World Journal of Pharmaceutical Sciences
ISSN (Print): 2321-3310; ISSN (Online): 2321-3086
Published by Atom and Cell Publishers © All Rights Reserved
Available online at: http://www.wjpsonline.org/
Original Article

Photocatalytic Degradation of Tetracycline in Aqueous Solutions by Kaolin nanoparticles

G. O. El-Sayed[1]*, H. A. Dessouki[1], H. S. Jahin[2] and S. S. Ibrahiem[2]

[1]Chemistry Department, Faculty of Science, Benha University, Benha, Egypt
[2]National Water Research Center, Central Lab. for Environ. Qual. Monit., Elqanater Elkhayria, Egypt

Received: 10-02-2015 / Revised: 16-03-2015 / Accepted: 31-03-2015

ABSTRACT

Kaolin has been synthesized in the nano-sized (30-60 nm) and examined as a photocatalyst for degradation of tetracycline in its aqueous solution. The photocatalytic behavior was performed under the effect of UV-radiation. The influences of various operational parameters such as catalyst dose, drug concentration, and time of exposure on percentage photodegradation of tetracycline chloride were investigated. The results reveal that the maximum degradation (97%) occurred after about 120 min irradiation. The degradation rate follows first order kinetics with a rate constant of 0.02 min^{-1}.

Keywords: tetracycline, photocatalytis, kaolin, nanoparticles

✦

INTRODUCTION

Antibiotics are organic compounds effective against bacterial infections, certain fungal infections and some kinds of parasites. Hazardous drugs are often prepared and administered to human and animal patients in hospitals, outpatient centers, physician's offices, veterinary hospitals and veterinary clinics. Generally, pharmaceuticals reach waterways through the discharge of wastewaters and effluents on environment, which often are not properly treated. Several alternatives to eliminate pharmaceutical compounds from water have been considered. These include reverse osmosis [1], adsorption onto activated carbons [2], ozonation [3], advanced oxidation processes, such as the Fenton or photo-Fenton system [4], ultrasound [5], peroxidation combined with UV light [6], photocatalysis using TiO_2 [7] or advanced oxidation hybrid processes [8]. Advanced oxidation processes (AOPs), are based on the production and use of hydroxyl radicals, which are strong oxidizing species that react with most organic contaminants [9]. The majority of pharmaceuticals are photo-active having the ability to absorb light as because their structures generally contain aromatic rings, heteroatoms, and other functional groups that enable them to absorb UV and visible radiation (direct photolysis) or to react with photosensitizing species (indirect photolysis) [10]. The AOPs involving UV irradiation seems to be effective for the degradation of many organic compounds [11,12], in which alkylic-oxidation, dealkylation, and dechlorination-hydroxylation (minor in catalytic oxidation process without UV-light) are the main pathways. One of the new methods of wastewater treatment containing dyes is their photocatalytic degradation in solutions illuminated with UV or solar radiation, which contains a suitable photocatalyst, mainly TiO_2. The removal of tetracycline (TC) by TiO_2 and the mesoporous binary system TiO_2–SiO_2 have been studied in batch [13]. The interactions of TC with nanoscale zerovalent iron (NZVI) modified by polyvinylpyrrolidone were investigated using batch experiments [14] as a function of reactant concentration, pH, temperature, and competitive anions. Batch tests were employed to estimate the optimal conditions for photocatalytic degradation of tetracycline using In_2S_3 under natural solar radiation [15]. The degradation of TC by the photo-Fenton process was evaluated under black-light and solar irradiation. The influences of iron source ($Fe(NO_3)_3$ or ferrioxalate), hydrogen peroxide and matrix were evaluated [16].

Tetracycline, is an antibiotic used in the treatment of infections caused by a wide range of anaerobic bacteria, protozoa and bacteroides, including trichomoniasis, amoebiasis, gingivitis and

---

***Corresponding Author Address:** Prof. Dr. Gamal Owes El-Sayed; Chemistry Department, Faculty of Science, Benha University, Benha, Egypt; E-mail:gamaloelsayed@yahoo.com*

vaginosis. In this study, the degradation of tetracycline using kaolin nanoparticles was examined. Operating factors such as initial drug concentration, photocatalyst dosage, and photocatalysis time were investigated in order to evaluate the extent of mineralization.

MATERIALS AND METHODS

Materials: All chemicals used throughout the experiments were of analytical grade. Tetracycline (Fig. 1) was obtained from EIPICO, Egypt. Double distilled water was used throughout all experiments.

Preparation and characterization of Kaolin nanoparticles: Nano kaolin is a product of kaolin, also known as white clay. Kaolin was established as supplementary cementitious material in concrete. The inclusion of kaolin in concrete enhances strength and durability and prolongs concrete life span. Nano kaolin can be developed by using sol gel technique which involves high energy milling [17]. The crystalline phases of Kaolin Nanoparticles were characterized by X-Ray diffractorometer (XRD, BrukerD8 Advance, Germany) using CuKα as the radiation source (40 kv, Step Size 0.020, scan rate 0.50 min^{-1}, 200≤700) and composition analysis was done by Energy Dispersive X-ray analysis (EDAX). The Nanoparticle size and zeta potential was estimated by particle size analyzer (SZ-100 Nanoparticle, Horiba,Germany) data. The particle size and morphology of the prepared nanoparticles particle were calculated by Transmission Electron Microscope (TEM, Hitachi VP-SEM S-3400N, Germany), given a particle size 30-60 nm (Fig. 2).

Experimental procedures: The batch experiments of tetracycline degradation were performed in a 250 mL glass beaker, where a total of 100 mL of tetracycline solution was used. The solution inside the beaker was exposed vertically to a UV-254 mercury lamp (15 W) at a fixed height (20 cm) as shown in Fig. 3. After the irradiation time, samples were withdrawn from the beaker and quickly analyzed.

Tetracycline concentration was quantified by an Aquamate V4.60 UV spectrophotometer (Thermo Scientific, USA) at wavelengths of 569 nm. The amount of the drug adsorbed per unit mass of the Kaolin was evaluated by using following equations:

$$q_e = (C_0 - C_e)\frac{V}{W} \quad (1)$$

Where, C_0 is the initial metal ion concentration, and C_e is the analyte concentration at equilibrium and V is the volume of metal ion solution in milliliters, W is the mass of adsorbent in grams. The percent of drug removal was evaluated from the equation:

$$\%Removal = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Adsorption experiments: The adsorption experiments were performed in dark using 100 ml aqueous solution of tetracycline of different concentrations (1-8 mg/L) at 25 °C. Each solution was loaded with 0.01 g nano kaolin and its pH was maintained at 3.35. This pH was chosen as the optimum pH as solubility studies of tetracycline indicated that it has its high solubility around pH 3.35 [18]. As shown in Fig. 4, the percent removal of tetracycline by adsorption is greatly affected by the initial concentration of the drug, which is a prove of the dependency of the adsorption efficiency on the initial concentration of the adsorbed species. The lower uptake at higher concentration results from increased ratio of initial adsorption number of species of the adsorbate to the available surface area. For a given adsorbent dose the total number of available adsorption sites is fixed thereby adsorbing almost the same amount of adsorbate, thus resulting in a decrease in the removal of adsorbate corresponding to an increase in initial adsorbate concentration.

Adsorption isotherms*:* Adsorption isotherm indicates a graphical representation of the relationship between the amount adsorbed by a unit weight of adsorbent and that of adsorbate remaining in a test solution at a constant temperature under equilibrium condition. This representation gives the information about the distribution of adsorbed solute between the liquid and solid phases at various equilibrium concentrations. Two adsorption isotherms were applied to the adsorption process; namely: Langmuir and Freundlich isotherms.

Langmuir isotherm model: This model describes the formation of a monolayer adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. This model assumes that there is no interaction between molecules adsorbed on neighboring sites [19]. Based upon these assumptions, Langmuir represented the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \quad (3)$$

where, C_e is the concentration at equilibrium (mg/L), q_e is the adsorption capacity at equilibrium in mg/g, Q_0 is the theoretical maximum adsorption capacity and K_L is the Langmuir adsorption constant (L/mg). The linear plot of C_e/q_e vs C_e shows that adsorption follows the Langmuir adsorption model (Fig. 5a). The values of q_e and K_L can be calculated (Table 1) from the slope and intercept of the plot, respectively.

Freundlich isotherm model: The Freundlich isotherm model The Freundlich equilibrium isotherm equation is an empirical equation used for the description of multilayer adsorption with interaction between adsorbed molecules. The Freundlich equation implies that adsorption energy exponentially decreases on the finishing point of adsorptional centres of an adsorbent:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F is the Freundlich isotherm constant (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1}, and n represents the adsorption intensity. The plot of ln C_e versus ln q_e gives a straight line (Fig. 5b) with slope 1/n and intercept ln K_F. The data obtained from Freundlich isotherm are shown in Table 1. As seen, the regression correlation coefficient calculated for Freundlich model (R^2=0.9749) is less than that of Langmuir model (R^2 = 0.9829). This indicates that the Langmuir model is more suitable for describing the sorption of tetracycline compared to Freundlich model.

Direct photolysis and photocatalysis: Photocatalytic mechanism suggests, both the photocatalyst and a light source are necessary for the degradation reaction to occur. Experiments were conducted for the removal of tetracycline from aqueous solution in the presence of kaolin nanoparticles alone and under the influence of UV radiation and in the presence of both (Fig. 6). As shown in the figure, maximum removal (97%) for initial tetracycline concentration of 1 mg/L occurred in presence of Kaolin nanoparticles (0.1 g/L) under the effect of UV radiation.

Effect of kaolin nanoparticles loading: The effect of photocatalyst concentration on the degradation rate of tetracycline has been investigated during exposure to UV light by employing different doses of Kaolin nanoparticles varying from 0.05 to 0.3 g/L for 1 mg/L drug. It is observed that the initial rate increases with the increase in catalyst concentration, becomes maximum and remains almost constant thereafter after about 120 min as shown in Fig. 7. The optimum catalyst concentration for the degradation of tetracycline is 0.2 g/L. The influence of photocatalyst dosage on the degradation of tetracycline can be explained in terms of the active sites on the kaolin surface available for photocatalytic degradation and the penetration of UV light into the nanoparticles suspension. As the dosage of photocatalyst was increased, an increase in the active surface area of kaolin was obtained. When the kaolin dosage was overdose, a shielding effect of excess particles occurred owing to an increase in the turbidity of the kaolin suspension [20]. Hence further addition of catalyst does not lead to the enhancement of the degradation rate.

Effect of initial tetracycline concentration: Initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. The influence of initial analyte concentration on the photocatalytic degradation of tetracycline is illustrated in Fig. 8. The examined range of the initial tetracycline concentration was varied from 1 to 8 mg/L. As the concentration increases, the degradation efficiency reduces. The possible reason is that, as the initial concentration of the drug increased, more drug molecules are adsorbed onto the surface of kaolin. But the adsorbed drug molecules are not degraded immediately because the intensity of the light and the catalyst amount is constant. Also with an increase in the drug concentration, the concentration of unadsorbed dye in the solution increases leading to lesser penetration of light through the solution on to the surface of kaolin thereby decreasing the degradation efficiency.

Kinetics of irradiation experiments: The rate constant value for tetracyclin degradation using kaolin nanoparticles was calculated using first order rate equation [21]:

$$ln \frac{C_0}{C_t} = kt \quad (6)$$

where, k is the first order rate constant.

A plot of ln(C_0/C_t) versus time represents a straight line, and the slope is equal to the apparent first order rate constant. Fig. 9 shows the plot depicting linear relationship between ln(C_o/C_t) and time and from the slope of the graph, rate constant value was calculated and was found to be 0.02 min^{-1}. The decrease in photocatalytic efficiency can be explained by the fact that transition metal ions substituted in Kaolin lattice act as recombination centers for electron holes [22].

CONCLUSION

Heterogeneous photocatalysis using Kaolin nanoparticles as photocatalyst was proven to be an effective method for the degradation of tetracycline in its aqueous solution. The experimental results demonstrated that increasing the substrate concentration, light exposure period, and Kaolin dosage in an appropriate range contributed to the photocatalytic degradation of tetracycline. The removal of the drug by adsorption on Kaolin nanoparticles was found to follow Langmuir isotherm model. The rate of photodegradation follows first order with a rate constant 0.02min^{-1}.

Table 1: Langmuir and Freundlich parameters of adsorption of tetracycline on Kaolin nanopsrticles

Langmuir isotherm			Freundlich isotherm		
Q_0 (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
52.63	3.275	0.9829	32.655	2.890	0.9749

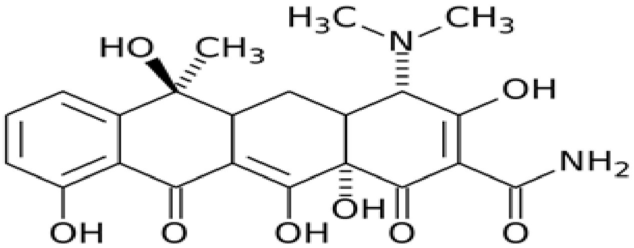


Fig (1): Molecular structure of Tetracycline

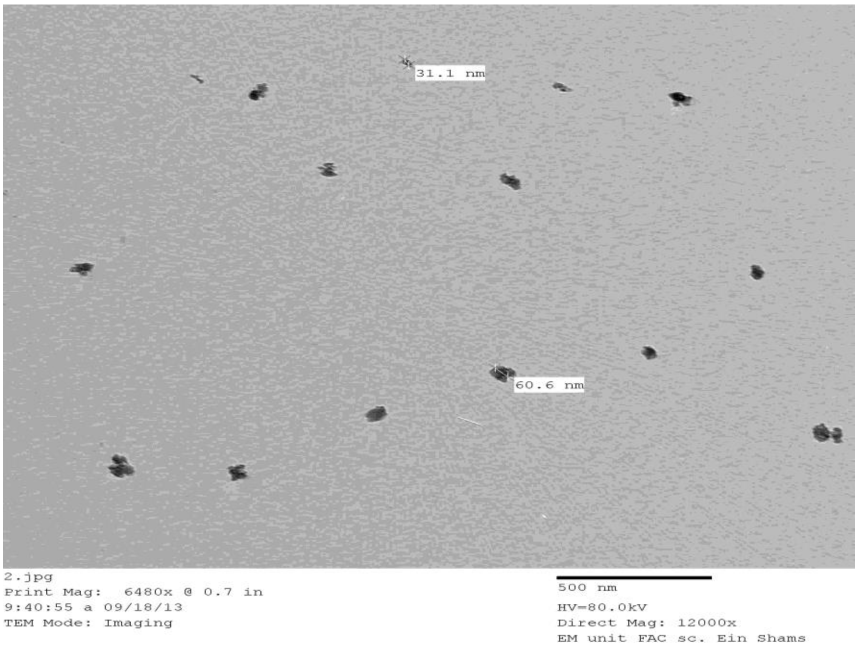


Fig. 2. TEM image of nano Kaolin nanoparticles

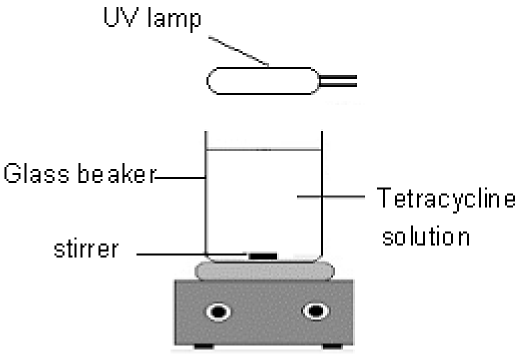


Fig. 3. Schematic diagram of the photocatalytic system

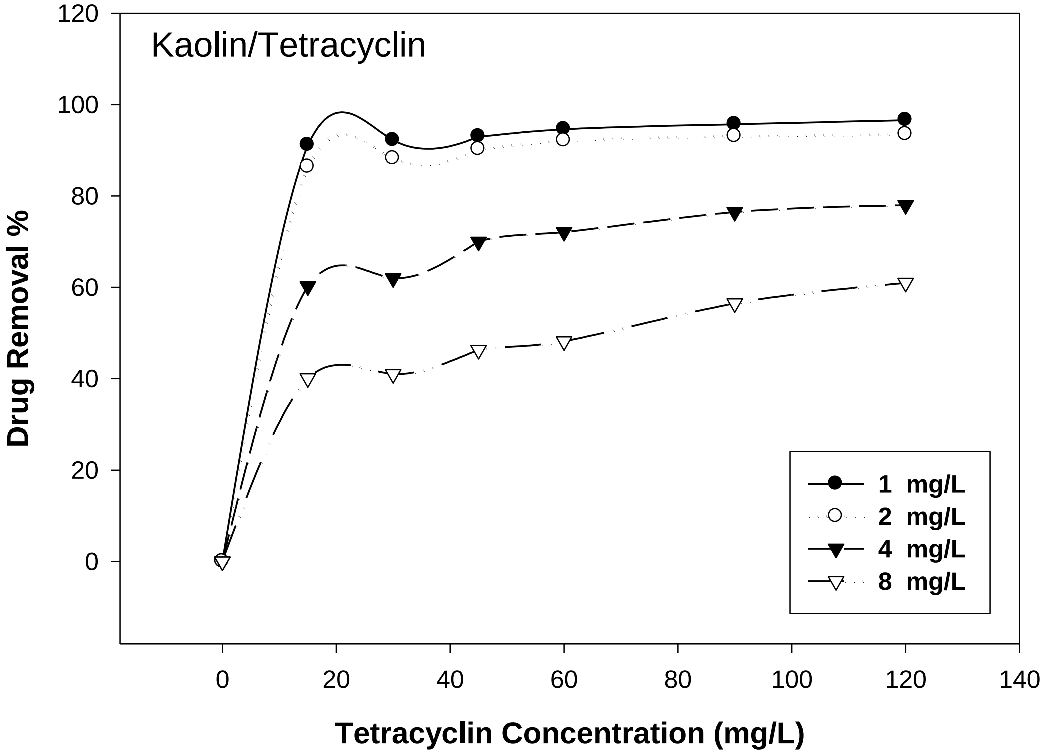
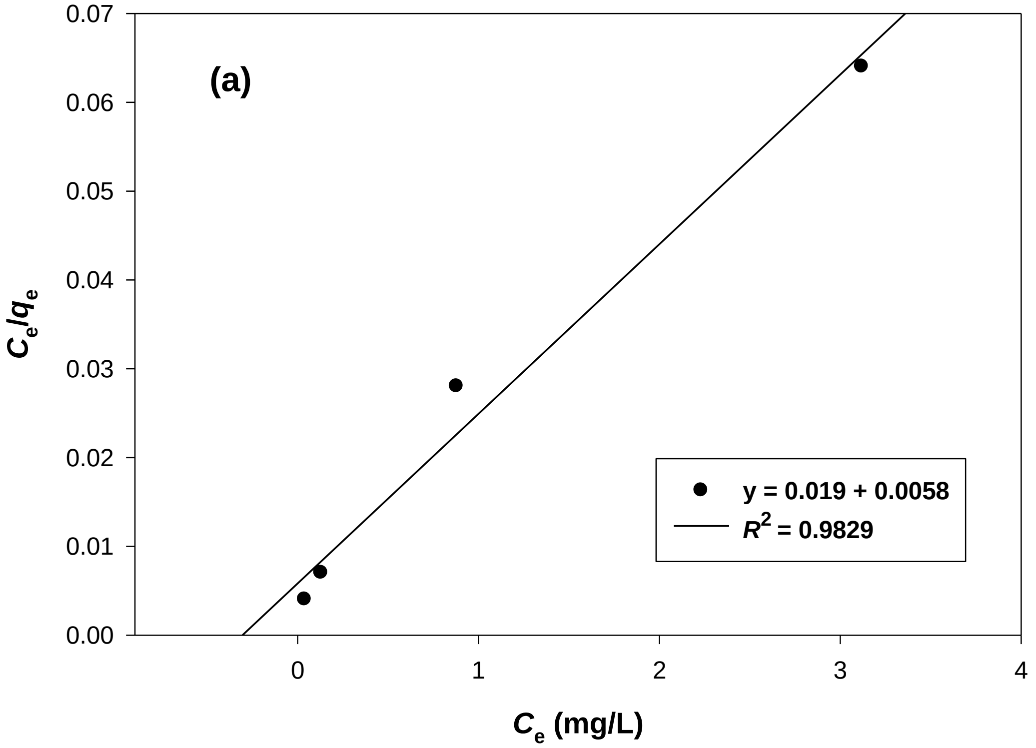


Fig. 4. Effect of initial concentration of tetracycline on percent removal



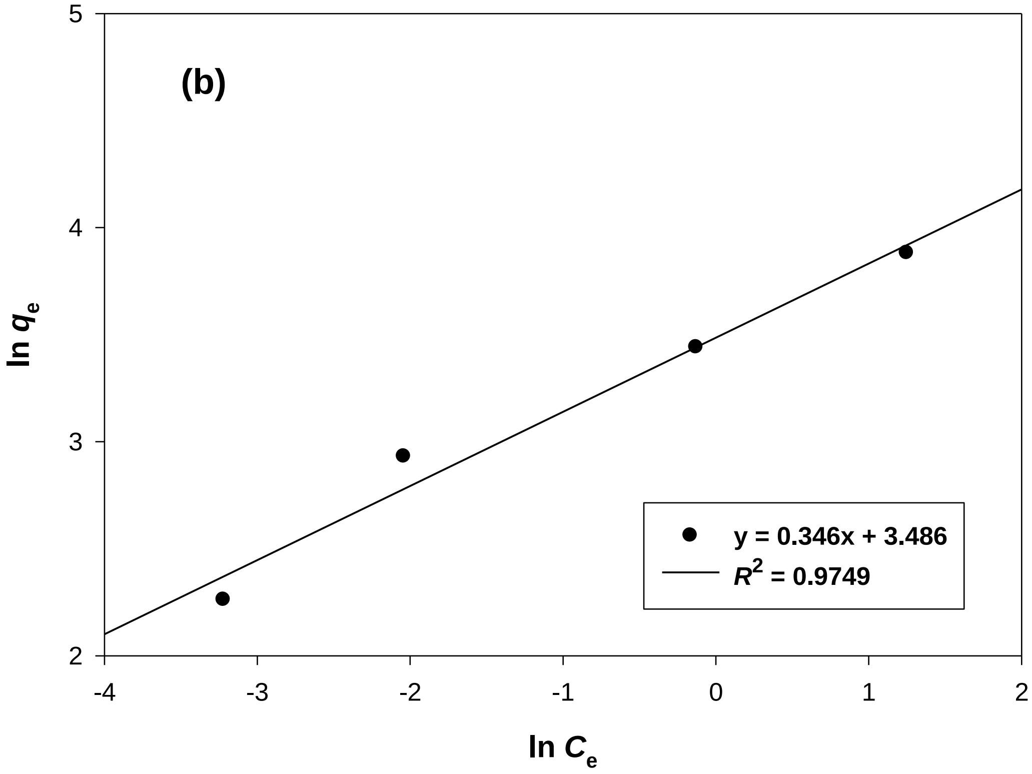


Fig 5: Plots of (a) Langmuir and (b) Freundlich isotherm models for adsorption of tetracycline on Kaolin nanoparticles.

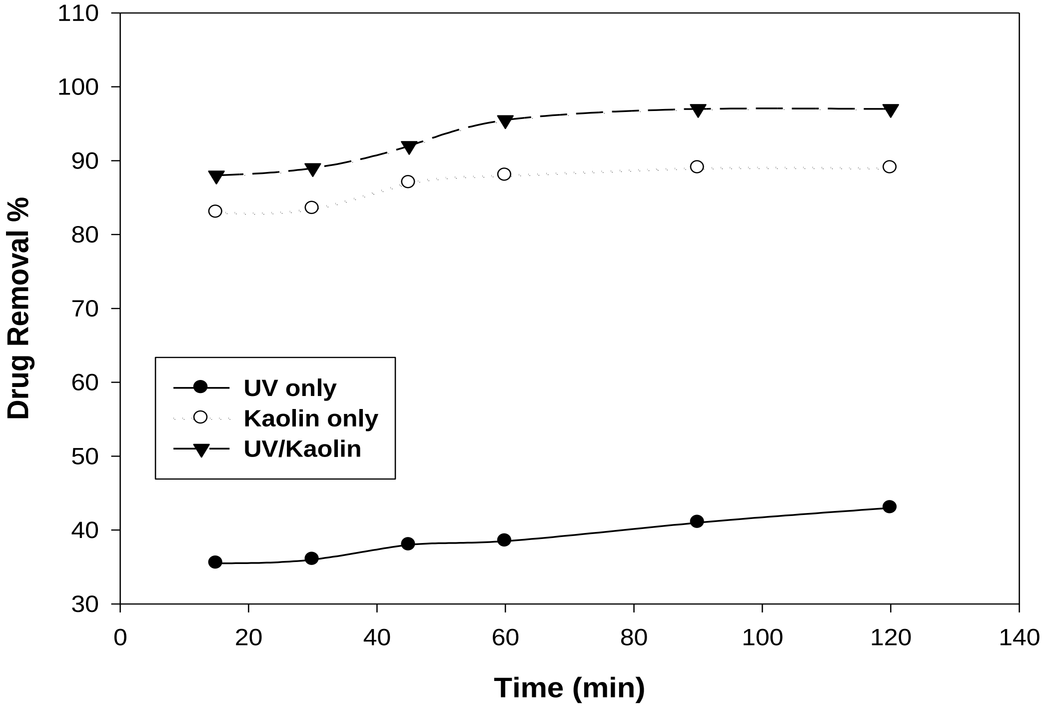


Fig. 6. Effect of degradation time of Tetracycline under different conditions

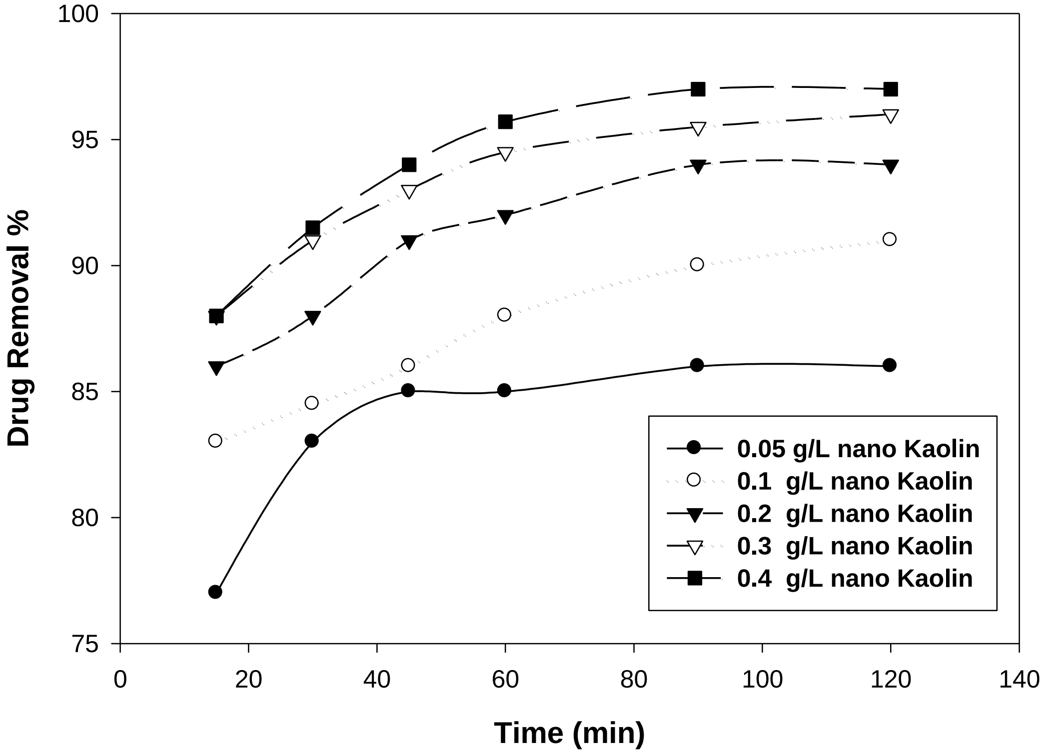


Fig. 7. Effect of kaolin dose on tetracycline photodegradation

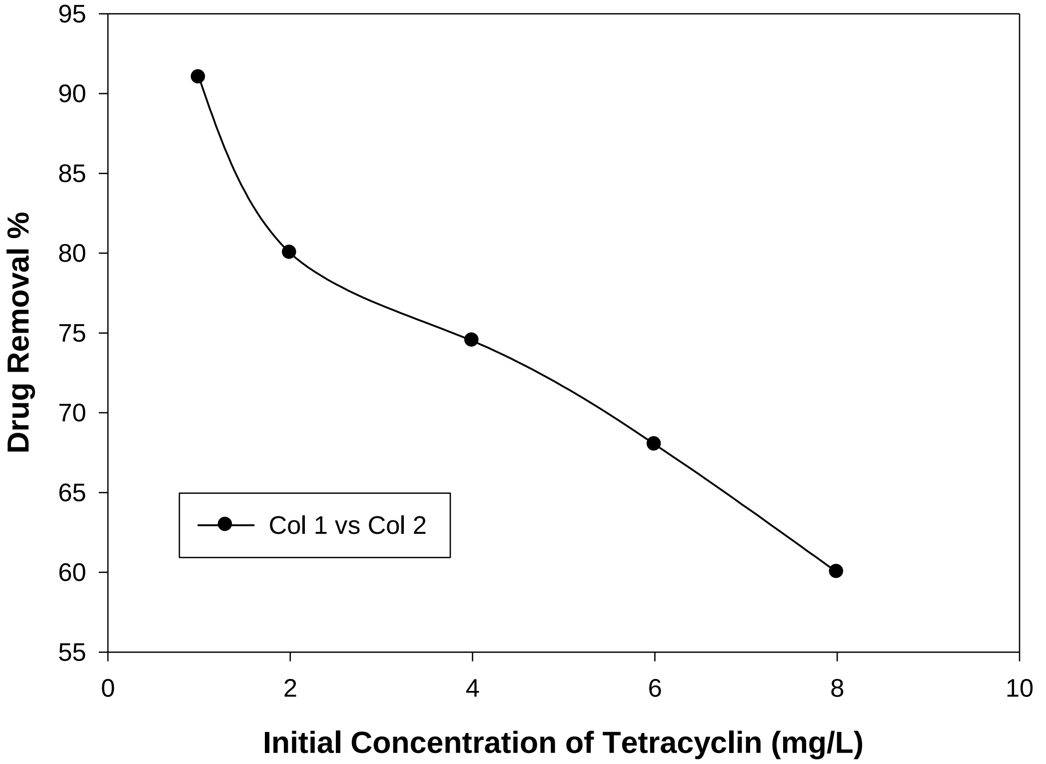


Fig. 8. Effect of initial tetracycline concentration of percent removal

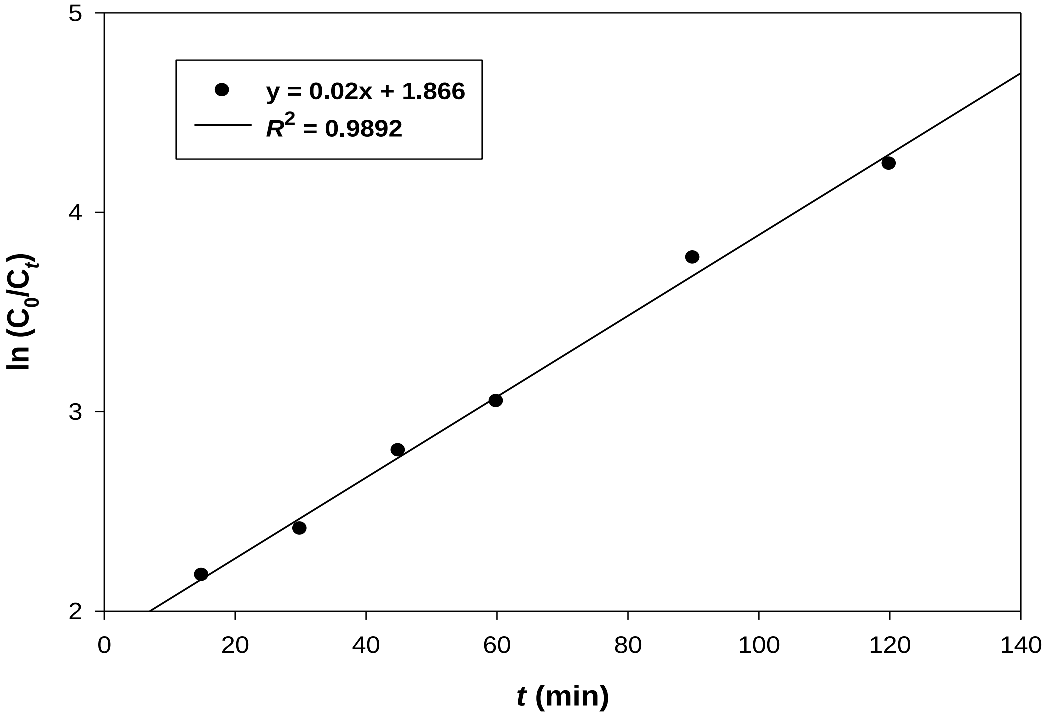


Fig. 9. Plot of ln (C_o/C_t) vs. time for the degradation of tetracycline (1 mg/L) using kaolin (0.1 g/L) as a photocatalyst

REFERENCES

[1] Radjenović J et al. Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment. Water Res 2008; 42: 3601-3610.

[2] Rivera-Utrilla J et al. Removal of nitroimidazole antibiotics from aqueous solution by adsorption/bioadsorption on activated carbon. J Hazard Mater 2009; 170: 298-305.

[3] Esplugas S et al. Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. J Hazard Mater 2007; 149: 631-642.

[4] Sirtori C et al. Decontamination industrial pharmaceutical wastewater by combining solar photo-Fenton and biological treatment. Water Res 2009; 43: 661-668.

[5] Isariebel Q-P et al. Sonolysis of levodopa and paracetamol in aqueous solutions. Ultrason Sonochem 2009; 16: 610-616.

[6] Yuan F et al. Degradation of selected pharmaceuticals in aqueous solution with UV and UV/H_2O_2. Water Res 2009; 43: 1766-1774.

[7] Palominos R et al. Photocatalytic oxidation of the antibiotic tetracycline on TiO_2 and ZnO suspensions. Catal Today 2009; 144: 100-105.

[8] Méndez-Arriaga F et al. Mineralization enhancement of a recalcitrant pharmaceutical pollutant in water by advanced oxidation hybrid processes. Water Res 2009; 43: 3984-3991.

[9] Giraldo AL et al. Degradation of the antibiotic oxolinic acid by photocatalysis with TiO_2 in suspension. Water Res. 2010; 44: 5158-5167.

[10] Prados-Joya G et al. Photodegradation of the antibiotics nitroimidazoles in aqueous solution by ultraviolet radiation. Water Res 2011; 45: 393-403.

[11] Chan KH, Chu W. Atrazine removal by catalytic oxidation processes with or without UV irradiation. Part II. An analysis of the reaction mechanisms using LC/ESI–tandem mass spectrometry. Appl Catal B: Environ 2005; 58: 165-174.

[12] Lifongo LL et al. Photodegradation of haloacetic acids in water. Chemosphere 2004; 55: 467–476.

[13] Brigante M, Schulz PC. Remotion of the antibiotic tetracycline by titania and titania–silica composed materials, J Hazard Mater 2011; 192: 1597-1608.

[14] Xiang-Dong Z et al. Photocatalytic degradation of tetracycline in aqueous solution by nanosized TiO_2. Chemosphere 2013; 92: 925-932.

[15] Ai C et al. Optimization of operating parameters for photocatalytic degradation of tetracycline using In_2S_3 under natural solar radiation. Solar Energy 2015; 113: 34-42.

[16] Bautitz IR et al. Degradation of tetracycline by photo-Fenton process—Solar irradiation and matrix effects, J Photochem Photobiol A: Chemistry 2007; 187: 33-39.

[17] Norhasri MSM et al. Sol Gel Characterization of Nano Kaolin, Advan Mater Res 2014; 856: 285-289.

[18] Wu Y, Fassihi R. Stability of metronidazole, tetracycline HCl and famotidine alone and in combination. Int J Pharm 2005; 290: 1–13.

[19] Langmuir I. The constitution and fundamental properties of solids and liquids. J Am Chem Soc 1916; 38: 2221–2295.

[20] Kaur S, Singh V. TiO_2 mediated photocatalytic degradation studies of Reactive Red 198 by UV irradiation. J Hazard Mater 2007; 141: 230–236.

[21] Rahman QI et al. Effective photocatalytic degradation of rhodamine B dye by ZnO nanoparticles. Mater Lett 2013; 91: 170–174.

[22] Kaur J, Singhaln S. Facile synthesis of ZnO and transition metal doped ZnO nanoparticles for the photocatalytic degradation of Methyl Orange. Ceramics Internat 2014; 40: 7417–7424.