

Adsorption and Photocatalytic Degradation of Pharmaceutical Amoxicillin using TiO₂ Nanoparticles in Aqueous Solutions: Oxidative Coupling as Spectrophotometric Method

Ayad F. Alkaim¹ · Aseel M. Aljobree²

^{1,2}College of science for women-Chemistry Department/ university of Babylon –Iraq

Corresponding author

Ayad F. Alkaim

alkaimayad@gmail.com

Abstract

Determination of Amoxicillin (AMX) drug using the oxidative coupling reaction of 4-amino antipyrine (4AAP) in the found of K₃[Fe(CN)₆] in the basic medium to give a red-colored chromophore that estimated spectrophotometrically at 508 nm. at 25°C. The good reagent concentration of 4-amino antipyrine of 0.3gm/100 ml and use potassium ferricyanide as oxidant of 0.3gm/100 ml. the photocatalytic degradation of an aqueous solution of Amoxicillin has studied in the several conditions in the found of TiO₂ Nano-particles Titanium dioxide suspension. The affect of several factor like weight of titanium dioxide, Amoxicillin concentration. Data appeared that, the photocatalytic degradation method was great at the beginning and then decreased with time. The photocatalytic degradation efficiency raise through increasing catalyst loading from 0.05 g to 0.2 g and lowering with the raise in catalyst loading. Appeared that the rate of photocatalytic degradation was increased with decreasing AMX drug concentration. also study Removal percentage (E%) of a real sample (mixture of pharmaceuticals compounds) from aqueous solution find when time raise the absorption lowering and give greater removal percentage (E%) .

Keywords: Adsorption , Removal , Photocatalytic , Pharmaceutical , Amoxicillin drug , Titanium dioxide nanoparticles , Oxidative coupling .

Introduction

One of the ecological contaminants is pharmaceutical products. Pharmaceutical are most utilized to enhance health human and utilized for animal treating and also in agriculture. Between the pharmaceutical products, antibiotics are the utmost and more utilized in the treating of bacterial infections in plants ,people and animals [1-3] .Antibiotics has been frequently useful in microbe inactivation , husbandry animal, chemical therapy, and agriculture. Amoxicillin (AMX), as a important broad-spectrum and semisynthetic antibiotic penicillin, have widely utilized in animal and drug veterinary [4-8]. advanced oxidation methods, like oxidation, oxidation ozone, light Fenton and semiconductor catalytic oxidation, require a great quantity of energy or substances to attain great enactment. Amid the numerous photo catalysts, TiO₂ consider utmost communal and affective because of its unique conduction band position and surface structure TiO₂ as an cheap, available commercially, and non-toxic photo catalyst has attracted raising attention for waste water treating [9, 10] . (TiO₂) has conceder as a hetero -generous photo catalyst and has demonstrated its potential of the degradation of organic composites in aqueous methods . A main difficulty encountered through this material is the time-consuming and uneconomic retrieval of Titanium dioxide and the need of great photo catalyst loadings [11-13].

Experimental

Preparation standard solutions

preparing of *Amoxicillin drug* (500 mg/L) stock solution . through dissolving 0.5gm of drug *Amoxicillin* in D.W .The solution was completing to 500 mL for D.W. Concentrations of drug was estimation via finding out the absorbance at the characteristic wavelength utilizing a double beam UV/Visible spectrophotometer (UV–Vis spectrophotometer, Shimadza 1650). Calibration curves was plotted among absorbance and concentration of the solution drug.

Materials

Commercial powder TiO_2 were purchased for (Germany /sigma-Aldrich,) *Amoxicillin drug* (AMX) was supported via Hila Company of samara factory . chemical formula: $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_5$ S, MW: 365.4 g/mol, λ_{max} 509 nm] The chemical structure of amoxicillin (Figure 1) . Wholly chemicals utilized in this study was analytical degree and utilized immediately without moreover purification.

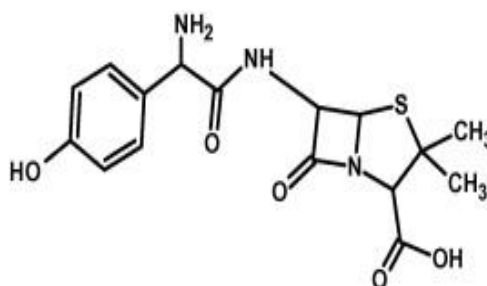


Figure 1: The chemical structure of amoxicillin ((2S.,5R.,6R.)-6-3,3-di-methyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid).[3]

Photo catalytic experiments

The photo catalytic activity of the TiO_2 nanoparticles photo catalyst was assessed via the degradation of AMX drug waste water. Wholly data was carry out in a photoreaction vessel, of 100 ml of whole efficiency . A 125 W great-pressure mercury lamp . The beaker was put below the light of the ultraviolet preserve the dimension among the light source and the surface of the solution planned via utilizing UV A-meter (Dr. Honle/Germany).Prior for each test, the lamp was turned on and warm up of around 10 minute to obtain a constant out put. Batch tests were performed as the following procedure, 0.15 g TiO_2 photo catalyst additional in to 100 mL solutions drug, the mix was stirred in dark about 20 minute to allow adsorption physical of drug molecules on catalyst particles reaching the equilibrium.

Sample collected at uniform term and was promptly centrifuged to remove analysis particles .Determination of Amoxicillin drug using the oxidative coupling reaction of 4- amino antipyrine in the found of potassium ferricyanide in the basic medium to gave a red-colored chromophore that determination spectrophotmetrically at 508 nm. The best concentration 0.3gm/100 ml of 4AAP was and 0.3gm/100 ml of the oxidant and calculated the calibration curve.

Effect of several factor like quantity of catalyst ($0.05\text{--}2.0\text{ g L}^{-1}$), and concentration of drug ($10\text{--}50\text{ mgL}^{-1}$) on the photo degradation capacity was studied. The removal

percentage E% of photo catalytic degradation of AMX drug and apparent first order rate constant was calculated utilizing the following relationships

$$\text{PDE (\%)} = (C_0 - C_t)/C_0 \times 100 \quad (1)$$

$$\left(\frac{C_t}{C_0}\right) = e^{-kt} \quad (2)$$

Where, C_0 and C_t are the primary and photolyzed conc. (mg/L), at the same order , (photo catalytic degradation efficiency) PDE, k is the apparent first order rate constant (min^{-1}) and t is time of irradiation (min.).

Results and discussion

Absorption spectra

The formation of panic-colored compound was employed in the quantitative detection of amoxicillin with 4- aminoantipyrine existence of $\text{K}_3[\text{Fe}(\text{CN})_6]$, when AMX was firstly mix with potassium ferricyanide in basic medium with reagent 4-aminoantipyrine, red-colored compound was formed with maximum absorbance in the visible at 509nm[8] as shown in Figure 2.

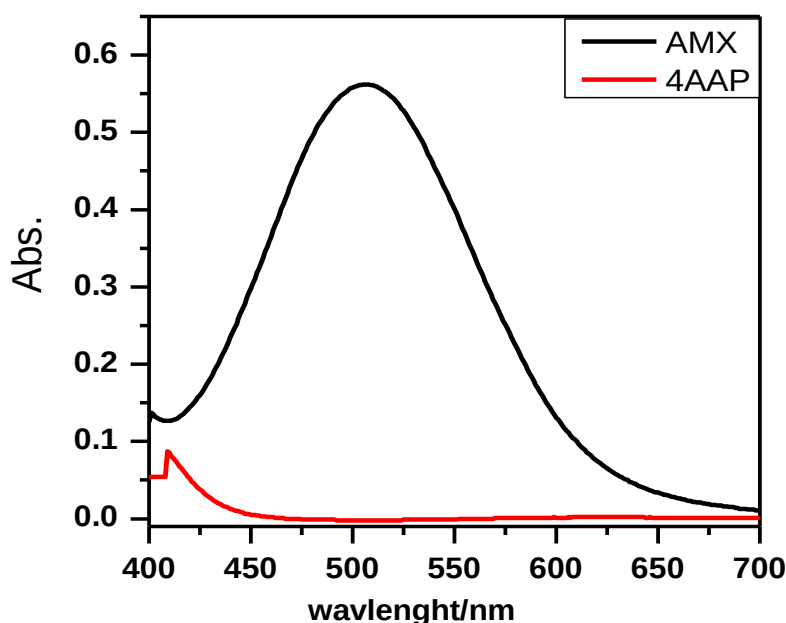


Figure 2: Absorption spectra solution of AMX of (100mgL^{-1}) against reagent blank.

Effect of reagent and oxidant concentration

The affects of various quantities of 4AAP reagent and oxidant potassium ferricyanide were studied. The highest absorbance and maximum color intensity of the complex were achieved with 0.3gm/100ml of reagent 4AAP and 0.3gm/100ml of oxidant potassium ferricyanide solutions [8] show in (Figure 3).

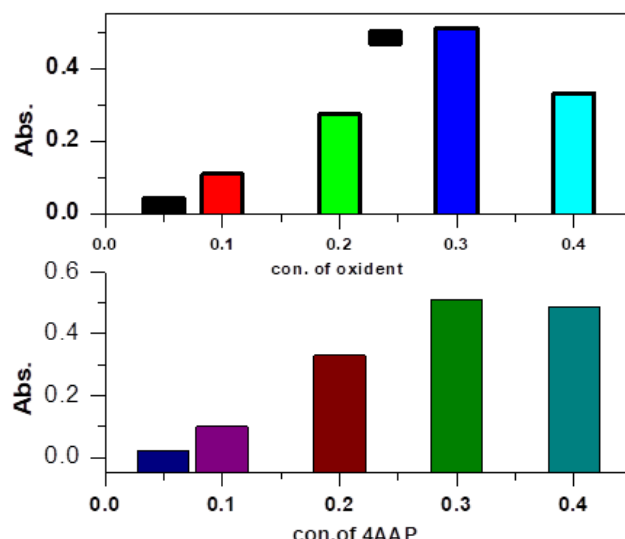


Figure 3 : Optimum absorption of compound in the presence of different conc. of reagent and oxidant .

Effect of weight dosage

The influence concentration of the photo catalyst ($0.05\text{--}2\text{ g/L}^{-1}$) in the photo catalytic degradation of drug AMX was inspected at an primary drug AMX conc. of 10 mg/l , ($0.94\text{ }\mu\text{ens. sec}^{-1}$) , light intensity flow rate of O_2 (5 mL. min^{-1}) and concentration buffer of the suspension pH 6.[14] Figure 4, data indicates that the rate of photo degradation raise via raising the quantity of TiO_2 to 2 g/L^{-1} . The data is consistent by several another research that they are the best quantity of loading catalyst [13, 15, 16]. When the conc. of the catalyst is under the best value, the affective surface of the catalyst and absorption of the light are the chief agent that estimation the photo catalytic degradation rate [16-18].

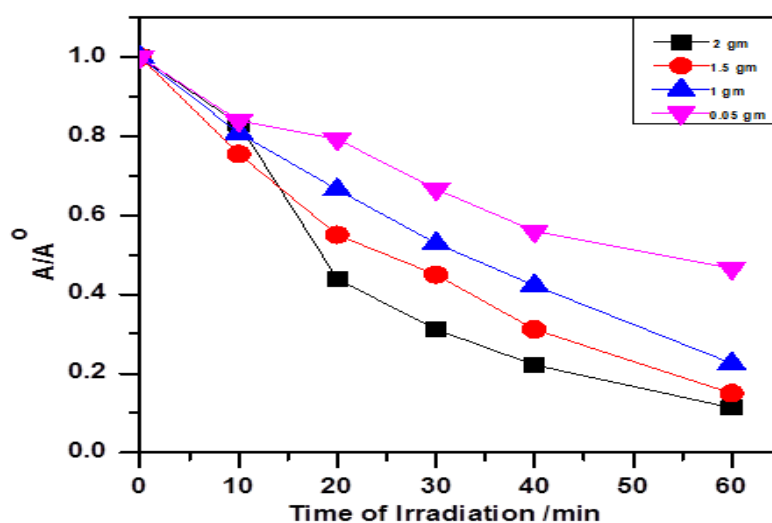


Figure 4. The effect weight of TiO_2 on Photocatalytic degradation of AMX drug *Exp.* Cond.: Temp. $25\text{ }^\circ\text{C}$, and L.I. 2.42 mW.cm^{-2}

The Effect of initial AMX drug concentration on photo catalytic degradation processes :

The effect of alteration primary (10 – 50 ppm) on Photo catalytic degradation method of AMX drug was studied utilizing 0.15/ 100 cm³ , the light intensity equal to 1.4 mW/cm², and temperature at 298 K . The data appear in Figure 5 .It has been observed that the rate of Photo catalytic degradation slowly lowering with the raising of primary concentration primary AMX drug. This behavior might be give details, the conc. 10 ppm was the most favorable conc. to cover the major area of the TiO₂ particles, thus absorbed maximum exciting photons to generate greater conc. of the activated TiO₂ semiconductor [13, 19, 20].

The concentration of drug AMX drug 10 ppm have the most favorable Photo catalytic degradation capacity give 98% of one hour [21, 22]. The data of the change in removal Photo catalytic degradation capacity (E %) concentration of AMX drug plotted in Figure 6.

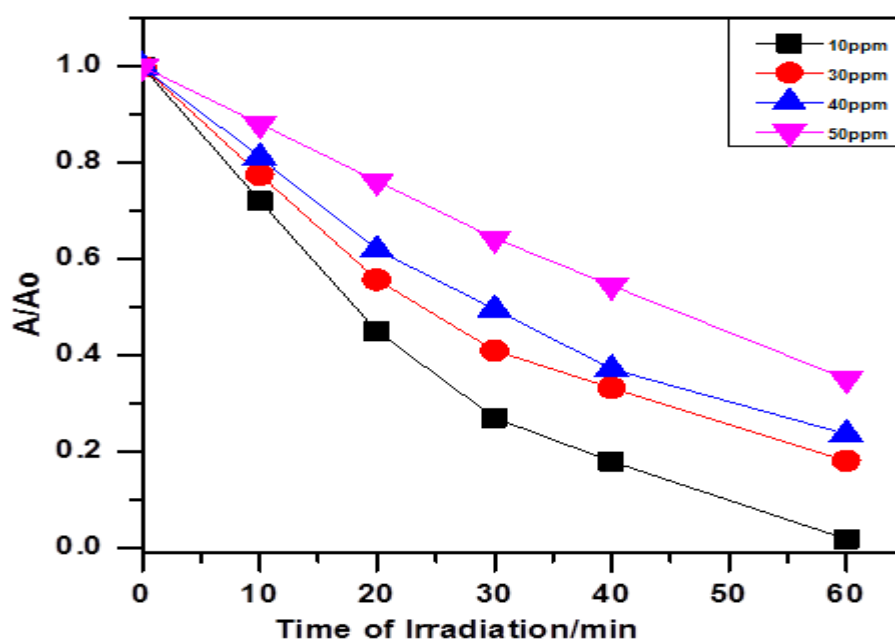


Figure 5 : Photo catalytic degradation of AMX drug at several primary concentration. Exp. Cond.: weight quantity 0.2 g.L⁻¹, Temp. 25 °C, and L.I. 2.42 m.W.cm-

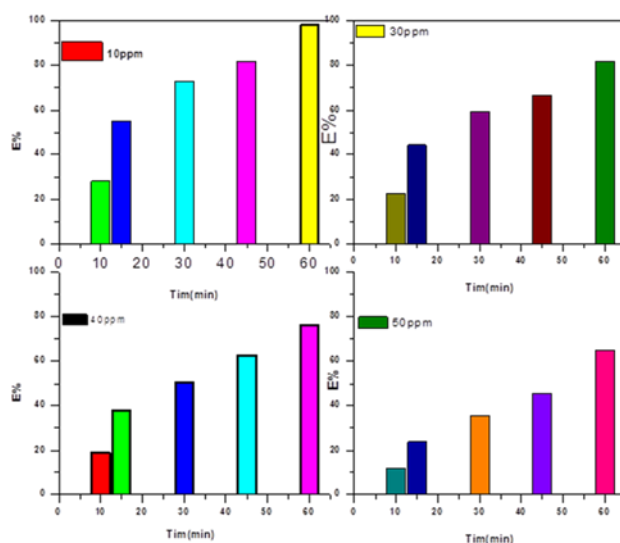


Figure 6 : percent removal AMX drug at several primary concentration. Exp. Cond.: weight quantity 0.2 g.L^{-1} , Temp. 25°C , and L.I. 2.42 m.W.cm^{-2} .

Removal of a real sample (mixture of pharmaceuticals compounds) from aqueous solution.

A real sample 100 ml of pharmaceutical contaminants of a refractory concentration was utilized in this study, after that additional about 0.2 g.L^{-1} of TiO_2 in beakers, and put under the light ultraviolet preserving the space among the surface of the solution and the light source controlled via utilizing UVA-meter (Dr. Honle/Germany) of one hour, then isolated were detached via centrifuge and measured the residual concentration through utilizing UV-Vis. spectrophotometer at selection wavelength at 273 nm without oxidative coupling appear in fig. 7. and find when time raise the absorption lowering and give great removal percentage (E%) [23, 24].

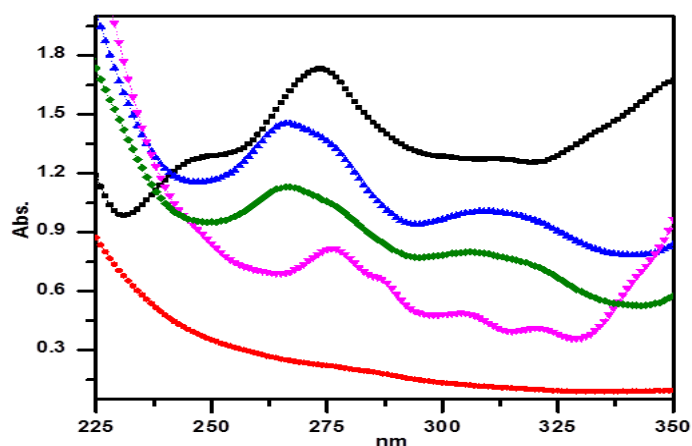


Figure 7: Effect Removal of the sample real (mixing of several pharmaceutical compounds) via utilizing Titanium dioxide nanoparticles.

Concoction

The maximum concentration 0.3gm/100 ml of 4-aminoantipyrine and 0.3gm/100 ml of $K_3[Fe(CN)_6]$ to gave great stability indeed greatly extra absorptivity to improve measurements and decrease mistake. The obtained data appear that AMX drug can be simply degraded via a TiO_2 helped method in aqueous dis-persions below UV irradiation. The optimum Photo catalytic degradation capacity of the conc. Amoxicillin drug 10 mg/l give to 98% after one hour . Removal percentage of the sample real (mixture of pharmeceuticals compounds) from aqueous solution find when time raised the absorption lowering and give greater removal percentage. The data indicated that the light intensity and catalyst loading, the primary concentration of drug effected the degradation capacity of TiO_2 powders obviously.

References:

1. Aljeboree, A.M. and A. Alshirifi, *Spectrophotometric Determination of phenylephrine hydrochloride drug in the existence of 4-Aminoan tipyrine: Statistical Study*. International Journal of Pharmaceutical Research, 2018. **10**(4).
2. Jafari, K., M. Heidari, and O. Rahmadian, *Wastewater treatment for Amoxicillin removal using magnetic adsorbent synthesized by ultrasound process*. Ultrasonics Sonochemistry, 2018. **45**: p. 248-256.
3. Aseel M. Aljeboree , A.N.A., *Adsorption of Pharmaceuticals as emerging contaminants from aqueous solutions on to friendly surfaces such as activated carbon: A review* J. Pharm. Sci. & Res. , 2018. **10**(9): p. 2252-2257
4. A. Pasamontes, M.P.C., *Determination of amoxicillin in pharmaceuticals using sequential injection analysis and multivariate curve resolution*. Analytica Chimica Acta, 2004. **515**(1): p. 159-165.
5. Aljeboree, A.M. and A.N. Alshirifi, *Oxidative coupling of Amoxicillin using 4-Aminoantipyrine: Stability and higher sensitivity*. Journal of Physics: Conference Series, 2019. **1294**(5): p. 052001.
6. Aseel M. Aljeboree, A.S.A., *Removal of Pharmaceutical (Paracetamol) by using CNT/ TiO_2 Nanoparticles*. Journal of Global Pharma Technology, 2019. **11**(01): p. 199-205.
7. Zhang, Y., et al., *Comparison of amoxicillin photodegradation in the UV/H₂O₂ and UV/persulfate systems: Reaction kinetics, degradation pathways, and antibacterial activity*. Chemical Engineering Journal, 2019. **372**: p. 420-428.
8. ASEEL M ALJEBOREE , ABBAS NOOR ALSHIRIFI, *Spectrophotometric Determination of phenylephrine hydrochloride drug in the existence of 4- Aminoantipyrine: Statistical Study*. International Journal of Pharmaceutical Research, 2018. **10**(4).
9. Song, J., et al., *KBrO₃ and graphene as double and enhanced collaborative catalysts for the photocatalytic degradation of amoxicillin by UVA/ TiO_2 nanotube processes*. Materials Science in Semiconductor Processing, 2016. **52**: p. 32-37.
10. Hua, W., E.R. Bennett, and R.J. Letcher, *Ozone treatment and the depletion of detectable pharmaceuticals and atrazine herbicide in drinking water sourced from the upper Detroit River, Ontario, Canada*. Water Research, 2006. **40**(12): p. 2259-2266.
11. Jiang, G., et al., *TiO_2 nanoparticles assembled on graphene oxide nanosheets with high photocatalytic activity for removal of pollutants*. Carbon. **49**(8): p. 2693-2701.
12. Kanakaraju, D., et al., *Titanium dioxide/zeolite integrated photocatalytic adsorbents for the degradation of amoxicillin*. Applied Catalysis B: Environmental, 2015. **166-167**: p. 45-55.
13. Alkaim, A.F., Alrobayi, Enas M ,Algubili, Abrar M and Aljeboree, Aseel M, *Synthesis, characterization, and photocatalytic activity of sonochemical/hydration–dehydration prepared ZnO rod-like architecture nano/microstructures assisted by a biotemplate*. Environmental technology, 2017. **38**(17): p. 2119-2129.
14. HUSSEIN, A.F.A.a.F.H., *PHOTOCATALYTIC DEGRADATION OF EDTA BY USING TiO_2 SUSPENSION*. Int. J. Chem. Sci., 2012. **10**(1): p. 586-598.
15. Enas M Alrobayi, A.M.A., Aseel M Aljeboree, Ayad F Alkaim, Falah H Hussein, *Investigation of photocatalytic removal and photonic efficiency of maxilon blue dye GRL in the presence of TiO_2 nanoparticles*. Particulate Science and Technology, 2017. **35**(1): p. 14-20.
16. A. Akyol, H. C. Yatmaz, and M. Bayramoglu, *Photocatalytic decolorization of Remazol Red RR in aqueous ZnO suspensions*. Appl Catal B: Environ, 2004. **54**(1): p. 19-24.
17. Ruwaida A Raheem, H.Y.A.-g., Aseel M Aljeboree, Ayad F Alkaim, *Photocatalytic degradation of reactive green dye by using Zinc oxide*. Journal of Chemical and Pharmaceutical Sciences, 2016. **9**(3): p. 1134-1138.
18. H. Wang, C. Xie, W. Zhang, S. Cai, Z. Yang, and Y. Gui, *Comparison of dye degradation efficiency using ZnO powders with various size scales*. J. Hazard Mater., 2007. **141**(3): p. 645-652.
19. R.P. Cavalcante, R.F.D., B. Bayarri, O. Gonzalez, J. Giménez, S. Esplugas, A. Machulek, *Photocatalytic mechanism of metoprolol oxidation by photocatalysts TiO_2 and TiO_2 doped with 5% B: primary active species and intermediates*. Appl. Catal. B Environ., , 2016. **194** p. 111-122.

20. AF Alkaim, T.K., FH Hussein, R Dillert, DW Bahnemann, *Solvent-free hydrothermal synthesis of anatase TiO₂ nanoparticles with enhanced photocatalytic hydrogen production activity*. Applied Catalysis A: General 2013. **466** p. 32-37.
21. Wang, C., Zhang, Y., Zhu, T., Wang, P., and Gao, S., *Photocatalytic degradation of methylene blue and methyl orange in a Zn(II)- based Metal-Organic Framework*. Desalination Water Treat, 2016. **57**: p. 17844-17851.
22. Aljeboree, A.M., et al., *Photocatalytic Degradation of Textile Dye Cristal Violet Wastewater using Zinc Oxide as a Model of Pharmaceutical Threat Reductions*. Journal of Global Pharma Technology, 2019. **11**(3): p. 138-143.
23. Aljeboree, A.M., *Removal of Vitamin B6 (Pyridoxine) Antibiotics Pharmaceuticals From Aqueous Systems By ZnO*. International Journal of Drug Delivery Technology 2019. **9**(2): p. 125-129.
24. Aseel M. Aljeboree, H.Y.A.-G., Mohammed H. Said and Ayad F. Alkaim, *THE EFFECT OF DIFFERENT PARAMETERS ON THE REMOVAL OF VITAMIN B12 DRUG (AS A MODEL BIOCHEMICAL POLLUTANTS) BY AC/ CLAY*. **Biochem. Cell. Arch.** , 2019. **19**(1): p. 000-000.