



Sulfate removal from water using TiO₂ nanoparticles

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ABSTRACT: In this study, titanium dioxide nanoparticles were used for the removal of sulfate ions. The initial properties of the nanoparticles before and after sulfate adsorption were examined using instrumental techniques. The effects of parameters such as concentration, pH, time, and temperature on sulfate removal were measured, and the optimal conditions for each parameter were applied in the adsorption isotherm. The calculation of thermodynamic constants revealed a negative ΔG° (free energy of gypsum), indicating a spontaneous reaction that does not require energy input. The ΔH° (enthalpy) of the reaction was positive, suggesting an endothermic nature of the removal process, while the positive ΔS° (entropy) indicated an increase in disorder during the reaction. The Freundlich and Langmuir isotherm models were fitted to the experimental data under optimal conditions, with the Langmuir isotherm equation providing a better fit with an R² value of 0.994. EDX analysis confirmed that the titanium dioxide nanoparticles primarily consisted of titanium and oxygen before sulfate adsorption, while sulfur was observed after adsorption, indicating surface adsorption of sulfate. Furthermore, the maximum adsorption capacity of titanium dioxide nanoparticles for sulfate was calculated as 10.24 mg/g based on the Langmuir equation. By comparing this adsorbent with others, it can be concluded that these nanoparticles are effective in sulfate removal from water.

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1- Introduction

Despite 70 percent of the Earth's surface being covered by water, less than one percent of it is suitable for human consumption. With this scarcity of freshwater resources, unfortunately, multiple human factors are constantly polluting this limited water volume. Among the wide range of mineral and organic pollutants, sulfate plays a significant role. Generally, sulfate removal processes include chemical precipitation, crystallization, cation exchange, biological treatments, membrane separation, electrodialysis, and surface adsorption [1]. Among these methods, surface adsorption has the advantage of being easy to use, highly efficient, cost-effective, and more selective [1]. Various adsorbents have been proposed for sulfate removal, including silica gel, zirconium, activated carbon, clays, and resins [2].

Titanium dioxide nanoparticles (TiO₂) are composed of very fine particles of titanium dioxide. These nanoparticles are used in many scientific and industrial fields due to their unique properties such as high specific surface area, high catalytic activity, light absorption, and strong electrochemical properties [3]. Titanium dioxide also has three crystal phases: anatase, rutile, and brookite. Two important properties of this material are its photocatalytic and surface adsorption

capabilities, which are utilized for pollutant removal, especially in water and wastewater treatment [4]. Nano-scale adsorbents have a large specific surface area due to their small size, providing ample surface sites for adsorption. However, there is limited research on nano-scale adsorbents for sulfate removal. The use of titanium dioxide nanoparticles for sulfate adsorption offers numerous advantages if successful. These materials exhibit high chemical stability and can be used over time without a significant reduction in their adsorption properties. Additionally, they can be recycled and reused, leading to resource efficiency. Furthermore, this sulfate adsorption method, utilizing nanoparticles with high adsorption capacity, allows for shorter contact times [3]. Therefore, considering the aforementioned points, this research was conducted with the following objectives:

1- Preliminary investigation of the ability of titanium dioxide (with an emphasis on surface adsorption) to remove sulfate by examining influential parameters such as nanoparticle concentration, solution pH, contact time, and temperature. This was performed on an aqueous solution with an initial concentration of 20 mg/l of sulfur (equivalent to 60 mg/l of sulfate).

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Table 1. Coefficients related to Freundlich and Langmuir models on sulfate adsorption

nano-particles	Freundlich constants			Langmuir constants		
	R ²	K _F	n	R ²	q _{max}	K _L
TiO ₂	0.973	0.178	0.718	0.994	10.24	0.028

2- Determination of the optimal adsorption conditions, conducting adsorption isotherms, and ultimately determining the adsorption capacity.

3- Utilization of instrumental methods to accurately characterize the properties of titanium dioxide particles (TiO₂) before and after sulfate adsorption. This characterization includes techniques such as XRD (X-ray diffraction), SEM-EDX (scanning electron microscopy-energy-dispersive X-ray spectroscopy), and BET (Brunauer-Emmett-Teller) analysis.

2- Materials and methods:

In this study, Merck Germany was used to prepare the potassium sulfate solution from potassium sulfate salt. Nano-sized titanium dioxide particles (Anatase-TiO₂) were obtained from Nabond China. The sulfate measurement was performed using the turbidity method with barium sulfate and a spectrophotometer at a wavelength of 480. Optimization experiments, consisting of four parameters (concentration, temperature, pH, and time), were conducted. The characterization of the nanoparticles was carried out using scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), and BET instrument. In the final stage, with the consideration of optimal conditions including 1 g/L adsorbent concentration, pH 3, 90 minutes contact time, and 20°C, sulfate adsorption isotherms were performed at concentrations of 0, 5, 10, 15, 20, and 25 mg/L. 0.125 g (1 g/L concentration) of the adsorbent was mixed with 25 mL of solutions with concentrations ranging from 0 to 25 mg/L at pH 3. Then, the mixture was incubated at 20 degrees Celsius for 90 minutes, and the sulfate adsorption capacity for titanium dioxide adsorbent was calculated. In this study, two main isotherm models, Freundlich and Langmuir, were used to describe the adsorption data and determine the adsorption capacity. The linear forms of these models are presented as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (1)$$

Where C_e is the equilibrium concentration of the solute in the solution (mg/L), q_e is the amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g), K_L is the Langmuir constant (L/g), and q_{\max} is the maximum adsorption capacity

(mg/g). The Langmuir model is applicable for homogeneous adsorption, and each molecule requires activation energy for adsorption.

The Freundlich equation is an empirical surface adsorption model. The linear form of the Freundlich equation is::

$$\text{Log}q_e = \text{Log}K_F + \frac{1}{n}\text{Log}C_e \quad (2)$$

Where C_e and q_e are the same as in the Langmuir equation, k_F and n are the Freundlich constants. In the Freundlich model, it is assumed that adsorption occurs in multiple layers, with a non-uniform distribution on heterogeneous surfaces..

To understand the dynamics of the removal reactions, kinetic information can be investigated. The study of adsorption kinetics is useful for predicting the adsorption rate for process design and modeling. In this study, pseudo-first-order and pseudo-second-order kinetic equations were used to study the kinetics of sulfate adsorption on titanium dioxide nanoparticles. The linear form of the pseudo-first-order equation is:

$$\text{Log}q_e - \left(\frac{K_1}{2.303} t \right) \text{Log} (q_e - q_t) = \quad (1)$$

q_e and q_t represent the adsorption capacity of sulfate at equilibrium and at the desired time, respectively (mg/g), and k_1 is the rate constant (min⁻¹). The linear form of the pseudo-second-order equation is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e} \right) t \quad (4)$$

In above Equation, k_2 is the pseudo-second-order rate constant (g/mg·min)

In equations, the parameters q_e and k_1 or k_2 can be determined from the slope and intercept of the linear plot of $\text{Log} (q_e - q_t)$ versus t or t/q_t versus t .

3- Results and discussion

The initial characteristics of nanoparticles before and after sulfate adsorption were investigated using XRD, SEM-EDX, and BET techniques. The impact of parameters such as adsorbent dosage, pH, time, and temperature on sulfate removal was measured. The maximum sulfate removal was achieved at a concentration of 1 g/L of adsorbent, resulting in 3.44 mg/g or 22.17%. Removal efficiency at pH 3 was 2.22 mg/g or 22.2%. At a contact time of 90 minutes, it was 4.25 mg/g or 42.5 %. As well as, the removal efficiency was 2.51 mg/g or 25.1 %, at a temperature of 20 °C. In the SEM analysis, the average size of titanium dioxide nanoparticles increased from 33.7 nm before sulfate adsorption to 48.3 nm after adsorption. The EDX analysis revealed that titanium and oxygen were the main elements present in the titanium dioxide nanoparticles before sulfate adsorption, while sulfur was observed after adsorption, indicating surface adsorption of sulfate. The specific surface area, average pore diameter, and pore volume of the titanium dioxide nanoparticles were determined by BET analysis as 45.4 m²/g, 22.3 nm, and 0.253 cm³/g, respectively.

Thermodynamic calculations showed a negative ΔG° value (free energy change), indicating the spontaneous nature of the adsorption reaction. The ΔH° value (enthalpy change) was positive, indicating an endothermic reaction and the ΔS° value (entropy change) was positive, indicating an increase in disorder during the reaction. Adsorption isotherms and isotherm models, including Freundlich and Langmuir, were used to determine the adsorption capacity of the titanium dioxide nanoparticles under optimal conditions. The data were fitted, and the Langmuir isotherm equation provided a better fit with a coefficient of determination (R^2) of 0.994, explaining the adsorption mechanism more effectively (Table 1).

4- Conclusion:

The maximum adsorption capacity of the titanium dioxide nanoparticles was calculated as 10.24 milligrams of sulfate (SO₄²⁻-S) per gram of adsorbent according to the Langmuir equation. Comparing this adsorbent with others, it can be concluded that these nanoparticles exhibit effective sulfate removal characteristics from water based on the mentioned properties.

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References

- [1] S. Mahdavi, Nano-TiO₂ modified with natural and chemical compounds as efficient adsorbents for the removal of Cd²⁺, Cu²⁺, and Ni²⁺ from water, *Clean technologies and environmental policy*, 18(1) (2016) 81-94.
- [2] H. Ma, M. Wang, J. Zhang, S. Sun, Preparation mechanism of spherical amorphous ZrO(OH)₂/AlOOH hybrid composite beads for adsorption removal of sulfate radical from water, *Materials Letters*, 247 (2019) 56-59.
- [3] K. Fialova, M. Motlochova, L. Cermakova, K. Novotna, J. Bacova, T. Rousar, J. Subrt, M. Pivokonsky, Removal of manganese by adsorption onto newly synthesized TiO₂-based adsorbent during drinking water treatment, *Environmental Technology*, 44(9) (2023) 1322-1333.
- [4] R. Djellabi, M.F. Ghorab, T. Sehili, Simultaneous removal of methylene blue and hexavalent chromium from water using TiO₂/Fe(III)/H₂O₂/sunlight, *CLEAN-Soil, Air, Water*, 45(6) (2017) 1500379.

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