Removal of Antibiotic Tetracycline (TCs) from aqueous solutions by using Titanium dioxide (TiO2) nanoparticles as an alternative material

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Abstract. In this work Titanium dioxide (TiO2) can be used as a sorbent for drug eliminate from industrial Water treatment ,drinking water such as tetracycline (TCs) . Several operational standards like primary drug concentration, large dose, pH, and the temperature of the solution by use of TiO2 in the adsorption of drug TCs. The best result of the percentage removal E% (51-87%), (59-94%) and (70-97%) at temperature (288to 323K).The removal rate decreased with an increase in drug concentrations from 93,706 to 60.227% and Raising the concentration of the pipette adsorbent enhances rising ratio of eliminate till fullness of the adsorbent. This study appears that the adsorption emphasize on mechanism of decomposition TiO2 applied as a substitutional, economical and environmentally harmless condenser for water purification.

Keywords: Pharmaceuticals, Titanium dioxide (TiO2), Adsorption, Removal, Tetracycline, Antibiotic.

Introduction

personal care products(PPCPs) and Pharmaceuticals are chemical materials utilized in personal healthcare, cosmetics and medical materials [1-4]. With improved quality of human life and world population growth , Using PCBs is growing quickly. As an outcome, the contamination of ground water and surface was appeared like a dangerous problem in last years, [1-3]. The worst thing, PPCPs have been found in the sources of raw water from drinking water treatment plants [5], fishes and water resources as well as in tissues of vegetables. Thus, PPCPs have a detrimental impact not only on human health, as well on aquatic environment. It contains a great variety of organic compounds, including combines of daily personal care products (PCPs) and pharmaceutical drugs like lotions, soaps, toothpaste, sunscreens, perfumes [6-8].

Antibacterial material secluded from Streptomyces aureofaciens known as tetracycline antibiotics (TCs); TCs inhibit Gram-positive and Gram-negative bacteria, mycoplasmas, chlamydiae, protozoan parasites and, rickettysiae [9].Like a model PPCP (personal care products and Pharmaceuticals), TCs contains mainly, oxytetracycline, tetracycline and chlortetracycline. TCs largely utilized in the curing livestock breeding and animal illnesses, and This led metabolized is full of animals and humans in the
presence of a large number of remains in the aquatic environment [10]. The frame of TCs and the pKa identical between various deprotonation illustrated in Table 1[11, 12]. It is clear that the pH has a Critical part in the elimination operation of TCs.

### Table 1. Physical and chemical structure of the main features of Tetracycline

| Molecular structure | Name                        | R<sub>1</sub> | R<sub>2</sub> | R<sub>3</sub> | R<sub>4</sub> | pK<sub>a1,2,3</sub> |
|---------------------|-----------------------------|--------------|--------------|--------------|--------------|---------------------|
|                     | Minocycline                 | N(CH<sub>3</sub>)<sub>2</sub> | H            | H            | H            | 2.8, 7.8, 9.3       |
|                     | Epitetracycline, Tetracycline | H            | CH<sub>3</sub> | OH           | H            | 3.3, 7.8, 9.6       |
|                     | Chlortetracycline           | Cl           | CH<sub>3</sub> | OH           | H            | 3.3, 7.5, 9.3       |
|                     | Meclocycline                | Cl           | O =          | OH           |              | 4.1, 6.9, 9.6       |
|                     | Demeclocycline              | Cl           | H            | OH           | H            | 3.4, 7.4, 9.4       |
|                     | Doxycycline                 | H            | H            | CH<sub>3</sub> | OH           | 3.0, 8.0, 9.2       |
|                     | Oxytetracycline             | H            | CH<sub>3</sub> | OH           | OH           | 3.2, 7.5, 8.9       |

**MATERIALS AND METHODS**

**Preparation solutions Tetracycline TCs and Linearity of Calibration Curve.**

TiO<sub>2</sub> was supplied from Sigma-Aldrich/Germany, Tetracycline TCs standard solution (100 mg L<sup>−1</sup>) were Freshly prepared aqueous solution of the pure drugs in a volumetric flask of 1000 mL by dissolving 0.1 g of drug TCs in distilled water. Beer’s law was form to keep 10–80 mg L<sup>−1</sup> TCs the scope of concentration investigated. Fig 1 display the linear regression of the information obtained from the standardization of charts of TCs utilized relationship analysis A=a +bc, where A is absorption at the height of the relevant in a 1.0 cm quartz cell, a and b are the intersection and the incline from the calibration charts, sequentially, and c is condensation of TCs (mgL<sup>−1</sup>) .

![Graph](image)

**Fig. 1:** Calibration curve of Tetracycline.
Adsorption experimental methods and measurements

Adsorption studies were performed in a batch method to check the influence of experimental factors (adsorbent dosage, pH, primary drug conc. and temperature) on the adsorption of drug on Titanium dioxide. The influence of experimental standards (10–80 mg L⁻¹), pH (Ranging from 3–11), adsorbent dosage (0.5-3 gm), temperature (15–50°C) the absorption of the drug were applied in impulse method of process in connection time of 24 hr. The influence of pH was studied by modifying pH of the drug solution and add 0.1 N HCl or 0.1 N NaOH. The decision and solid stage were discrete by centrifugation at 2500 rpm for 10 min in centrifuge, repeated twice to confirm that there is no scattered particles in absorption measurements and analyzed using a UV–vis spectrophotometer at a wavelength of 370 nm. The determination of the final concentration of the solution of the calibration curve. The condensation is maintained at the capacitor phase (qe/mg.g⁻¹) illustrating using the following equation:

\[ q_e = (C_o - C_e) \frac{V}{W} \] (1)

where \( C_o \) is the Primary drug condensation and \( C_e \) is the equilibrium drug condensation (mg L⁻¹), \( V \) is the volume of resolution (L) and \( W \) is Mass capacitor (gm), the percentage of drugs removed (R%) from the solution was illustrating using the following equation:

\[ R(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \] (2)

THE RESULTS AND THE DISCUSSION

The influence of Titanium dioxide Dose:

Influence of dose on drug elimination TCs (50 ppm) have been shown in Fig. 2. The raising of adsorbent dose from 0.5 to 3 g, the percentage of drug removal enhanced from 58.041 to 92.237% after 24hr of adsorption time[13]. This result attributed to as that the increase of adsorbent dose with decrease in adsorption density and increases the number of spots obtainable for adsorption spot is due basically to the lack of adsorption sites in adsorption reactions [14].

![Fig 2: influence of a large quantity of adsorbent TiO₂ to remove the percentage and quantity of adsorbed TCs drug(Exp. Condition: Temp. = 25°C, contact time 24 h, and pH of solution 6).](image-url)
Effect of Initial Concentration of TCs Drug:

Different concentrations of TCs 10-80 mgL\(^{-1}\) were chosen to study the influence of initial concentration of drug onto TiO\(_2\). The amounts of drug adsorbed at neutral pH, adsorbent dosage 2gm and 298.15K are given in Figure 3. With increasing initial concentration of TCs from 10 to 80 mgL\(^{-1}\) [13]. The removal rate decreased with an increase in drug concentrations from 93.706 to 60.227% but also increases adsorption ability with Increasing the concentration of the primary drug because it increases the number of collisions between the drug ions and the TiO\(_2\) after 24 hr of equilibrium adsorption time [14, 15].

![Image of Figure 3](image)

**Fig.3: influence of primary concentration on removal of percentage and amount of adsorbent TCs drug onto TiO\(_2\) (Exp. Condition: Temp. = 25°C, contact time 24 h, and pH of solution 6).**

Effect of pH

The measure of the acidity or basicity (pH) drug resolution is relies on pH of primary drug resolution. Some experiments were performed effect of primary pH of drug resolution on the adsorption ability and the removal rate (R%) of the TiO\(_2\) at 25 °C with 50 mg L\(^{-1}\) solutions to study the drug adsorption on TiO\(_2\) as a function of solution pH, the outcomes appear in the Fig.4.

Percentage of drug removal TCs an increases were as follows: from (7.692%) to (92.853%) for an increase in pH from 3.0 to 11. Thus it is obviously from the results that the adsorption operation is pH solution dependent, the adsorption ability and the percentage of TCs adsorbed rising with pH and being at the ultimate at pH 6. Many reasons probably attributed to the adsorption of TCs drug by the TiO\(_2\) comparative to pH [16, 17]. The exterior of TiO\(_2\) contains a large number of interactive sites, when the pH is less, the exterior of the TiO\(_2\) obtains positively charged so that making the H+ ions compete effectively with drug cations causing a reduction in the quantity of drug adsorbed (mg g\(^{-1}\)). the pH of the adsorption system rises the attractiveness of electrons due to positive drug molecules and active sites negatively charged to the adsorbed surfaces or may be rising the number of negatively charged adsorbent sites [18, 19].
Fig. 4: Influence of solution pH on the removal percentage onto TiO$_2$ (Exp. Condition: Temp. = 25°C, contact time 24 h, and pH of solution 6).

**Effect of solution temperature:**

The influence of solution temperature (288 to 323 K) on drug uptake TCs using TiO$_2$, shows Fig. (5a, 5b and 5c). The results indicate that the adsorption efficiency and percentage removal E% of TCs onto the adsorbent surface of TiO$_2$ was found depended of the temperature. It is clear that the percentage removal E% and adsorption efficiency increased because the solution temperature increased. That percentage removal E% (51-87%), (59-94%) and (70-97%) adsorption efficiency (5-21 mg g$^{-1}$), (5-24 mg g$^{-1}$) and (5-28 mg g$^{-1}$) at temperature (288 to 323 K) at the same order [20, 21].

Fig. 5: Influence of resolution temperature on adsorption of TCs drug using the exterior of TiO$_2$ a) Temp 15°C b) Temp 25°C c) Temp 50°C

**Conclusion**

In this work, the efficiency of the most widely study TiO$_2$ for the removal of drug have been discussed. Influence of different factors like pH, adsorbent dose, The condensation of the pollutant and the temperature on the adsorption operation was also discussed. the best result of pH 6 percentage removal E% (92.853%) Highlighting the mechanism of adsorption and adsorption efficiencies give indication the adsorption process was spontaneously.
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