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RESEARCH ARTICLE

ADSORPTIVE AND PHOTOCATALYTIC REMOVAL OF METHYLENE BLUE AND TETRACYLINE RESIDUE BY COVALENT ORGANIC FRAMEWORK FUNCTIONALIZED WITH TITANIUM DIOXIDE NANOSHEETS ADSORBENT FROM WATER

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ABSTRACT

In this research work, a covalent organic framework adsorbent functionalized with titanium dioxide was synthesized. Then, Effect of pH, amount of adsorbent, agitation time, and initial concentration of methylene blue and tetracycline pollutants on the process of pollutant removal from water were investigated. The effect of ultraviolet light on the performance of the adsorbent was studied. The adsorbent's ability to remove pollutants was compared in the presence and absence of UV light. The synthesized adsorbent consists of two parts. The main part includes the covalent organic framework that shows effective surface adsorption, and the other part is titanium dioxide, which is connected to the structure of the adsorbent by covalent bonding. The titanium dioxide is activated when exposed to ultraviolet light and increases the removal percentage of the adsorbent under optimal conditions. Functionalization of the covalent organic framework with titanium dioxide created a dual-purpose and efficient adsorbent to remove pollutants.

KEYWORDS

Covalent organic framework, Titanium dioxide, Optimization, Methylene blue, Tetracycline

1. INTRODUCTION

With the increase in world population, the need for safe water for developing human societies is inevitable (Pavithra and Jaikumar, 2019). On the other hand, industrialization and urbanization have caused extensive pollution of surface and underground water resources (Gopinath et al., 2020; Eskizeybek et al., 2012). Pollutants in water and wastewater usually include heavy metals and organic compounds such as dyes and drugs, which are a serious threat to people and the environment (Kanchana and Vijayalakshmi, 2020; Rauf and Ashraf, 2012). Five major industries are responsible for creating color in environmental effluents. The textile industry with 54%, the paper dyeing industry with 21%, the pulp dyeing industry with 10%, the leather industry with 8% and the paint production industry with 7% introduce polluting dyes into the environment (De Gisi et al., 2016; Mainya et al., 2013). These non-degradable organic dyes are often carcinogenic. Increasing the concentration of these colors in water leads to resistance to the penetration of sunlight into the depths of the water and destroys the food chain of aquatic animals (Rauf et al., 2010; Liu, et al., 2012). Methylene blue can be mentioned as an example of these colored pollutants. Methylene blue is a dark blue powder that causes various effects on the body such as cyanosis, kidney failure, tachycardia, hemolytic anemia, hyperbilirubinemia, gastritis, digestive and nervous disorders, and skin and eye tissue irritation (Contreras, et al., 2019; Sun, et al., 2019; Abdelrahman, et al., 2019; Jawad, et al., 2020; Cusioli et al., 2020; Staroń et al., 2019). Tetracycline is a widely used antibiotic due to its wide range of use against infections caused by gram-positive and gram-negative bacteria, mycoplasma, fungi, rickettsia and parasites (Daghrir and Drogui, 2013). Tetracycline is the second most widely used antibiotic (Gu and Karthikeyan, 2005). Due to its low cost, wide spectrum and oral administration, it is widely used (Jeong, 2010). Tetracycline is widely found in surface and underground water, and its release in the environment leads to this antibiotic residue in the environment. It can also cause the creation of antibiotic-resistant microorganisms. (Pulicharl et al., 2017; Sanganyado and Gwenzi, 2019). The weak and incomplete metabolism of this antibiotic in the human body causes this compound to enter the environment actively. Therefore, it is necessary to remove the residue of this antibiotic from the environment (Selvakumar et al., 2019; Xiong et al., 2019; Wei et al., 2020). To deal with these problems, suitable methods of water purification with high efficiency and low cost and design and manufacture of adsorbents with features such as high adsorption capacity, fast adsorption speed, economic efficiency, low toxicity for the environment, ease of separation, strength and reusability is necessary to removal of environmental pollutants (Che al., 2018; Ajmal et al., 2014; Lu et al., 2020).

Today, covalent organic frameworks as a new type of porous material with high adsorption capacity, resistance to heat and acidic and basic environments, and the ability to act with diverse and selective functional groups, as new adsorbents for removing various pollutants, have been noticed. (Wang and Zhuan, 2020; Cote et al., 2005; Zhang, 2018; Medina et al., 2017). Functionalization of the covalent organic frameworks is carried out by different methods (El-Kaderi et al., 2007; Das et al., 2015). The covalent connection of these compounds with semiconductors, creates a strong attraction for the removal of pollutions. (Jiang et al., 2018; Zhou et al., 2019., Lu et al., 2019). The surface adsorption characteristics of the covalent organic framework along with the properties of photocatalytic degradation of semiconductors, simultaneously caused removal and destruction of contaminants in aqueous solutions (Liu et al., 2018; Thote et al., 2014; Cheng et al., 2018; Shen et al., 2022; Wang et al., 2022; Guo et al., 2020; Sun et al., 2021; Sun et al., 2019; Liu et al., 2022). Comparing the effectiveness of simple and functionalized covalent organic framework

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adsorbents in removing various pollutants reveals the necessity of functionalizing these compounds. The design and construction of covalent organic frameworks functionalized with semiconductors such as titanium dioxide and the creation of efficient dual-purpose adsorbents are one of the main goals of this research. Synthesis of covalent organic framework functionalized with titanium dioxide was carried out and the removal of two pollutants, tetracycline and methylene blue, was optimized in different experimental conditions. Optimizing the pH and time of contact with the adsorbent and the amount of adsorbent and the concentration of pollutants were investigated. The removal of methylene blue and tetracycline was investigated in the presence and absence of ultraviolet light. The comparison of the adsorbent in removing methylene blue and tetracycline pollutants clearly showed the ability of the synthesized adsorbent.

2. Experimental

2.1 Chemicals and storage solutions

Chemicals and solvents used in this thesis with an analytical purity higher than 99% were obtained from Merck (Germany) and used without purification. All aqueous solutions were prepared by double distilled pure water. The stock solution of analytes such as tetracycline and methylene blue was prepared by dissolving the appropriate amount of their powder in double distilled water, and the other solutions used with specific concentrations were prepared by diluting the stock solution with double distilled water.

2.2 Instrumentation

The absorption spectra of the solutions were performed using an Agilent model 8453 UV-Vis single-beam spectrophotometer. The pH of the solutions was measured using a pH meter model 827 made by Metrohm, Switzerland. An ultrasonic water bath was used for the synthesis of nanomaterials and also for dispersing them in the studied solutions. Fourier transform infrared spectrometer Perkin Elmer Spectrum GX model was used to record the infrared spectra of covalent organic frameworks.

2.3 Synthesis of covalent organic framework functionalized with titanium dioxide

Titanium dioxide nanosheets were synthesized. Then, aminopropyltriethoxysilane-functionalized TiO2 nanosheets were prepared. Terephethaldehyde as a precursor was added to this compound and a combination of amine and aldehyde was carried out. Finally, melamine and terephthaldehyde were added to this compound and a covalent organic framework functionalized with titanium dioxide was synthesized according to the method described in the literature (Li, 2020).

3. Results and Discussion

3.1 Fourier transform infrared of adsorbent

To characterize the functionalized covalent organic framework and confirm step by step each of the synthesized structures, are shown in Figure 1. In the infrared Fourier transform spectra for compounds (A) TiO2, (B) APTES-TiO2 and (C) CHO-TiO2, there are specific peaks at the wave numbers of 498 cm^{-1} and 3500 cm^{-1}, which are respectively caused by Ti-O bond and surface hydroxyl groups. Are. In comparison with the spectrum of TiO2 nanosheets, the spectrum of APTES-TiO2 shows clear peaks at the wave numbers of 1630 cm^{-1} and 2930 cm^{-1}, which belong to the N-H vibration in the NH_2 and CH_2 groups in APTES, respectively. A peak at 928 cm^{-1} wave number indicates the stretching vibration of Ti-O-Si, which is caused by the connection of silanol groups of APTES to the hydroxyl groups of TiO2 nanosheets.

In comparison with the APTES-TiO2 spectrum, the CHO-TiO2 spectrum shows additional peaks at 1620 cm^{-1} and 1460 cm^{-1}, which respectively indicate the formed C=N group and C=C of the benzene ring of terephthaldeyde molecule. The peak at 1560 cm^{-1} wave number caused by N-H groups of APTES-TiO2 compound has disappeared in CHO-TiO2, which indicates the successful binding of terephetaldehyde. Also, the absorption spectra in the wavenumbers 2920 cm^{-1} and 1620 cm^{-1}, respectively, are caused by C-H and C=O bonds of terephthalaldehyde compound. In the last step, the precursor CHO-TiO2 reacts with two monomers, terephthalaldehyde and melamine, and the final composition of the covalent organic framework functionalized with titanium dioxide is obtained.

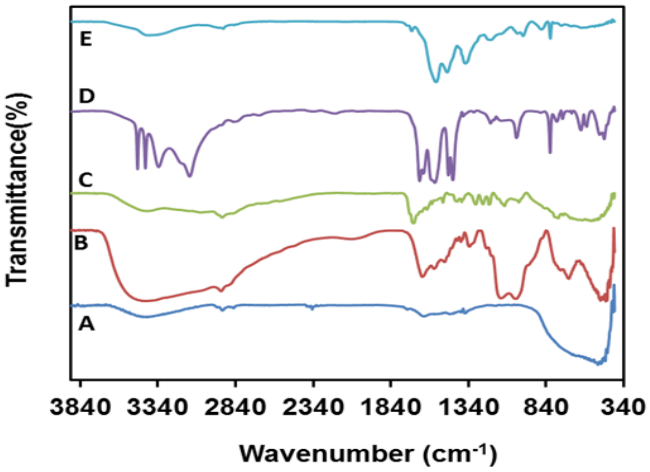

Figure 1: Infrared Fourier transform spectra for compounds (A) TiO2, (B) APTES-TiO2 CHO-TiO2 (C), COF-TiO2 (D), COF (E).

3.2 EDAX of adsorbent

EDAX of a covalent organic framework functionalized with titanium dioxide is presented in Figure 2. The results obtained from this analysis show that the organic covalent framework functionalized with titanium dioxide is composed of 25% carbon element, 18.05% nitrogen element, 28.02% oxygen element, 5.17% silicon element and 23.77% titanium element.

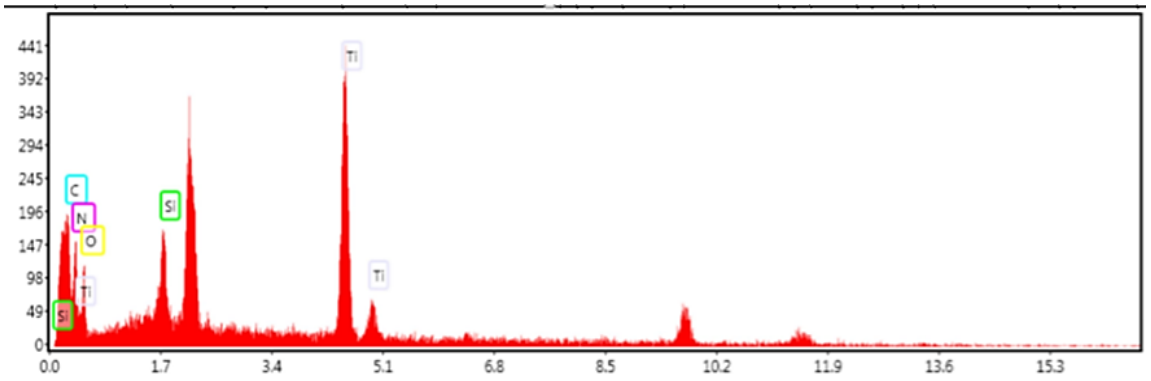

Figure 2: EDAX spectrum of covalent organic framework functionalized with titanium dioxide.

3.3 Determination of point zero charge

To determine the point of zero charge of the covalent organic framework functionalized with titanium dioxide, 0.01 grams of this compound was added to 10 ml volumes of 0.01 molar sodium nitrate solution, whose pH was previously adjusted by sodium hydroxide solution and 0.01 molar nitric acid. was added at room temperature. Then the solutions were closed and stirred for 24 hours. At the end, the final pH of the solutions was measured and the difference between the initial and final values (ΔpH) was calculated. As shown in figure3, the ΔpH diagram was drawn in terms of initial pH and pH_{PZC} was obtained from the intersection point of the chart with the horizontal axis. The value of pH_{PZC} for the synthesized compound was 3.63.

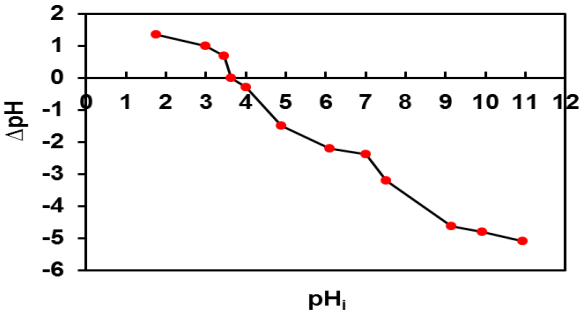

Figure 3: ΔpH diagram versus initial pH for covalent organic framework functionalized with titanium dioxide.

3.4 Optimizing of different parameters for removal of methylene blue

3.4.1 Effect of pH

To investigate the effect of pH on the surface absorption of methylene blue by the adsorbent, one should first pay attention to the structure of the adsorbent under investigation. This absorber consists of two parts. The first part includes the covalent organic framework, which has a surface covered with N-H groups, has a high specific surface area and many holes, and shows a good surface absorption for the methylene blue molecule. As demonstrated by the percentage curve of removal of methylene blue at different pH values and in the absence of ultraviolet light in Figure 4, the surface absorption of methylene blue is carried out on the part of the covalent organic framework. By increasing the pH of the methylene blue solution, the pair of electrons on the surface of the adsorbent is exposed to the methylene blue molecule with the dominant cationic form, and thus the percentage of removal increases at alkaline pHs until the maximum percentage of methylene blue removal on the adsorbent is observed at a pH equal to 10.

As the curve of percentage removal of methylene blue at different pH values and in the presence of ultraviolet light shows, the solution of methylene blue along with the absorbent is exposed to ultraviolet light under completely identical conditions. In this case, in addition to the effect of the covalent organic framework on the surface absorption of methylene blue, the second part of the absorber, which is the titanium dioxide group, destroys a part of the methylene blue molecules against ultraviolet light, and thus, the removal percentages of methylene blue at different pH levels slightly increase. Gives. According to the x-ray energy diffraction spectrum of the absorbent, which determined the amount of titanium in the absorber to be 23.77%, it is clear that this increase in the removal percentage of methylene blue by the absorbent is due to the amount of titanium dioxide attached to the covalent organic framework.

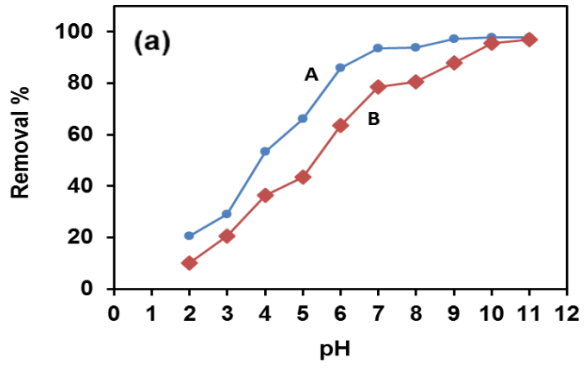

Figure 4: The effect of solution pH on the removal percentage of methylene blue by the covalent organic framework functionalized with titanium dioxide, diagram A with ultraviolet light and diagram B in the absence of ultraviolet light (conditions: 0.02 g of absorbent, stirring time 15 minutes, initial concentration of methylene blue 150 mg L^{-1}, initial volume 10 ml).

3.4.2 Effect of mass of adsorbent

To investigate the effect of the amount of adsorbent, equal amounts of a covalent organic framework, in the range of 0.005 g to 0.03 g, were added to two identical flasks containing 10 ml of methylene blue solution of 150 mg L^{-1} at a pH of 10 and then for 15 minutes. They were stirred by a magnetic stirrer in the presence and absence of ultraviolet light. Then the suspensions were centrifuged for 20 minutes. Absorption of the supernatant solutions was measured and the removal percentage of methylene blue was obtained in both cases. The results are shown in Figure 5. The removal percentage of methylene blue increases with increasing amounts of absorbent, both in the absence of ultraviolet light and in the presence of ultraviolet light. This phenomenon is due to the fact that with increasing amounts of adsorbent, more active sites and surface area are exposed to the analyte. When the adsorbent is exposed to ultraviolet light, the titanium dioxide part of the adsorbent is activated. The percentage of methylene blue removal increases slightly in all amounts of adsorbents compared to when there is no ultraviolet light. The amount of 0.02 grams of absorbent was obtained as the optimal amount. The following experiments were performed with this amount of absorbent.

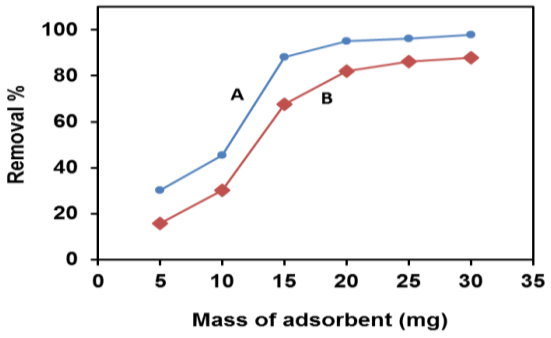

Figure 5: The effect of absorbent amount on the removal percentage of methylene blue by covalent organic framework functionalized with titanium dioxide, diagram A with ultraviolet light and diagram B in the absence of ultraviolet light (conditions: pH: 10, stirring time 15 minutes, initial concentration of methylene blue 150 mg L^{-1}, initial volume 10 ml).

3.4.3 Effect of agitation time

To investigate the effect of contact time on the removal of methylene blue by the adsorbent, an amount of 0.02 g of covalent organic framework powder was added to two identical bottles, each of which contained 10 ml of methylene blue solution of 150 mg L^{-1} at a pH of 10. One human was exposed to ambient light and the other to ultraviolet light. The solutions were stirred between 10 and 70 seconds by a magnetic stirrer and then centrifuged for 20 minutes and the absorbance of the supernatant solution was measured. Finally, the percentage of methylene blue removal was calculated at the mentioned times. As Figure 6 shows, for the solution exposed to ultraviolet light, the removal percentage reaches its maximum value in 30 seconds. Meanwhile, for the other solution, the highest percentage of methylene blue removal was obtained in 1 minute. The synthesized adsorbent consists of two parts of the covalent organic framework, which has a large specific surface area and many holes, and is considered a suitable adsorbent for methylene blue, and the titanium dioxide part, which is activated in the vicinity of ultraviolet light and causes an increase in the removal percentage of methylene blue. It is formed in a shorter time. This high surface absorption rate represents the very high ability of the covalent organic framework functionalized with titanium dioxide to interact and remove methylene blue.

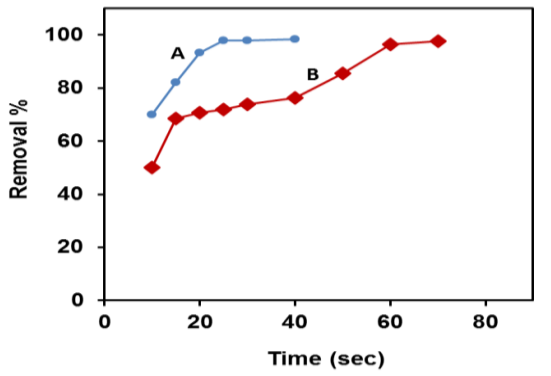

Figure 6: The effect of contact time on the removal percentage of methylene blue by the covalent organic framework functionalized with titanium dioxide, diagram A with ultraviolet light and diagram B in the absence of ultraviolet light (conditions: pH: 10, 0.02 g of absorbent, initial concentration of methylene blue150 mg L^{-1}, initial volume 10 ml).

3.4.4 *Effect of initial concentration of methylene blue*

To investigate the effect of the initial concentration on the removal of methylene blue by the adsorbent, two series of methylene blue solutions with concentrations ranging from 150 mg L^{-1} to 300 mg L^{-1} were prepared. Then their pH was adjusted to 10. 0.02 grams of covalent organic framework absorbent powder functionalized with titanium dioxide were added to the solutions of the first and second series under completely identical conditions. The solutions of the first series were exposed to ultraviolet light and the solutions of the second series were exposed to ambient light. Both series of solutions were stirred for 1 minute by a magnetic stirrer and then centrifuged for 20 minutes. At the end, the concentrations of the supernatant solutions were measured and the removal percentage of methylene blue was calculated in both series. As Figure 7 shows, with increasing methylene blue concentration, the removal percentage decreases. This phenomenon occurs because the surface adsorption sites are saturated at higher analyte concentrations. In the case of solutions exposed to normal ambient light, this decrease in removal percentage indicates that the part of the organic covalent framework, which contains many holes and a large specific surface area, is being saturated. The same phenomenon has caused the reduction of methylene blue removal percentage in the solutions of the second series that were exposed to ultraviolet light. Of course, due to the presence of the agent attached to the covalent organic framework, titanium dioxide, which is activated by exposure to ultraviolet light, this reduction in removal percentage occurs at a slower rate. According to the test results, the concentration of 150 mg L^{-1} was obtained as the optimal value of the initial concentration for methylene blue solution.

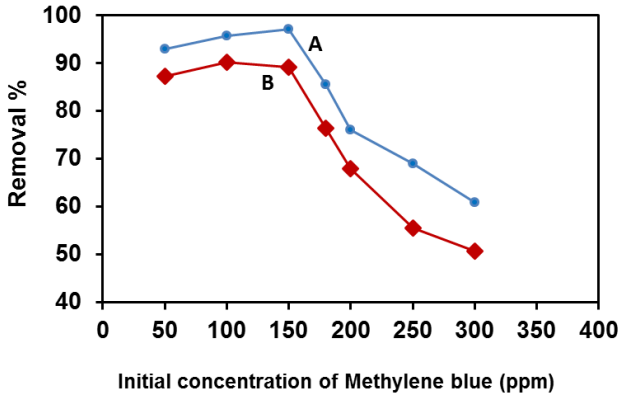

Figure 7: The effect of the initial concentration of methylene blue solution on the removal percentage of methylene blue by the covalent organic framework functionalized with titanium dioxide, diagram A with ultraviolet light and diagram B in the absence of ultraviolet light (conditions: pH: 10, 0.02 g of absorbent, stirring time equal to 1 minute, initial volume 10 ml).

3.5 Optimizing of different parameters for removal of tetracycline

3.5.1 Effect of pH

To investigate the effect of pH on the surface absorption of tetracycline by the adsorbent, we must first pay attention to the structure of the adsorbent and the structure of tetracycline. This absorber consists of two parts. The first part includes the covalent organic framework, which has a surface covered with N-H groups and has a high specific surface area and many holes. Tetracycline molecule has different charges in different pH ranges. tetracycline has a positive charge at pHs less than 3.3. In the pH range between 3.3 and 7.7 it is in the form of a dipolar ion, and at pHs higher than 7.7 it has a negative charge. At pHs higher than the pH_{PZC} of the adsorbent (3.63), the adsorbent surface has a negative charge, and the free electron pairs of the nitrogens on the adsorbent surface are exposed to the positive charge of the tetracycline molecule, and the electrostatic attraction increases the surface absorption of the tetracycline molecule on the adsorbent surface and increases the removal percentage of this pollutant from the solution. As can be seen in Figure (8), with the increase of pH, in the presence of ultraviolet light and the absence of ultraviolet light, the percentage of tetracycline removal increases, and at the optimum pH of 7, the maximum percentage of tetracycline removal will be observed. With the increase in pH, the tetracycline molecule becomes negatively charged, the electrostatic interaction of the absorbent surface with tetracycline decreases, and for this reason, the percentage of removal is observed. In the presence of ultraviolet light, titanium dioxide attached to the covalent organic framework is activated and causes an increase in the percentage of tetracycline removal in the desired pH range. The design and synthesis of the covalent organic framework functionalized with titanium dioxide increases the percentage of removal and the efficiency of the adsorbent in removing organic pollutants such as tetracycline.

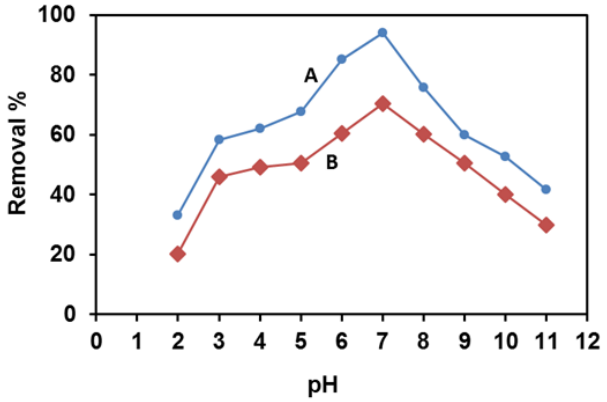

Figure 8: The effect of solution pH on the percent removal of tetracycline by covalent organic framework functionalized with titanium dioxide, diagram A with ultraviolet light and diagram B in the absence of ultraviolet light (conditions:0.02 g of adsorbent, stirring time 15minutes, initial concentration of tetracycline mg L^{-1} 170, initial volume 10 ml).

3.5.2 *Effect of mass of adsorbent*

To investigate the effect of the amount of adsorbent, amounts of 0.005 g to 0.035 g were added to two series of 170 mg L^{-1} tetracycline solution at pH 7 under completely identical conditions. The first series of prepared solutions were stirred by a magnetic stirrer for 15 minutes in normal ambient light and then centrifuged for 20 minutes. As can be seen in Figure (9), in the absence of ultraviolet light, the percentage of tetracycline removal increases with the increase in the amount of absorbent. This phenomenon is because with increasing amounts of adsorbent, more active sites and surface area are exposed to the analyte. Finally, the curve reaches a constant value, where the removal percentage has reached its maximum. The amount of 0.03 grams of absorbent is determined as the optimal amount of absorbent. When the adsorbent is exposed to ultraviolet light, the titanium dioxide part of the adsorbent is activated. The percentages of tetracycline removal increase slightly in all amounts of adsorbent compared to when there is no ultraviolet light. The optimum amount of absorbent in this case is 0.02 grams. It is clear that the design and synthesis of covalent organic framework adsorbent functionalized with titanium dioxide. In addition to causing higher removal percentages in all amounts of adsorbent, consumes a lower amount of adsorbent to reach the maximum removal of tetracycline.

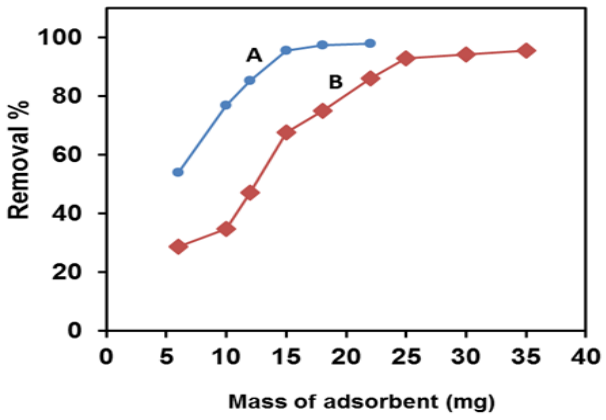

Figure 9: The effect of the amount of adsorbent on the percentage of tetracycline removal by the covalent organic framework functionalized with titanium dioxide, diagram A with ultraviolet light and diagram B in the absence of ultraviolet light (conditions: pH: 7, stirring time 15 minutes, initial concentration of tetracycline 170 mg L^{-1}, initial volume 10 ml).

3.5.3 Effect of agitation time

To investigate the effect of agitation time on the removal of tetracycline by the adsorbent, 0.03 g of adsorbent powder was added to two series of

170mg L^{-1}tetracycline solution under the same conditions and at a pH of 7. One series of solutions was exposed to ambient light and another series of solutions was exposed to ultraviolet light. The solutions were stirred by a magnetic stirrer for 10 to 120 seconds and then centrifuged for 20 minutes and the absorbance of the supernatant solutions was measured. Finally, the percentage of tetracycline removal was calculated at the mentioned times. As Figure 10 shows, for solutions exposed to ultraviolet light, the removal percentage reaches its maximum value in 1 minute. Meanwhile, for solutions exposed to normal ambient light, the highest percentage of tetracycline removal was obtained in 2 minutes. This phenomenon occurs because the synthesized adsorbent is composed of two parts. The first part is the covalent organic framework, which has a large specific surface area and many holes and is considered a suitable adsorbent for tetracycline. The other part is titanium dioxide, which is connected to the covalent organic framework by covalent bonding. Titanium dioxide is activated in the vicinity of ultraviolet light and increases the percentage of tetracycline removal in shorter times. This high surface adsorption speed represents the very high ability of the covalent organic framework functionalized with titanium dioxide to interact and remove tetracycline.

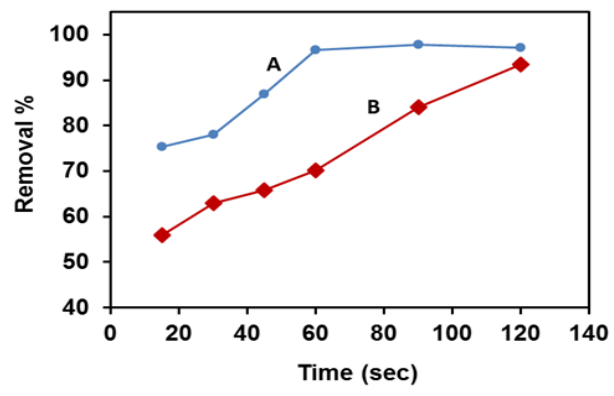

Figure 10: The effect of contact time on the removal percentage of tetracycline by organic covalent framework functionalized with titanium dioxide, diagram A with ultraviolet light and diagram B in the absence of ultraviolet light (conditions: pH: 7, adsorbent 0.03 g, initial concentration of tetracycline 170 mg L^{-1}, initial volume 10 ml).

3.5.4 Effect of initial concentration of tetracycline.

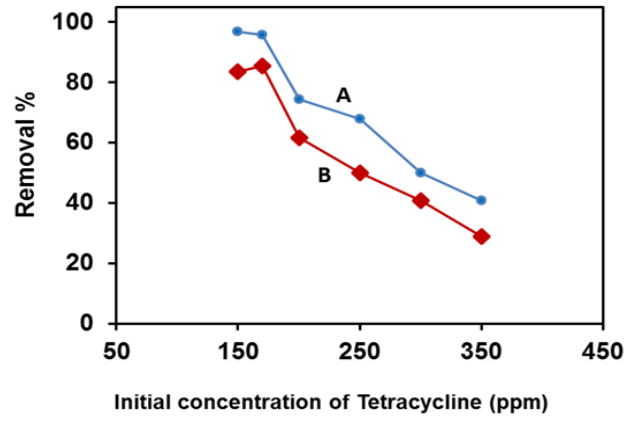

Figure 11: The effect of the initial concentration of tetracycline solution on the percentage of tetracycline removal by the covalent organic framework functionalized with titanium dioxide, diagram A with ultraviolet light and diagram B in the absence of ultraviolet light (conditions: pH: 7, 0.03 g of adsorbent, stirring time equal to 2 minutes, initial volume of 10 ml).

To investigate the effect of the initial concentration on the removal of tetracycline by the adsorbent, 0.03 g of adsorbent was added to two series of tetracycline solutions with concentrations between 150 mg L^{-1} and 350 mg L^{-1} at a pH of 7. The solutions of the first series were exposed to ultraviolet light and the solutions of the second series were exposed to normal ambient light. Both series of solutions were stirred for 2 minutes by a magnetic stirrer and then centrifuged for 20 minutes. At the end, the concentrations of the supernatant solutions were measured and the percentage of tetracycline removal in both series was calculated. As Figure (11) shows, with the increase in tetracycline concentration, the removal percentage decreases. This phenomenon occurs because the surface adsorption sites are saturated at higher analyte concentrations. In the case of solutions exposed to normal ambient light, this decrease in removal percentage indicates that the part of the covalent organic framework, which contains many holes and a large specific surface area, is being saturated. The same saturation of the covalent organic framework in the solutions of the second series that were exposed to ultraviolet light has also caused a decrease in the percentage of tetracycline removal. Of course, due to the agent attached to the covalent organic framework of titanium dioxide, which is activated when exposed to ultraviolet light, this reduction in removal percentage occurs at a slower rate. According to the test results, the concentration of 170 mg L^{-1} was obtained as the optimal value of the initial concentration for the tetracycline solution.

4. Conclusions

In this research, the synthesis of a covalent organic frame work functionalized with titanium dioxide was carried out. Then, the ability and performance of the adsorbent in removing methylene blue and tetracycline pollutants were investigated. Different experimental parameters were optimized to achieve the most effective conditions for using the adsorbent. The covalent binding of titanium dioxide to the covalent organic framework, in addition to creating strong adsorption against environmental conditions, can remove more significant amounts of tetracycline and methylene blue in a shorter period and using fewer amounts of adsorbent. All the results show that the new adsorbent shows excellent capabilities in removing environmental pollutants such as tetracycline and methylene blue.

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Conflict of Interest

The authors of this work declare that they have no conflicts of interest.

References

Abdelrahman, E. A., Hegazey, R., and El-Azabawy, R. E. 2019. Efficient removal of methylene blue dye from aqueous media using Fe/Si, Cr/Si, Ni/Si, and Zn/Si amorphous novel adsorbents. J. Mater. Res. Technol, 8, Pp. 5301-5313.

Ajmal, A., Majeed, I., Malik, R. N., Idriss, H., and Nadeem, M. A. 2014. Principles and mechanisms of photocatalytic dye degradation on TiO 2 based photocatalysts: a comparative overview. RSC Adv, 4, Pp. 37003-37026.

Che, H., Liu, C., Hu, W., Hu, H., Li, J., Dou, J., Shi, W., Li, C., and Dong, H. 2018. NGQD active sites as effective collectors of charge carriers for improving the photocatalytic performance of Z-scheme gC 3 N 4/Bi 2 WO 6 heterojunctions. Catal. Sci. Technol, 8, Pp. 622-631.

Cheng, Y. J., Wang, R., Wang, S., Xi, X. J., Ma, L. F., and Zang, S. Q. 2018. Encapsulating [Mo3S13]2- clusters in cationic covalent organic frameworks: enhancing stability and recyclability by converting a homogeneous photocatalyst to a heterogeneous photocatalyst. ChemComm,54, Pp 13563-13566.

Contreras, M., Grande-Tovar, C. D., Vallejo, W., and Chaves-López, C. 2019. Bio-removal of methylene blue from aqueous solution by Galactomyces geotrichum KL20A. Water, 11, Pp. 282.

Cote, A. P., Benin, A. I., Ockwig, N. W., O'Keeffe, M., Matzger, A. J., and Yaghi, O. M. 2005. Porous, crystalline, covalent organic frameworks. Science, 310, Pp. 1166-1170.

Cusioli, L. F., Quesada, H. B., Baptista, A. T., Gomes, R. G., and Bergamasco, R. 2020. Soybean hulls as a low-cost biosorbent for removal of methylene blue contaminant. Environ. Prog. Sustain. Energy, 39, Pp. 13328.

Daghrir, R., and Drogui, P. 2013. Tetracycline antibiotics in the environment: a review. Environ. Chem. Lett, 11, Pp. 209-227.

Das, G., Biswal, B. P., Kandambeth, S., Venkatesh, V., Kaur, G., Addicoat, M., Heine, T., Verma, S. and Banerjee, R. 2015. Chemical sensing in two

dimensional porous covalent organic nanosheets. Chem, 6, Pp. 3931-3939.

De Gisi, S., Lofrano, G., Grassi, M., and Notarnicola, M. 2016. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. Sustain. Mater. Technol, 9, Pp. 10-40.

El-Kaderi, H. M., Hunt, J. R., Mendoza-Cortés, J. L., Côté, A. P., Taylor, R. E., O'Keeffe, M., and Yaghi, O. M. 2007. Designed synthesis of 3D covalent organic frameworks. Science, 316, Pp. 268-272.

Eskizeybek, V., Sarı, F., Gülce, H., Gülce, A., and Avc, A. 2012. Preparation of the new polyaniline/ZnO nanocomposite and its photocatalytic activity for degradation of methylene blue and malachite green dyes under UV and natural sun lights irradiations. Appl. Catal. B: Environ, 119, Pp. 197-206.

Gopinath, K. P., Madhav, N. V., Krishnan, A., Malolan, R., and Rangarajan, G. 2020. Present applications of titanium dioxide for the photocatalytic removal of pollutants from water: A review. J. Environ. Manage, 270, Pp. 110906.

Gu, C., and Karthikeyan, K. 2005. Interaction of tetracycline with aluminum and iron hydrous oxides. Environ. Sci. Technol, 39, Pp. 2660-2667.

Guo, S., Yang, P., Zhao, Y., Yu, X., Wu, Y., Zhang, H., Yu, B., Han, B., George, M. W., and Liu, Z. 2020. Direct Z-Scheme Heterojunction of SnS2/Sulfur-Bridged Covalent Triazine Frameworks for Visible-Light-Driven CO2 Photoreduction. ChemSusChem, 13, Pp. 6278-6283.

Jawad, A. H., Abdulhameed, A. S., and Mastuli, M. S., 2020. Acid-factionalized biomass material for methylene blue dye removal: a comprehensive adsorption and mechanism study. J. Taibah Univ. Sci, 14 Pp. 305-313.

Jeong, J., Song, W., Cooper, W. J., Jung, J., and Greaves, J. 2010. Degradation of tetracycline antibiotics: mechanisms and kinetic studies for advanced oxidation/reduction processes. Chemosphere,78 Pp. 533-540

Jiang, Q., Sun, L., Bi, J., Liang, S., Li, L., Yu, Y., and Wu, L. 2018. MoS2 Quantum Dots-Modified Covalent Triazine-Based Frameworks for Enhanced Photocatalytic Hydrogen Evolution. ChemSusChem, 11, Pp. 1108-1113.

Kanchana, S., and Vijayalakshmi, R. 2020. Photocatalytic degradation of organic dyes by PEG and PVP capped Cu, Ni and Ag nanoparticles in the presence of NaBH4 in aqueous medium. J. water environ. Nanotechnol, 5, Pp. 294-306.

Li, C. C., Gao, M. Y., Sun, X. J., Tang, H. L., Dong, H., and Zhang, F. M. 2020. Rational combination of covalent-organic framework and nano TiO2 by covalent bonds to realize dramatically enhanced photocatalytic activity. Appl. Catal. B: Environ, 266, Pp. 1185-1186.

Liu, H., Chu, J., Yin, Z., Cai, X., Zhuang, L., and Deng, H. 2018. Covalent organic frameworks linked by amine bonding for concerted electrochemical reduction of CO2. Chem. Sci, 4, Pp. 1696-1709.

Liu, J., Feng, C., Li, Y., Zhang, Y., Liang, Q., Xu, S., Li, Z., and Wang, S. 2022. Photocatalytic detoxification of hazardous pymetrozine pesticide over two-dimensional covalent-organic frameworks coupling with Ag3PO4 nanospheres. Sep. Purif. Technol, 288, Pp. 120644.

Liu, T., Li, Y., Du, Q., Sun, J., Jiao, Y., Yang, G., Wang, Z., Xia, Y., Zhang, W., and Wang, K. 2012. Adsorption of methylene blue from aqueous solution by graphene. Colloids Surf. B: Biointerfaces, 90, Pp. 197-203.

Lu, G., Huang, X., Wu, Z., Li, Y., Xing, L., Gao, H., Dong, W., and Wang, G. 2019. Construction of covalently integrated core-shell TiO2 nanobelts@ COF hybrids for highly selective oxidation of alcohols under visible light. Appl. Surf. Sci, 493, Pp. 551-560.

Lu, Z. Y., Ma, Y. L., Zhang, J. T., Fan, N. S., Huang, B. C., and Jin, R. C. 2020. A critical review of antibiotic removal strategies: Performance and mechanisms. J. Water Process Eng, 38, Pp. 101681.

Mainya, N. O., Tum, P., and Muthoka, T. M. 2013. Photodegradation and adsorption of methyl orange and methylene blue dyes on TiO2. Int. J. Sci. Res, 4, Pp. 3185-3189.

Medina, D. D., Petrus, M. L., Jumabekov, A. N., Margraf, J. T., Weinberger, S., Rotter, J. M., Clark, T., and Bein, T. 2017. Directional charge-carrier transport in oriented benzodithiophene covalent organic framework thin films. ACS nano, 11, Pp, 2706-2713.

Pavithra, K. G., and Jaikumar, V. 2019. Removal of colorants from wastewater: A review on sources and treatment strategies. Ind. Eng. Chem. Res, 75, Pp. 1-19.

Pulicharla, R., Hegde, K., Brar, S. K., and Surampalli, R. Y. 2017. Tetracyclines metal complexation: Significance and fate of mutual existence in the environment. Environ. Pollut, 221, Pp. 1-14.

Rauf, M. A., and Ashraf, S. S. 2012. Survey of recent trends in biochemically assisted degradation of dyes. Chem. Eng. J, 209, Pp. 520-530.

Rauf, M. A., Meetani, M. A., Khaleel, A., and Ahmed, A. 2010. Photocatalytic degradation of methylene blue using a mixed catalyst and product analysis by LC/MS. Chem. Eng. J, 157, Pp. 373-378.

Sanganyado, E., and Gwenzi, W. 2019. Antibiotic resistance in drinking water systems: Occurrence, removal, and human health risks. Sci. Total Environ, 669, Pp. 785-797.

Selvakumar, K., Raja, A., Arunpandian, M., Stalindurai, K., Rajasekaran, P., Sami, P., Nagarajan, E., and Swaminathan, M. 2019. Efficient photocatalytic degradation of ciprofloxacin and bisphenol A under visible light using Gd2WO6 loaded ZnO/bentonite nanocomposite. Appl. Surf. Sci, 481, Pp. 1109-1119.

Shen, H., Shang, D., Li, L., Li, D., and Shi, W. 2022. Rational design of 2D/2D covalent-organic framework/TiO2 nanosheet heterojunction with boosted photocatalytic H2 evolution. Appl. Surf. Sci, 578, Pp. 152024.

Staroń, P., Chwastowski, J. and Banach, M., 2019. Sorption behavior of methylene blue from aqueous solution by raphia fibers. Int. J. Environ. Sci. Technol, 16, Pp. 8449-8460.

Sun, C., Karuppasamy, L., Gurusamy, L., Yang, H. J., Liu, C. H., Dong, J., and Wu, J. J. 2021. Facile sonochemical synthesis of CdS/COF heterostructured nanocomposites and their enhanced photocatalytic degradation of Bisphenol-A. Sep. Purif. Technol, 271, Pp. 118873.

Sun, G., Zhang, M., Liu, X., Gao, Q., Jiang, W., Zhou, Y., Wang, H., Cui, M., Qiu, J., and Xu, J. 2019. Isolation and characterization of the pymetrozine-degrading strain Pseudomonas sp. BYT-1. J. Agric. Food Chem, 67, Pp. 4170-4176.

Sun, L., Hu, D., Zhang, Z., and Deng, X. 2019. Oxidative degradation of methylene blue via PDS-based advanced oxidation process using natural pyrite. Int. J. Environ. Res. Public Health, 16, Pp. 4773.

Thote, J., Aiyappa, H. B., Deshpande, A., Díaz Díaz, D., Kurungot, S., and Banerjee, R. 2014. A Covalent Organic Framework-Cadmium Sulfide Hybrid as a Prototype Photocatalyst for Visible-Light-Driven Hydrogen Production. Chem. Eur. J, 20, Pp. 15961-15965.

Wang, J., and Zhuan, R. 2020. Degradation of antibiotics by advanced oxidation processes: An overview. Sci. Total Environ., 701, Pp. 135023.

Wang, L., Huang, G., Zhang, L., Lian, R., Huang, J., She, H., Liu, C., and Wang, Q. 2022. Construction of TiO2-covalent organic framework Z-Scheme hybrid through coordination bond for photocatalytic CO2 conversion. J. Energy Chem, 64, Pp. 85-92.

Wei, X., Feng, H., Li, L., Gong, J., Jiang, K., Xue, S., and Chu, P. K. 2020. Synthesis of tetragonal prismatic γ-In2Se3 nanostructures with predominantly {110} facets and photocatalytic degradation of tetracycline. Appl. Catal. B: Environ, 260, Pp. 118218.

Xiong, T., Yuan, X., Wang, H., Wu, Z., Jiang, L., Leng, L., Xi, K., Cao, X., and Zeng, G. 2019. Highly efficient removal of diclofenac sodium from medical wastewater by Mg/Al layered double hydroxide-poly (m-phenylenediamine) composite. J. Chem. Eng, 366, Pp. 83-91.

Zhang, S., Zheng, Y., An, H., Aguila, B., Yang, C. X., Dong, Y., Xie, W., Cheng, P., Zhang, Z., Chen, Y., and Ma, S. 2018. Covalent organic frameworks with chirality enriched by biomolecules for efficient chiral separation. Angew. Chem. Int. Ed, 57, Pp. 16754-16759.

Zhou, G., Zheng, L. L., Wang, D., Xing, Q. J., Li, F., Ye, P., Xiao, X., Li, Y., and Zou, J. P. 2019. A general strategy via chemically covalent combination for constructing heterostructured catalysts with enhanced photocatalytic hydrogen evolution. ChemComm, 55, Pp. 4150-4153.