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Sorption Potential of Different Forms of TiO₂ for the Removal of Two Anticancer Drugs from Water

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Abstract: Anticancer drugs pose a potential risk to the environment due to their significant consumption and biological effect even at low concentrations. They can leach into soils and sediments, wastewater, and eventually into drinking water supplies. Many conventional technologies with more effective advanced oxidation processes such as photocatalysis are being extensively studied to find an economical and environmentally friendly solution for the removal of impurities from wastewater as the main source of these pharmaceuticals. Since it is impossible to treat water by photocatalysis if there is no sorption of a contaminant on the photocatalyst, this work investigated the amount of imatinib and crizotinib sorbed from an aqueous medium to different forms of photocatalyst. In addition, based on the sorption affinity studied, the applicability of sorption as a simpler and less costly process was tested in general as a potential route to remove imatinib and crizotinib from water. Their sorption possibility was investigated determining the maximum of sorption, influence of pH, ionic strength, temperature, and sorbent dosage in form of the suspension and immobilized on the fiberglass mesh with only TiO₂ and in combination with TiO₂/carbon nanotubes. The sorption isotherm data fitted well the linear, Freundlich, and Langmuir model for both pharmaceuticals. An increasing trend of sorption coefficients Kₘ was observed in the pH range of 5–9 with CRZ, showing higher sorption affinity to all TiO₂ forms, which was supported by Kᵢ values higher than 116 (µg/g)/(mL/µg)¹/ₙ. The results also show a positive correlation between Kₘ and temperature as well as sorbent dosage for both pharmaceuticals, while CRZ sorbed less at higher salt concentration. The kinetic data were best described with a pseudo-second-order model (R² > 0.995).

Keywords: sorption process; imatinib; crizotinib; TiO₂ suspension; TiO₂ immobilized onto glass mesh; TiO₂/carbon nanotubes

1. Introduction

Environmental pollution is a ubiquitous problem that humanity has been dealing with for many years. When considering the impact of various factors on the environment, more and more attention is paid to pharmaceuticals. These are biologically active compounds used to treat and prevent diseases, alleviate of symptoms, etc., in human and veterinary medicine [1,2]. The modernization of technology and science has led to the promotion of quality of life through the increased production of medicines whose consumption is increasing every day [3]. Since information about their fate is still limited and there are no environmental laws, they can reach different sources in the environment and undergo processes, such as sorption, photolysis, hydrolysis or even biodegradation. These processes can often produce transformation or degradation products that are more toxic than the
parent compound. The fact that they are still present in the environment at low concentrations is not reassuring due to their unknown long-term effects on the aquatic and terrestrial world [1,4].

In addition to commonly studied classes of pharmaceuticals such as antibiotics [5–9], anticancer drugs are also a frequent research topic due to the increasing incidence of this disease and the potential carcinogenic, mutagenic, and teratogenic effects on the environment. They usually enter the environment as partially metabolized compounds via urine and feces discharged into municipal wastewater and hospitals [10,11]. Examples of such anticancer drugs include imatinib and crizotinib, tyrosine kinase inhibitors used to treat leukemia and lung cancer, respectively. Imatinib has been found in wastewater treatment plant (WWTP) effluent at concentrations ranging from 54 to 180 ng/L and is characterized as a highly persistent compound in water that does not degrade [12,13]. A similar fate is expected for crizotinib given the BIOWIN values calculated using the EPI Suite program (BIOWIN 3 = 1.0010, BIOWIN 5 = −0.4293, BIOWIN 7 = −0.3096). Moreover, these calculated modules predict the resistance of CRZ to biodegradation, aerobic and anaerobic, in terms of BIOWIN values of less than 0.5 [13]. Therefore, these two pharmaceuticals, along with other anticancer drugs, are not expected to be removed by conventional water treatment methods [14,15]. The development of advanced oxidation processes, as more efficient methods for the water treatment, is often the focus of many studies when pharmaceuticals are compounds of interest [11,16]. One such method for removing pharmaceuticals and other organic compounds from water is photocatalysis, which uses a catalyst that is excited by some type of radiation to form highly oxidative radicals (e.g., OH) that react with the pollutant to degrade ultimately into CO$_2$ and water [17]. However, for a photocatalytic reaction to occur at all, sorption of the drug on active sites on the surface/pores of the photocatalyst is a necessary step [18]. The most commonly used photocatalyst is TiO$_2$ due to its easy availability, low cost, non-toxicity, stability, and photochemical efficiency. It can be in the suspended form in water or immobilized on a solid support, which is also a more effective method because the immobilized catalyst can be much more easily removed from water after purification and its reuse is possible, which reduces processing costs [19,20].

Due to all advantages provided by pure TiO$_2$, there are UV light limitations which are trying to be solved for many years by producing different composites with carbonaceous materials. One of these interesting support materials is carbon nanotubes (CNTs), which have been introduced as adsorbent and whose molecular structure allows greater surface area and more π–π interactions with aromatic organic pollutants. CNTs showed good suitability for sorption removal of some antibiotics, such as lincomycin, sulfamethoxazole, and sulfapyridine [6,21]. The creation of new materials consisting of TiO$_2$ and CNTs improves the photocatalytic performance of TiO$_2$, which can increase the photocatalytic activity of TiO$_2$ due to its usually higher specific surface area, good sorbent properties, reduced h$^+$/e$^-$ recombination, and the possibility of light absorption at higher wavelengths, ultimately leading to more successful environmental applications [22,23]. Such a combination of composites has a wide range of application, from photoelectronics to water purification by photocatalysis, but high cost of CNTs still limits their wide application [6,24,25].

Considering the above, the aim of this work was to determine the potential of TiO$_2$ as a sorbent in suspended and immobilized form for the removal of imatinib and crizotinib from water for the first time. In addition to using pure TiO$_2$ immobilized on glass fibers, the efficiency of immobilized TiO$_2$ in combination with carbon nanotubes, a material with a higher specific surface area, was also investigated. The sorption affinity of each compound to a given sorbent using different operating parameters (pH, ionic strength, temperature, and sorbent dosage) is described by the linear, Freundlich, and Langmuir sorption isotherms. The kinetic study of pharmaceutical sorption was determined by Lagergren’s pseudo-first-kinetic-order, pseudo-second-kinetic-order, and intraparticle diffusion model.
2. Materials and Methods

2.1. Chemicals and Reagents

The studied pharmaceuticals imatinib (IMT) and crizotinib (CRZ) with high purity were supplied by Pliva. Table 1 shows the structures of the active ingredients and their physicochemical properties. NaOH (p.a.) was purchased from Gram-mol, Zagreb, Croatia. HCl was purchased from VWR Chemicals, SAD, NaCl from Lach Ner, Czech Republic, acetonitrile from J. T. Baker, Netherlands, and formic acid from T.T.T. d.o.o., Sv. Nedjelja, Croatia.

Table 1. Physicochemical properties of pharmaceuticals [14,26,27].

| PhAc | IMT | CRZ |
|------|-----|-----|
| Formula | C29H31N7O | C21H22Cl2FN5O |
| CAS | 152459-95-5 | 877399-52-5 |
| Mr | 493.6 | 450.1 |
| pKₐ | 8.07; 3.73; 2.56; 1.52 | 5.6; 9.4 |
| log K_{ow} | 2.89 | / |

The standard stock solution (1000 mg/L) of IMT was prepared by dissolving a precisely weighed amount of the powder in MilliQ water while CRZ was dissolved in acetonitrile. The working standard solutions (5; 10; 15; 20; 25 mg/L) were prepared by diluting the standard solution of pharmaceuticals in MilliQ water. HCl and NaOH were used to adjust the pH. In the experiments in which the influence of ionic strength was studied, the working standard solutions were prepared using NaCl (0.001; 0.01 and 0.1 M) instead of water.

2.2. Sorbent Preparation and Characterization

Titanium dioxide (TiO₂) was supplied by Evonik (Aeroxide®, TiO₂ P25 with a crystalline content of 75% anatase and 25% rutile), and the multi-walled carbon nanotubes (CNT) were obtained from Chengdu Organic Chem. Co. (outside diameter from 5 nm to 30 nm, purity > 95% and length from 10 µm to 30 µm). The suspension was prepared by weighing 0.01 g TiO₂ in 10 mL of pharmaceutical aqueous solution. Before immobilization of the catalyst to the support, glass fiber (GF) meshes were cut and adapted to the dimensions of the glass vessels with an average area of 10.17 cm². The procedure for sol-gel preparation and characterization of two types of immobilized photocatalysts (TiO₂-GF and TiO₂/CNT-GF) on a round-cut glass fiber mesh was the same as described in previously published papers [28,29]. The average weight of the immobilized TiO₂ film was 0.0037 g/cm² and 0.072 g/cm² for TiO₂/CNT, respectively. Adding such a mesh to a drug volume of 10 mL yielded an average concentration of 3.76 g/L. Analogous to the above calculations, the concentration of TiO₂/CNT-GF mesh was 73.2 g/L, higher than that of TiO₂-GF at the beginning, so it is expected that sorption will be higher with this type of catalyst.

In order to get insight in sorbent, clean GF mesh, pure TiO₂, mesh with TiO₂-GF and TiO₂/CNT-GF were recorded by a scanning electron microscope (SEM-QUANTA FEG-250, Zaragoza, Spain) operated at 20 kV. Figure 1 shows SEM images and by comparing the surfaces of TiO₂ (b) and TiO₂ after binding to glass fibers (c), it can be seen that agglomeration has occurred. Furthermore, TiO₂/CNT-GF (d) bonds noticeably produce even larger agglomerates. As it is well known, (I) the surface plays an important role in the sorption process, and (II) the agglomeration reduces the surface area. These are important facts in this paper.
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Figure 1. The SEM images: (a) clean GF mesh, (b) TiO$_2$, (c) TiO$_2$-GF mesh, and (d) TiO$_2$/CNT-GF mesh.

2.3. Sorbent Studies

Batch sorption experiments were performed in glass vessels by shaking in a laboratory shaker (Innova 4080 Incubator Shaker, New Brunswick Scientific, Minneapolis, MN, USA) that allowed continuous contact (200 rpm) between a specific type of TiO$_2$ and 10 mL of aqueous IMT/CRZ solution. After shaking, the solutions were centrifuged and filtered through 0.20-µm membrane syringe filters (Scheme 1).

Scheme 1. Schematic description of sorption experiment procedure.

To determine the time required to reach sorption equilibrium, initial experiments were performed by shaking 5, 15, and 25 mg/L IMT/CRZ solution with TiO$_2$ at 25 °C for various time periods (10, 20, 30, 40, 50, 60, 120, 240, 360, 1080, and 1440 min). Based on these experiments, a contact time of 24 h was sufficient to establish equilibrium between IMT/CRZ and TiO$_2$ suspension and CRZ sorbed onto TiO$_2$/CNT, while other forms of immobilized TiO$_2$ on fiber glass mesh were agitated for 4 h.
Five concentration levels were used (5; 10; 15; 20; 25 mg/L) for the isotherm experiments to test the influence of pH, ionic strength, temperature, and sorbent dosage. The initial pH was adjusted to pH 7 prior to each of the aforementioned experiments, except for the pH influence where pH values 3, 5, 9, and 11 were also tested. All experiments were performed in duplicate.

2.4. Instrumental Procedure

IMT and CRZ samples were analyzed with the HPLC-DAD, Agilent 1100 System (Santa Clara, CA, USA) using Kinetex C18 stationary phase (150 × 4.6 mm, particle size 3.5 µm). The mobile phase with a flow rate of 0.5 mL/min consisted of 0.1% formic acid in Milli-Q water (eluent A) and 0.1% formic acid in acetonitrile (eluent B). Gradient elution began with 80% of eluent A. Within the next 6 min, the composition of eluent A decreased to 20%. After holding 20% of A for 1 min, the initial phase composition was returned and maintained for 7 min. The injection volume was 25 µL. Detection was monitored at 258 nm for IMT and 270 nm for CRZ, respectively.

2.5. Data Analysis

Sorption isotherms are models that predict the nature and mechanism of interaction between sorbates and sorbent. The obtained sorption data were analyzed using the linear and two-parameter models: Freundlich and Langmuir isotherms. The isotherm constants were obtained by linearizing the model using linear regression as the simplest method for data analysis.

Through the linear model, the sorption coefficient $K_d$ is expressed as the ratio between the amount of drug in the sorbent ($q_e$, mg/g) and the solution ($C_e$, mg/L) [30]:

$$q_e = K_d \times C_e$$

(1)

The empirical Langmuir model (2) was used to describe whether the sorption process is a homogenous process that forms in a monolayer on a fixed number of active sites with no interactions between the sorbed molecules. It is given in a linear form [31]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L}\right) \frac{1}{C_e}$$

(2)

where $q_m$ (mg/g) and $K_L$ (L/mg) represent the maximum sorption capacity (mg/g) and the equilibrium constant referred to sorption energy and the affinity between TiO$_2$ and pharmaceuticals. Calculating $R_L$, a dimensionless constant, the nature of sorption can be inferred; $R_L$ values above 1 indicate an unfavorable process, whereas sorption is favored at $R_L$ between 0 and 1 [32].

The Freundlich isotherm can be applied to describe the sorption equilibrium for heterogeneous surfaces with possibility of multilayer formation, where all sorption from all sites occurs at the point with the highest binding energy [31,33].

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

(3)

$K_F$ is the Freundlich constant indicating the relative sorption capacity ($\mu g$/g) (mL/µg)$^{1/n}$ and $1/n$ is the heterogeneity parameter which indicates the sorption intensity with values ranging from 0 to 1 [34]. Values above 1 indicate cooperative sorption, while lower values than 1 are caused by chemisorption [35].
2.6. Sorption Kinetic Models

The Lagergren’s pseudo-first kinetic model (Equation (4)), Ho’s pseudo-second kinetic model (Equation (5)), and Weber and Morris intraparticle diffusion model (Equation (6)) were used to evaluate the mechanism and describe the phases of the sorption process.

\[ \ln(q_e - q_t) = ln q_e - k_1 t \]  (4)

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \]  (5)

\[ q_t = k_{id} t^{1/2} \]  (6)

$q_t$ and $q_e$ represent the amount of sorbed analyte at time $t$ and at equilibrium state ($\mu$g/g), $k_1$ is the constant rate of pseudo-first-order (min$^{-1}$), $k_2$ is the constant rate of pseudo-second-order kinetic model (g/$\mu$g min), while $k_{id}$ is the intraparticle diffusion rate constant ($\mu$g/g min$^{1/2}$) [33].

The sorption process can be described by a few stages. The first stage involves the transfer of sorbate near the surface of the sorbent. The second stage is called external diffusion followed by intraparticle diffusion as the third stage. The last stage includes chemical and physical reactions on the surface of the sorbent [36].

3. Results and Discussion

3.1. Kinetic Study

The maximum time required to reach sorption equilibrium was examined by shaking pharmaceutical solutions with three initial pharmaceutical concentrations (5, 15, and 25 mg/L) for 11 different time periods. The TiO$_2$ suspension reached equilibrium with both pharmaceuticals after 24 h. IMT and CRZ were not significantly sorbed on immobilized TiO$_2$ after 4 h, whereas CRZ was required to remain in contact with TiO$_2$/CNT-GF for 24 h. Review of the literature revealed similar results for multi-walled CNTs as sorbents in the case of sulfapyridine and sulfamethoxazole, which also reached equilibrium after 4 h, while ciprofloxacin moved even longer than CRZ (72 h) [21,37]. For all three types of sorbents, sorption in the initial phase is a dominant and fast process, while sorption after reaching equilibrium was a slow process over time. The initial concentrations did not affect the contact time between pharmaceutical and TiO$_2$.

Tables 2 and 3 show the parameters from the kinetic study in which the pseudo-first- and pseudo-second-order models were tested for IMT and CRZ, respectively. For the pseudo-first-order model, the linear correlation coefficient $R^2$ does not show good agreement, while the $R^2$ for pseudo-second-order kinetic model was very high ($R^2 > 0.99$). The theoretical values $q_{e,cal}$ were closer to the experimental values $q_{e,exp}$ obtained at all concentrations used. Thus, the pseudo-second-order model is the better model for describing the sorption kinetics of the two pharmaceuticals on all three types of TiO$_2$ photocatalyst.

The intraparticle diffusion constants obtained and values related to the boundary layer thickness indicate that the sorption process occurs mainly in three stages. After contact with an aqueous solution of pharmaceutical and the solid phase, the compound migrates into the sorbent boundary layer. The second stage involves intraparticle diffusion between the porous material and the IMT/CRZ. Sorption at the active sites of the sorbents and equilibrium state are usually reached in the third stage, which is confirmed by the smallest slope, $k_{p3}$ (Tables 4 and 5) [33,38].
Table 2. Sorption kinetic parameters for IMT.

| IMT          | Initial Concentration, mg/L | qe,exp, µg/g | Pseudo-First-Order | Pseudo-Second-Order |
|--------------|-----------------------------|--------------|--------------------|--------------------|
|              |                             |              | qe,calc, µg/g      | k1, min⁻¹        | R²                | qe,calc, µg/g | k2, g/µg min | R²                |
| suspended TiO₂ | 5                          | 14.62        | 8.47              | 0.0059            | 0.9488           | 14.90        | 2.03 × 10⁻⁴   | 0.9990           |
|              | 15                          | 28.40        | 8.50              | 5 × 10⁻⁵          | 0.6238           | 29.67        | 4.26 × 10⁻⁴   | 0.9981           |
|              | 25                          | 32.47        | 10.76             | 3 × 10⁻⁵          | 0.6731           | 34.25        | 3.13 × 10⁻⁴   | 0.9969           |
| TiO₂-GF      | 5                          | 27.37        | 4.73              | 0.0002            | 0.6430           | 28.57        | 8.36 × 10⁻⁴   | 0.9989           |
|              | 15                          | 118.50       | 6.52              | 0.0004            | 0.6385           | 125          | 2.96 × 10⁻⁴   | 0.9999           |
|              | 25                          | 168.25       | 8.94              | 0.0002            | 0.6516           | 174.44       | 1.67 × 10⁻⁴   | 0.9995           |
| TiO₂/CNT-GF  | 5                          | 32.35        | 4.87              | 0.0003            | 0.5734           | 36.76        | 1.72 × 10⁻⁴   | 0.9792           |
|              | 15                          | 68.18        | 8.23              | 0.0002            | 0.6100           | 85.47        | 4.20 × 10⁻⁴   | 0.8151           |
|              | 25                          | 104.65       | 10.48             | 0.0002            | 0.6309           | 161.29       | 1.05 × 10⁻⁵   | 0.5285           |

Table 3. Sorption kinetic parameters for CRZ.

| CRZ          | Initial Concentration, mg/L | qe,exp, µg/g | Pseudo-First-Order | Pseudo-Second-Order |
|--------------|-----------------------------|--------------|--------------------|--------------------|
|              |                             |              | qe,calc, µg/g      | k1, min⁻¹        | R²                | qe,calc, µg/g | k2, g/µg min | R²                |
| suspended TiO₂ | 5                          | 15.88        | 8.00              | 0.0059            | 0.9460           | 15.77        | 9.87 × 10⁻³   | 0.9997           |
|              | 15                          | 46.32        | 7.91              | 4 × 10⁻⁵          | 0.6230           | 46.30        | 1.13 × 10⁻³   | 0.9996           |
|              | 25                          | 67.39        | 10.21             | 5 × 10⁻⁵          | 0.7200           | 68.03        | 4.12 × 10⁻⁴   | 0.9989           |
| TiO₂-GF      | 5                          | 42.39        | 2.86              | 0.0002            | 0.4222           | 42.55        | 7.15 × 10⁻⁴   | 1.0000           |
|              | 15                          | 120.57       | 5.72              | 0.0002            | 0.7360           | 121.95       | 5.37 × 10⁻⁴   | 0.9996           |
|              | 25                          | 207.93       | 8.99              | 0.0004            | 0.9133           | 212.77       | 7.43 × 10⁻⁴   | 0.9954           |
| TiO₂/CNT-GF  | 5                          | 30.29        | 3.90              | 6 × 10⁻⁵          | 0.3427           | 30.40        | 7.07 × 10⁻³   | 1.0000           |
|              | 15                          | 86.52        | 7.35              | 0.0002            | 0.6480           | 88.50        | 3.39 × 10⁻⁴   | 0.9996           |
|              | 25                          | 121.43       | 9.96              | 0.0002            | 0.7592           | 128.21       | 1.07 × 10⁻⁴   | 0.9954           |

Table 4. Intraparticle diffusion model for IMT.

| Sample       | c₀, mg/L | k₁, µg/g min⁻¹/² | R² | k₂, µg/g min⁻¹/² | R² | k₃, µg/g min⁻¹/² | R² | C₁   | C₂   | C₃   |
|--------------|----------|------------------|----|------------------|----|------------------|----|------|------|------|
| suspended TiO₂ | 5        | 2.484            | 0.9731 | 5.757            | 0.1139 | 0.8928            | 10.73 | 0.1018 | 0.9800 | 10.92 |
|              | 15       | 3.257            | 0.9751 | 8.884            | 0.5956 | 0.9853            | 12.35 | 0.2395 | 0.9997 | 19.34 |
|              | 25       | 3.475            | 0.9577 | 9.525            | 0.4854 | 0.9901            | 15.42 | 0.4181 | 0.9788 | 17.96 |
| TiO₂-GF      | 5        | 0.7496           | 0.9828 | 7.675            | 1.6248 | 0.9915            | 2.012  | 0.0121 | 0.8842 | 27.19 |
|              | 15       | 12.317           | 0.9942 | 4.801            | 4.8479 | 0.9873            | 44.82  | 0.1761 | 0.9614 | 115.88 |
|              | 25       | 12.738           | 0.9840 | 40.46            | 8.4091 | 0.9867            | 35.57  | 0.0867 | 0.9994 | 166.9 |
| TiO₂/CNT-GF  | 5        | 1.732            | 0.9623 | 4.491            | 2.7714 | 0.9100            | 8.461  | 0.0018 | 0.8187 | 32.33 |
|              | 15       | 5.338            | 0.9557 | 18.016           | 5.5006 | 0.9850            | 15.58  | 0.0402 | 0.9712 | 67.58 |
|              | 25       | 5.018            | 0.9373 | 17.199           | 10.283 | 0.9694            | 51.27  | 0.1127 | 0.9920 | 102.87 |

This step is very fast and does not control the rate of the whole sorption process. From the obtained results, it can be concluded that the sorption of IMT and CRZ on TiO₂ samples is a complex process controlled mainly by external and intraparticle diffusion. The C values increased from the first to the third stage, with values greater than 0 confirming the first step of surface sorption as the rate-limiting step [39].

3.2. Modeling of Sorption Isotherms—Influence of pH

The sorption parameters of the three types of sorbents fitted to the linear, Freundlich, and Langmuir isotherms are shown in Table 6 for IMT and Table 7 for CRZ, respectively.
Table 5. Intraparticle diffusion model for CRZ.

| Sample            | c_0, mg/L | Intraparticle Diffusion | First Stage | Second Stage | Third Stage |
|------------------|-----------|-------------------------|-------------|--------------|-------------|
|                  |           |                         | k_p1, µg/g min^{1/2} | R^2 | C_1 | k_p2, µg/g min^{1/2} | R^2 | C_2 | k_p3, µg/g min^{1/2} | R^2 | C_3 |
| Suspended TiO_2  | 5         | 0.4913                  | 0.9539      | 11.00        | 0.0330      | 0.9046      | 14.51 | -               | -               | - |
|                  | 15        | 2.318                   | 0.9776      | 17.81        | 0.6452      | 0.9935      | 31.13 | 0.1536          | 0.9508          | 40.21 |
|                  | 25        | 2.814                   | 0.9465      | 20.05        | 1.779       | 0.9395      | 27.35 | 0.3887          | 0.9971          | 52.47 |
| TiO_2-GF         | 5         | 1.261                   | 0.9530      | 30.34        | 0.1787      | 0.8709      | 39.17 | 0.0045          | 0.9976          | 42.22 |
|                  | 15        | 5.441                   | 0.9524      | 60.15        | 0.6495      | 0.9812      | 98.46 | 0.0220          | 1.000           | 119.73 |
|                  | 25        | 14.914                  | 0.9918      | 0.7623       | 4.138       | 0.9168      | 80.25 | 2.803           | 0.9994          | 102.09 |
| TiO_2/CNT-GF     | 5         | 2.009                   | 0.8401      | 15.59        | 0.1506      | 0.9554      | 26.73 | 0.0210          | 0.9436          | 29.54 |
|                  | 15        | 17.532                  | 0.9269      | 2.124        | 1.948       | 0.9928      | 43.26 | 0.3957          | 0.9324          | 72.35 |
|                  | 25        | 10.690                  | 0.9609      | 17.21        | 3.713       | 0.9979      | 31.72 | 1.048           | 0.9345          | 83.87 |

Table 6. Sorption isotherm parameters for IMT as an influence of pH.

| Isotherm Parameter | Suspended TiO_2 | TiO_2-GF | TiO_2/CNT-GF |
|-------------------|-----------------|----------|--------------|
| Linear K_d (mL/g) | 162.2           | 213.8    | 672.3        |
|                   | 0.9960          | 0.9980   | 0.9910       |
|                   | R^2             | 0.9990   | 0.9990       |
| Langmuir q_m (mg/g) | 5.0             | 5.0      | 20           |
|                   | 0.5             | 0.4      | 0.07         |
|                   | R^2             | 0.8896   | 0.9199       |
|                   | K_L (mL/g)      | 0.015    | 0.5          |
|                   | 2027.2          | 1944.5   | 1563.5       |
|                   | R^2             | 0.9750   | 0.9990       |
| Freundlich n      | 3.0             | 2.6      | 1.4          |
|                   | 0.95            | 0.95     | 0.95         |
|                   | R^2             | 0.9990   | 0.9990       |
|                   | K_F (µg/g)(mL/µg)^1/n | 174.2  | 2025.8       |
|                   | 1742            | 2105.7   | 116.5        |
|                   | R^2             | 0.9982   | 0.9482       |

Table 7. Sorption isotherm parameters for CRZ as an influence of pH.

| Isotherm Parameter | Suspended TiO_2 | TiO_2-GF | TiO_2/CNT-GF |
|-------------------|-----------------|----------|--------------|
| Linear K_d (mL/g) | 103.5           | 233.8    | 234.4        |
|                   | 0.9965          | 0.9970   | 0.9993       |
|                   | R^2             | 0.9993   | 0.9993       |
| Langmuir q_m (mg/g) | 10.0            | 5.0      | 20.0         |
|                   | 0.015           | 0.5      | 0.5          |
|                   | R^2             | 0.9968   | 0.8665       |
|                   | K_L (mL/g)      | 174.2    | 2025.8       |
|                   | 1742            | 2105.7   | 116.5        |
|                   | R^2             | 0.9982   | 0.9482       |
| Freundlich n      | 1.2             | 2.6      | 2.7          |
|                   | 0.99            | 1.3      | 1.2          |
|                   | R^2             | 0.9982   | 0.9482       |

The linear isotherm showed the best fit to the obtained data for all TiO_2 experiments at different pH values (R^2 > 0.99) suggesting the domination of partition interactions [40].
The sorption coefficient $K_d$ showed an increasing trend with increasing pH values for IMT and CRZ on TiO$_2$ in three forms (Figure 2). According to the literature [41,42], the zeta potential of TiO$_2$ is between 6 and 6.5, so TiO$_2$ is positively charged at pH 5; it is probably predominantly negatively charged at pH 7 and 9. The $pK_a$ value of IMT nitrogen atom of piperazine is about 7.8–8.07 [27,43], which means that IMT is positively charged in acidic medium and predominantly negatively charged under alkaline conditions. At pH 5, electrostatic repulsive interactions predominated causing the least sorption, while at higher pH values, electrostatic attractive forces were promoted between neutral IMT and more negatively charged TiO$_2$. At pH 9, the sorption affinity of the pharmaceutical was highest, while at pH 7 (value close to the isoelectric point of the sorbent), agglomeration was possible on the TiO$_2$ surface resulting in lower sorption affinity [41,44]. A similar trend in sorption affinity was obtained with CRZ which has two $pK_a$ values: 5.6 and 9.4. It can exist in positive, neutral, and negative forms under different pH conditions [26]. Therefore, the increase in sorption coefficient is accompanied by an increase in pH, which is due to the different species present in the medium causing repulsive forces at pH 5 or attractive forces at pH 9. It has been shown that the efficiency of drug removal can be strongly influenced by the presence of different ionizable species of the drug by changing the process conditions, i.e., sorption can be positively influenced by an increase in pH as in this study or negatively influenced in the case of ciprofloxacin and multi-walled CNT (above pH 7) [37], and cefdinir in the pH range of 4–10 using TiO$_2$ as a sorbent [45].

To investigate the sorption capacity and multilayer formation on heterogeneous surfaces, the parameters $n$ and $K_F$ were calculated from the logarithmic form of the Freundlich isotherm [46,47]. In the case of sorption of both pharmaceuticals to TiO$_2$ in suspension, the $n$ values are higher than 1, indicating that this type of sorbent is favorable for the removal of IMT and CRZ at low concentrations [48,49]. The sorption of IMT on TiO$_2$-GF mesh is described by $n$ close to 1 (at pH 5 and 9), confirming the linearity of the isotherm and the constant affinity for sorption in the applied concentration range. At the surface of TiO$_2$/CNT-GF, sorption was a cooperative process with the same $n$ values for each pH showing the decrease in affinity of IMT sorption due to the filled active binding sites [50]. CRZ showed a constant sorption potential with higher sorbate concentration on both immobilized catalysts with $n$ values close to unity. The sorption capacity coefficients $K_F$ were highest for the suspension, confirming the highest affinity for sorption of IMT in this form. Other $K_F$ values are relatively low (19.3–27.2 ($\mu g/g$)(mL/$\mu g$)$^{1/n}$), indicating the mobility of pharmaceutical in the sorbent [51]. CRZ generally showed higher tendency to sorb to all TiO$_2$ forms. The Langmuir model in conjunction with the Freundlich isotherm also fitted the experimental data very well, as in the case of cefdinir and TiO$_2$ suspension [45], indicating the complexity of sorption considered as a possible monolayer, and heterogenous

![Figure 2](https://example.com-figure2.png)

**Figure 2.** pH influence on IMT and CRZ sorption (1—suspended TiO$_2$, 2—TiO$_2$-GF, 3—TiO$_2$/CNT-GF).
multilayer process [45,48,52]. At pH 9, the highest values of maximum saturated monolayer sorption capacity \( q_{ml} \) (except for immobilized TiO\(_2\) at pH 7) of the three TiO\(_2\) modifications were obtained, indicating a higher sorption capacity at the mentioned pH, which is in agreement with the determined \( K_d \) values. In general, the TiO\(_2\) suspension showed the better capacity to sorb both pharmaceuticals, which was expected due to the higher number of active sites on the catalyst surface and easier mass transfer while immobilization of material by trapping active sites may decrease the surface activity [22]. Higher mass of TiO\(_2\) does not necessarily bring higher sorption performance, rather the performance of the sorbent or catalyst plays a major role. The results are also consistent with the results of the SEM analysis (Figure 1), which shows the agglomeration occurred during the binding of TiO\(_2\) and TiO\(_2\)/CNT to GF meshes, resulting in a decrease in the active surface area of the sorbent. However, to avoid problems in sample reuse and filtration, it is better to immobilize only TiO\(_2\) and not to use it in combination with nanotubes because the different active sites of the two materials may cause heterogeneous sorption [45].

3.3. Influence of Ionic Strength

Standard solutions of pharmaceuticals at a natural pH 7 were prepared in the presence of 0.001 M, 0.01 M, and 0.1 M NaCl instead of MilliQ water to determine the sorption capacity by changing the concentration of the inorganic salt.

A slight increasing trend of IMT sorption with higher ionic strength for all three sorbent samples (Figure 3) can be attributed to possible neutralization of the TiO\(_2\) surface by positive ions, which allows non-electrostatic interactions between pharmaceutical and sorbent [53]. Increased sorption may also be the result of increased solubility of the pharmaceutical due to addition of soluble salts in aqueous solution [48]. The higher concentration of Na\(^+\) ions affecting the decrease in CRZ sorption on TiO\(_2\) may be the result of decreased active sites due to competitive sorption between Na\(^+\) and CRZ, and weak electrostatic repulsion interactions due to equal charges of sorbent and sorbate, including ambient pH [54]. Determining the effect of ionic strength provides important information on how much the removal of organic contaminants from water is affected by the presence or addition of different ions. These results may also indicate that the sorption of IMT and CRZ is also affected by different substances in the water matrix, which needs to be confirmed by additional experiments.

![Figure 3. Ionic strength as influencing parameter on IMT and CRZ sorption (1—suspended TiO\(_2\), 2—TiO\(_2\)-GF, 3—TiO\(_2\)/CNT-GF).](image-url)

3.4. Effect of Sorbent Dosage

For each type of sorbent, experiments were performed with three different sorbent dosages (Figure 4): the lower mass and the higher mass of the sorbent used in the experiments described above. The percentage of sorption was not affected too much by higher dosage of sorbent; a slight increase in \( K_d \) with higher mass was observed, which was due to
The pH of the solutions was adjusted to a neutral environment (pH 7). It was found that temperature has different influences on sorption to TiO$_2$ in different forms (Table 8). The sorption of IMT on the suspension decreased with increasing temperature. For the sorption of IMT on TiO$_2$-GF, the effect of temperature was not noticeable due to a slight increase in active sites and $K_d$ values. A similar temperature effect was found for the sorption of CRZ on all TiO$_2$ forms; increasing the temperature led to an increase in molecular diffusion to the surface of the photocatalyst and then promoted pharmaceutical binding [56]. Similar sorption thermodynamics depending on the type of sorbent used as for IMT was also reported for ciprofloxacin [37].

Figure 4. Effect of sorbent dosage (1—suspended TiO$_2$, 2—TiO$_2$-GF, 3—TiO$_2$/CNT-GF: 1: min—0.5 g/L, average—1.0 g/L, max—1.5 g/L; mass layer of 2: min—2.3 g/L, average—3.7 g/L, max—5.2 g/L; mass layer of 3: min—47.8 g/L, average—73.2 g/L, max—107.6 g/L).

3.5. Sorption Thermodynamics

To describe the nature of the sorption process by determining thermodynamic parameters, experiments were performed at temperatures of 25, 30, and 35 °C (298; 303; 308 K). The pH of the solutions was adjusted to a neutral environment (pH 7). It was found that temperature has different influences on sorption to TiO$_2$ in different forms (Table 8). The sorption of IMT on the suspension decreased with increasing temperature. For the sorption of IMT on TiO$_2$-GF, the effect of temperature was not noticeable due to a slight increase in active sites and $K_d$ values. A similar temperature effect was found for the sorption of CRZ on all TiO$_2$ forms; increasing the temperature led to an increase in molecular diffusion to the surface of the photocatalyst and then promoted pharmaceutical binding [56]. Similar sorption thermodynamics depending on the type of sorbent used as for IMT was also reported for ciprofloxacin [37].

Table 8. Thermodynamic parameters for IMT and CRZ sorption.

| Sample          | $K_d$, mL/g | $\Delta G^\circ$, kJ/mol | $\Delta H^\circ$, kJ/mol | $\Delta S^\circ$, J/mol |
|-----------------|------------|--------------------------|--------------------------|------------------------|
| IMT 298 K       | 213.8      | -13.3, -10.4, -10.0      | -57.9, -151.0            |
| 303 K           | 61.9       | 49.7                      |                          |
| 308 K           | 47.4       | 8.8                       |                          |
| 298 K           | -13.3      | -10.4, -10.0              | -57.9, -151.0            |
| 303 K           | -10.4      | -10.0                     |                          |
| 308 K           | -9.5       | -9.5                      |                          |
| CRZ 298 K       | 36.4       | -8.8, -9.3, -9.5          | 10.4, 64.6               |
| 303 K           | 40.3       | -8.8, -9.3, -9.5          | 10.4, 64.6               |
| 308 K           | 47.4       | -8.8, -9.3, -9.5          | 10.4, 64.6               |
| suspended TiO$_2$ 298 K | 82.3      | -10.9, -11.1, -1.8 | 2.9, 46.4               |
| 303 K           | 82.5       | -11.1                     |                          |
| 308 K           | 88.7       | -1.8                      |                          |
| TiO$_2$-GF      | 233.8      | -13.5, -14.3, -14.8       | 16.7, 101.7              |
| 298 K           | 268.8      | -13.5                     |                          |
| 303 K           | 271.7      | -14.3                     |                          |
| 308 K           | -10.1      | -11.6                     |                          |
| TiO$_2$/CNT-GF  298 K | 179.2     | -10.1, -11.6, -11.9       | 3.82, 55.8               |
| 298 K           | 180.9      | -11.6                     |                          |
| 303 K           | 197.6      | -11.9                     |                          |
| 308 K           | 357.0      | -9.7                      |                          |

Thermodynamic parameters, including Gibbs free energy, $\Delta G^\circ$, enthalpy, $\Delta H^\circ$, and entropy, $\Delta S^\circ$, were calculated using the following equations [57]:

$$\Delta G^\circ = -RT\ln K_d$$  

(7)
The sorption of IMT and CRZ on all sorbents is favorable and spontaneous physisorption process, which is confirmed by negative values of $\Delta G^\circ$, ranging from $-1.8$ to $-14.8$ kJ/mol for both pharmaceuticals [58]. The more negative the $\Delta G^\circ$ values, the higher sorption affinity of the pharmaceuticals, as a result of increased driving molecular forces such as Van der Waals forces [59]. The positive $\Delta H^\circ$ and $\Delta S^\circ$ values indicate that the sorption of CRZ onto three forms of TiO$_2$ and of IMT onto both types of immobilized TiO$_2$, is an endothermic reaction [60], where an increase in temperature leads to a higher sorption capacity. Based on the negative values of the thermodynamic parameters $\Delta H^\circ$ and $\Delta S^\circ$, it can be assumed that IMT sorption in suspension is an exothermic reaction in which randomness at the interface of TiO$_2$ and IMT solution decreases [33,59].

\[
\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}
\]  

(8)

3.6. Statistical Analysis

Statistical analysis was performed by calculating correlations between the parameters affecting sorption as independent variables (pH, ionic strength, temperature, sorbent dosage) and the dependent one—the sorption coefficient. Pearson’s correlation coefficient $r$ can range from $-1$ to $+1$, while $-$ or $+$ indicate the direction of correlation [61]. The sorption of IMT to all types of TiO$_2$ under different influences showed strong linear correlations with $r$ higher than 0.84. A slightly weaker correlation was found for the influence of ionic strength on IMT sorption to TiO$_2$-GF (Figure 5). A similar trend was also observed for CRZ, where a strong positive correlation ($r = 0.87–0.98$) indicated a proportional relationship between $K_d$ and pH, temperature, and sorbent dosage. The sorption of CRZ showed a negative medium-strong correlation when the ionic strength of the solution was changed.

![Figure 5](image-url)  

**Figure 5.** Determination of Pearson’s correlation coefficients between sorption influencing parameters.

4. Conclusions

In this manuscript, preliminary data on the removal of IMT and CRZ from an aqueous solution by sorption processes with TiO$_2$ suspension, TiO$_2$-GF, and immobilized TiO$_2$/CNT-GF were presented. The influence of contact time, solution pH, initial pharmaceutical concentration, ionic strength, sorbent dosage, and ambient temperature was studied to determine the affinity of IMT and CRZ for the photocatalyst used. Statistical analysis confirmed that the complexity of the sorption process is strongly influenced by the various parameters mentioned above. Since most of the pharmaceuticals present in the environment are expected to be in ionized form, the experiments were carried out at different pH values in the range of 5–9, to show what interactions may occur due to the physicochemical properties of sorbent and sorbate during the sorption process. The $K_d$ values obtained from the linear isotherm, the best model to describe the sorption processes for both pharmaceuticals ($R^2 > 0.99$), increased with increasing alkalinity of the aqueous medium. When
inorganic salt was added to the solution, an opposite behavior of the drugs was observed. The sorption affinity of CRZ decreased with increasing concentration of Na-cations, while IMT was slightly more sorbed on all three catalyst types. Increasing the mass of TiO$_2$ also increased the active sites on the catalysts, resulting in higher sorption affinity of the two drugs. Thermodynamic parameters indicated spontaneity of CRZ and IMT sorption on all catalyst forms used. Higher ambient temperature had positive effect on the sorption of pharmaceuticals on both types of immobilized TiO$_2$ and on the suspension for CRZ, while IMT added in suspension showed an exothermic response. The pseudo-second-order model best described the kinetics of the sorption process with $R^2$ values close to one. Despite the fact that the suspended form of TiO$_2$ had a higher sorption capacity, when the efficiency of the removal process, sorption or photocatalysis was considered together with the operating costs, including the preparation of the sorbent, it can be concluded that the suspension is not cost-effective in real water treatment applications at higher levels, considering the time-consuming and expensive separation without the possibility of reuse.

CRZ and IMT showed a similar and relatively good tendency to sorb to the TiO$_2$ photocatalyst, which can be considered for future research as a potential sorbent for pharmaceuticals removal from various types of water matrices. If a compound has a good affinity for the sorption catalyst, the sorption process should be considered as an economically and environmentally efficient method for the removal of contaminants, rather than a process that requires higher energy consumption.

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