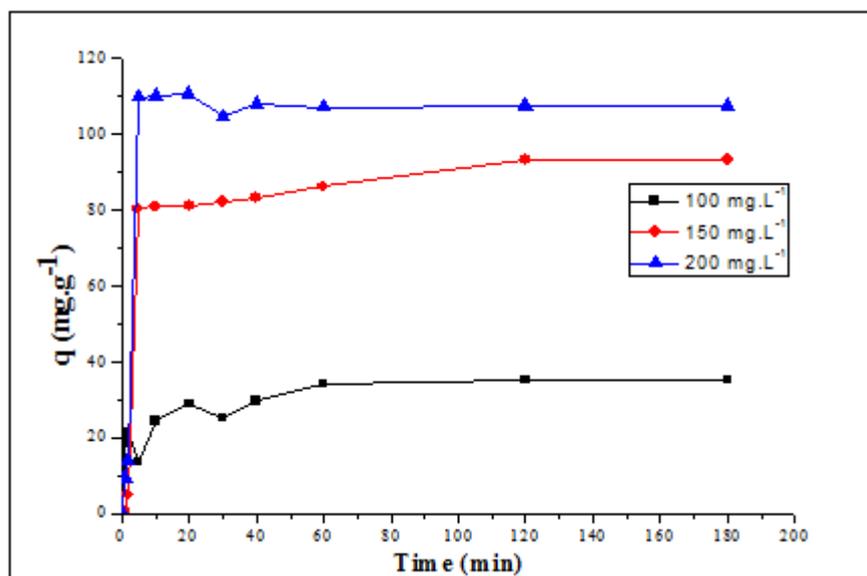


Figure 4. Kinetic study of the adsorption of 2-nitrophenol onto SP at different concentrations.

Effect of pH

Experiments were conducted using an initial concentration of 100 mg L⁻¹ and 2-nitrophenol uptake was investigated changing pH values 2, 4, 6 and 8.

The effect of the pH of the aqueous solution in the adsorption process can be attributed to the dependency of phenol ionization at different pH

values. The ratio of phenolate anion can be calculated as follows:

$$\phi_{\text{phenolate}} = [1 + 10^{(\text{pK}_a - \text{pH})}]^{-1} \quad (2)$$

From Eq (2) and with $pK_a = 7.23$, $\phi_{\text{phenolate}}$ increases as the pH value increases, and these results

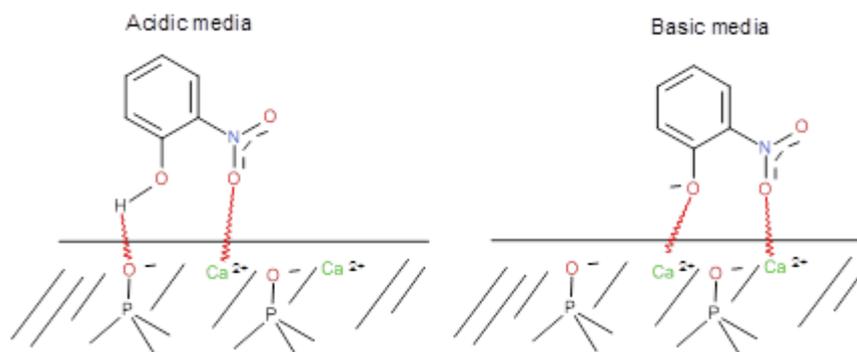


Figure 5. Schematic representation of the interactions between 2-nitrophenol and SP at different pH values.

At an acidic pH, 2-nitrophenol molecules are mostly neutral, and in this case, we observe a strong H-bonding interaction between the SP surface dominated by a negative charge with the oxygen atom O⁻ and H of 2-nitrophenol, which explains the increase in adsorption. Other weak interactions probably occur between substrate and solid as NO₂ and Ca²⁺.

At a basic pH, phenolate anions are formed by the dissociation of 2-nitrophenol. Thus, the strong H-bonding interaction between the oxygen atom of SP and the H of 2-nitrophenol is lost, hence lowering the adsorption capacity.

In general, the adsorption of 2-nitrophenol is much higher at low pH values than at high ones. This has been reported in many studies on the adsorption of phenols and nitrophenols on different adsorbents¹²⁻¹⁴. We can conclude that pH is an important factor affecting this adsorption.

Kinetic adsorption

The adsorption kinetics studies are thoroughly performed because of their importance in the investigation of the adsorption rate and mechanism. The pseudo-first-order and pseudo-second-order kinetic models are employed to fit experimental data obtained from the kinetics experiments. These two models can be expressed in a linear form as Eqs (3) and (4)¹⁵:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (3)$$

can explain the interaction between 2-nitrophenol and SP, as demonstrated in Fig.5.

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

Where q_t and q_e (mg g⁻¹) are the amounts of 2-nitrophenol adsorbed at any time (min) and at equilibrium, respectively. K_1 (min⁻¹) and K_2 (g mg⁻¹ min⁻¹) are the pseudo-first-order and pseudo-second-order model rate constants, respectively. The correlation coefficients (R^2), K_1 , K_2 and calculated $q_{e,cal}$ values are shown in Table 1.

The $q_{e,cal}$ of the pseudo-first-order model is 3.713 mg g⁻¹, and R^2 is 0.813. However, the $q_{e,cal}$ of the pseudo-second-order model is 38.461 mg g⁻¹, and R^2 is 0.961, suggesting that 2-nitrophenol adsorption onto the SP is according to the pseudo-second-order kinetic models.

Weber's intraparticle diffusion model is used to further identify the steps of the adsorption process. It can be expressed according to Eq (5)¹⁵:

$$q_t = k_i t_{1/2} + C \quad (5)$$

Where k_i (mg·g⁻¹ min^{-1/2}) is the rate constant of intraparticle diffusion, and C (mg g⁻¹) is the intercept and is a constant related to the thickness of the boundary layer. A plot of q_t versus $t_{1/2}$ should be a straight line with a slope k_i and intercept C when the adsorption mechanism follows the intraparticle diffusion process.

Table 1. Kinetic models for 2-nitrophenol adsorption onto the SP.

Models	Equation	Models Parameters	R^2
Pseudo-first order	$y = -0.013x + 1.312$	$q_{e,cal} = 3.713 \text{ mg g}^{-1}$ $K_1 = 0.013 \text{ min}^{-1}$	0.813
Pseudo-second order	$y = 0,026x + 0.263$	$q_{e,cal} = 38.461 \text{ mg g}^{-1}$ $K_2 = 0.098 \text{ min}^{-1}$	0.961
Intra-particule diffusion	$y = 3,072x + 7,940$	$K_i = 3.07 \text{ mg g}^{-1} \text{ min}^{-1/2}$ $C = 7.94 \text{ mg g}^{-1}$	0.780

There is no point passing through the origin. This indicates that although intraparticle diffusion was

involved in the adsorption process, it was not the sole rate-controlling step. This also confirms that the

adsorption of 2-nitrophenol on SP was a multi-step process involving adsorption on the external surface and diffusion into the interior¹⁵. It can be seen in Table 1 that other adsorption mechanisms along with diffusion contribute to the interactions between the 2-nitrophenol molecules and SP particles.

Considering these results, the kinetics of 2-nitrophenol adsorption on SP can be described in the order of fitting the pseudo-second-order which explains the chemisorption due to the hydrogen bond of 2-nitrophenol and the active functional groups present in the support confirmed by pH effect.

Adsorption isotherms

Adsorption isotherm represents the amount of material bound at the surface (the sorbate) as a function of the material present in the gas phase

and/or in the solution.

As classified in the Giles article¹⁶, the adsorption equilibrium data obtained for 2-nitrophenol, as shown in Fig. 6, are classified in the S1 curve. This one indicates the vertical orientation of adsorbed molecules at the surface.

It is shown in the same figure that the adsorption becomes more favorable as the concentration increases. In the initial part of this S1 curve, the concentration of solute is low which indicates that the solvent molecules compete with solute molecules for the adsorption sites. When some of solute molecules were adsorbed, they can improve the adsorption of solute molecules by side-by-side association, helping to hold them to the surface. This has been called co-operative adsorption¹⁶.

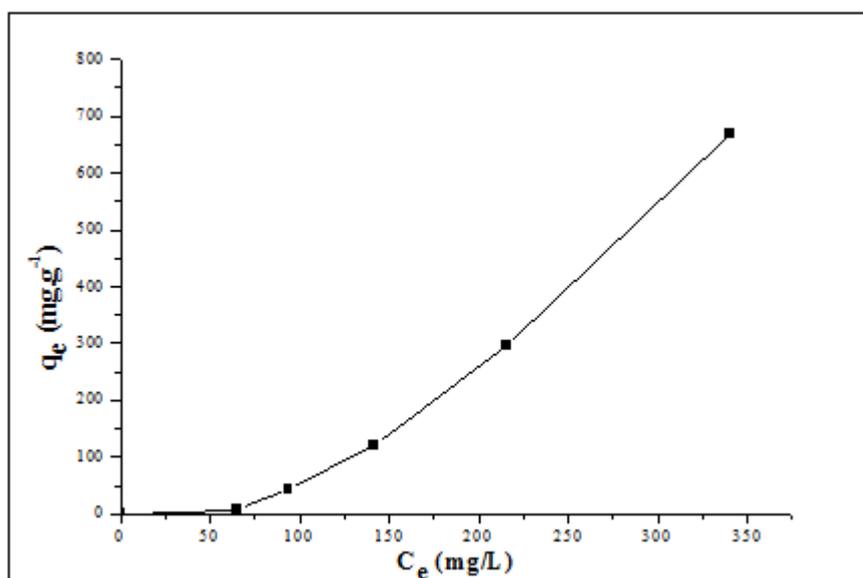


Figure 6. Sorption isotherm of 2-nitrophenol onto SP.

This curve shows that the molecule is monofunctional because the 2-nitrophenol attraction arises from its hydroxyl group, which is at the end of the molecule, and the intermolecular attraction array is in the adsorbed layer, presenting a strong competition from the 2-nitrophenol molecules for substrate sites.

The adsorption isotherm models of Langmuir, Freundlich, and Dubinin–Radushkevich are described below.

Langmuir isotherm

The Langmuir adsorption isotherm⁷ is based on the concept that solid surfaces have finite adsorption sites. When all of the adsorption sites are filled, the surface will no longer be able to adsorb solute from the solution. The Langmuir equilibrium equation is shown in Eq (6):

$$C_e/q = 1/b \cdot q_{\max} + C_e/q_{\max} \quad (6)$$

where C_e (mg L⁻¹) is the equilibrium concentration, q (mg g⁻¹) is the amount of adsorption per unit mass of SP at equilibrium, q_{\max} is the amount of adsorbate adsorbed per unit mass of SP, corresponding to complete monolayer coverage, and b is the Langmuir constant, which can be considered a measure of adsorption energy. A linear plot of C_e/q against C_e is used to give the values of q_{\max} and b from the slope and intercept of the plot, respectively.

The very low ($R^2 = 0.318$) correlation coefficient for 2-nitrophenol indicating a poor mathematical fit shows that the removal of 2-nitrophenol does not follow the Langmuir mode with $q_{\max} = 17.54$ mg g⁻¹ (Table.2). We can deduce from this model that the adsorbent has more than one type of site (micropores, macropores and mesopores) on the SP surface with heterogeneous distribution.

Table 2. Isotherms parameters models for 2-nitrophenol adsorption onto the SP.

Models	Equation	Models Parameters	R ²
Langmuir	$y = -0,057x + 16,10$	$b = 3.54 \cdot 10^{-3} \text{ L mg}^{-1}$ $q_{max} = 17.54 \text{ mg g}^{-1}$	0.318
Freundlich	$y = 3,152x - 11,37$	$n = 0.317$ $K_f = 1.15 \cdot 10^{-5} \text{ L g}^{-1}$	0.871
Dubinin Radushkevich	$y = -0,004x + 6,451$	$B = 0.004 \text{ mol}^2 \text{ kJ}^{-2}$ $q_s = 633.33 \text{ mg g}^{-1}$ $E = 11.18 \text{ kJ. mol}^{-1}$	0.980

Freundlich isotherm

In contrast to the Langmuir model, the Freundlich model assumes that the adsorbent surface energy is heterogeneous. It is assumed that the strongest binding sites are occupied first, and the binding strength decreases with the increasing degree of site occupation. The slope ranges between 0 and 1, which is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value approaches zero. The Freundlich adsorption isotherm expression is shown in Eqs (7) and (8) ⁷:

$$q_e = K_f x \frac{1}{n} C_e \quad (7)$$

$$\text{Ln}q_e = \text{Ln} K_f + \left(\frac{1}{n}\right) \text{Ln}C_e \quad (8)$$

Where K_f (L. g^{-1}) and n are Freundlich adsorption constants related to the adsorption capacity and intensity of the adsorbents, respectively. The constants were determined by the linear plot of $\text{Ln}q_e$ versus $\text{Ln}C_e$.

From Eq (8) and (Table.2), we can determine the constants of the Freundlich isotherm for the removal of 2-nitrophenol by SP with $R^2 = 0.871$.

The result obtained with the Freundlich isotherm is better than those obtained with the Langmuir model with intraparticle diffusion on SP. The weakness of these models is that they do not consider the possible competition between the interactions of several elements with the same site.

Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface and the characteristic porosity of the adsorbent. This model, which does not assume a homogenous surface or a constant adsorption potential as with the Langmuir model, was also applied to the analysis of the experimental data. The model has often successfully fitted high solute activities and the intermediate range of concentration data. The linear form of the Dubinin–Radushkevich isotherm is given in Eq (9):

$$\text{ln}(q_e) = \text{ln}(q_s) - (B_{DR} \varepsilon^2) \quad (9)$$

Where q_e = amount of adsorbate in the adsorbent at

equilibrium (mg g^{-1}), q_s = theoretical isotherm saturation capacity (mg g^{-1}), B_{DR} = Dubinin–Radushkevich isotherm constant ($\text{mol}^2 \text{ kJ}^{-2}$), and ε is the Polanyi potential. The approach was typically applied to distinguish the physical and chemical adsorption of ions with its mean free energy, E , per molecule of adsorbate (for removing a molecule from its location in the sorption space to infinity), which can be computed using the following relationship¹⁷:

$$E = \frac{1}{\sqrt{2B_{DR}}} \quad (10)$$

Where B_{DR} is denoted as the isotherm constant. Meanwhile, the parameter ε can be calculated as follows:

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (11)$$

Where R , T and C_e represent the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), absolute temperature (K) and adsorbate equilibrium concentration (mg L^{-1}), respectively. The constants were determined by the linear plot of $(\text{Ln}q_e)$ versus ε^2 .

From (Table.2), the constant q_s (633 mg g^{-1}) and B_{DR} ($0.004 \text{ mol}^2 \text{ kJ}^{-2}$) were determined from the appropriate plot ($R^2 = 0.98$) using Eq 9. The mean free energy, $E = 11.18 \text{ kJ mol}^{-1}$ indicates a chemical adsorption process. Therefore, the Dubinin–Radushkevich isotherm gives the best fit to the experimental data.

Adsorption mechanism

To understand SP / 2-nitrophenol interactions, the kinetic and isotherms results were developed.

Considering the Langmuir coefficient correlation ($R^2 = 0.318$), it assumes the following:

- Adsorption is not monolayer (the adsorbed layer is not one molecule in thickness);
- Adsorption cannot occur at a finite (fixed) number of definite localized sites that are identical and equivalent.
- It is possible to form a lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites.

Therefore, the Freundlich isotherm with $0.317 < n < 1$ confirms the intraparticle diffusion and the heterogeneous surface, which is in agreement with the Dubinin–Radushkevich isotherm.

From the kinetics according to Weber's intraparticle diffusion model and as shown in the effect of contact time, two stages are involved in the adsorption of 2-nitrophenol by SP, as follows:

- From the time 0 to 25 min during which the adsorption of 2-nitrophenol is on the external surface of SP, which is the instantaneous adsorption stage (film-diffusion);
- From 25 min to 2 h, which is characterized by the transport of 2-nitrophenol within the SP pores (particle diffusion) with a limited rate.

According to the BET and MEB analysis, the multi-layer adsorption on the SP and capillary condensation in the presence of an irregular surface are corroborated. We can suppose that the adsorption process on SP is controlled not only by the interaction with the surface (especially with a low specific area) but also the formation of an intrabond between SP and 2-nitrophenol, which explains the high adsorption capacity attained in the Dubinin-Radushkevich isotherm.

Therefore, the mechanism that can be proposed is that SP adsorbs 2-nitrophenol, forming a bond between the hydrogen of O-H and the polar oxygen sites on the SP surface and the oxygen of NO₂ with calcium on the SP surface, which explains the pH effect. A similar mechanism of interaction between 2-nitrophenol and other adsorbents has been shown by Kalayci (formation of hydrogen bonds)¹⁸ and Wahab (bond formation between the oxygen of NO₂ and calcium)¹⁹. In addition, the solvent effects can be considered in adsorption studies, and water molecules can be adsorbed on the surface oxygen groups by hydrogen bonding, which is unfavorable for the adsorption of 2-nitrophenol if some activate sites are occupied.

In general, the adsorption mechanism is complex, which might also involve other factors, such as the dispersive force¹⁹, temperature^{20, 21} and ion-exchange interactions¹⁹.

Conclusion

The present study leads to the following conclusions:

- The adsorption kinetics shows that the adsorption equilibrium is obtained in 2 h.
- The percentage removal increases with an increase in the initial 2-nitrophenol concentration.
- The adsorption of 2-nitrophenol decreases as the pH increases. The maximum removal obtained is at pH 2 and 4.
- The equilibrium data are tested using the Langmuir, Freundlich and Dubinin-Radushkevich isotherm models, and the best fit is obtained with the Dubinin-Radushkevich model.
- The pseudo-second-order kinetic model could better describe the adsorption kinetics, and the intraparticle diffusion model demonstrated that intraparticle diffusion is not the rate-limiting step.

The adsorbent system suggested in this study is simple, rapid, and inexpensive on a laboratory scale. These results reveal the natural phosphate, as well as other materials, as a potential adsorbent system suitable for the reduction of the content of nitrophenolic compounds in wastewater.

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