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Next-Generation 5% GD-Ni Functionalized Alginate Beads for Innovative Visible-Light Photocatalytic Degradation of Tetracycline

Norezatul Shahirah Ahmad Zamanhuri[1], Norzahir Sapawe[1,*], Muhammad Farhan Hanafi[2], Diyana Faziha Mohamad[1], Mohammad Luqman Ismail[1], Lusi Ernawati[3], Siti Fatimah Ibrahim[4]

[1] Universiti Kuala Lumpur, Branch Campus Malaysian Institute of Chemical and Bioengineering Technology (UniKL MICET), Lot 1988 Vendor City, Taboh Naning, 78000 Alor Gajah, Melaka, Malaysia
[2] Department of Chemical Engineering and Energy Sustainability, Faculty of Engineering, Universiti Malaysia Sarawak (UNIMAS), 94300 Kota Samarahan, Sarawak, Malaysia
[3] Department of Chemical Engineering, Institut Teknologi Kalimantan, 76127, Balikpapan, Indonesia
[4] School of Chemical and Process Engineering, University of Leeds, LS2 9JT Leeds, United Kingdom

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ABSTRACT

Tetracycline (TC) is a typical traditional antibiotic with high prevalence and persistence, commonly used in livestock farming; and its poor degradability and impact on antibacterial resistance in aquatic ecology are great environmental challenges. The conventional wastewater treatment observed insufficient to remove them, making sustainable remediation technologies even more necessary. The calcium-alginate beads were co-doped with gadolinium (Gd) and nickel (Ni) to develop the photocatalyst via the sol-gel and precipitation approach. The improved visible-light photocatalytic performance of Gd^{3+}/Ni^{2+} modified is attributed to the improved light-harvesting, inhibited electron-hole recombination and preferred generation of ROS. Photodegradation experiments and tests showed that the initial TC concentration, pH, and dosage were the major factors affecting the catalytic activity. The optimal degradation efficiency (81%) was obtained within 120 min (pH 5, catalyst dosage of 3 g/L, and 20 mg/L) in the best conditions. In addition, the photocatalytic degradation of TC using 5% Gd-Ni bead catalysts was also properly expressed by the Langmuir–Hinshelwood kinetic model, so that the reaction rate constant (KR value) and the equilibrium adsorption constant (KLH) were compared. Due to its excellent performance, low toxicity and reusability, the 5% Gd–Ni/alginate system showed their potential use as a sustainable photocatalyst for AOPs in the elimination of pharmaceutics of concern.

1. Introduction

Pharmaceutical contaminants such as antibiotics are continuously polluted in aquatic environment, leading to a serious threat to the ecosystem and human health globally. Of these, tetracycline (TC) is the most detected antibiotic in wastewater, surface water, as well as in drinking

* *Corresponding author.*
E-mail address: norzahir@unikl.edu.my

water. Due to its extensive use in human and veterinary medicine and lack of biodegradability, it has led to the generation of antibiotic-resistant bacteria and the disruption of microbial communities in aquatic environments [1,2]. Most traditional wastewater treatment facilities fail to remove these types of micropollutants; therefore, advanced oxidation processes (AOPs) have been developed to remove them [3].

Among various AOPs, photocatalysis is promising technology for the degradation of organic pollutants at mild conditions with the assistance of light irradiation. Overview of photocatalysis including basic reactions in the photocatalytic process, electron-hole pairs were generated when a semiconductor material is photoexcited, and these could then react with water and/or oxygen to form reactive oxygen species (ROS) such as hydroxyl radicals (•OH) and superoxide anions ($O_2•^-$). The ROS degrades complex organic substances to less harmful end-products such as CO_2 and H_2O [4,5].

However, the application of traditional photocatalysts (e.g., TiO_2 and ZnO) is limited due to their wide band gaps, making them only active under ultraviolet (UV) illumination. To enhance photocatalytic activity in the visible region, the doping of semiconductors with rare-earth and transition metal ions has also been explored. Gd^{3+} is known to enhance energy transfer and prolong lifetimes of charge carriers because of the 4f electronic structure of a rare-earth element gadolinium. Nickel (Ni^{2+}) is an active electron acceptor which reduces the charge recombination and enhances the catalytic efficiency [6,7]. The proposed synergistic co-doping of Gd and Ni is beneficial to increasing light-harvesting in visible light range and improving the photocatalytic activity remarkably.

Equally important in the design of a photocatalyst is the selection of a support matrix for the immobilization of the active catalyst. Alginate, a bio-based polymer extracted from brown algae, has several attractive characteristics such as biodegradability, low toxicity, and hydrogel formation with multivalent cations by means of ionic crosslinking. These traits permit efficient sequestration of metal ions as well as nanoparticles, enhance catalyst reclamation and recycling and minimize secondary pollution [8].

The use of photocatalysts in alginate beads is an environment-friendly and applicable alternative in green chemistry. The combination of Gd and Ni in an alginate framework to form a green Gd/Ni/alginate is an eco-friendly, reusable, and visible-light-responsive multifunctional photocatalyst composite. Such biohybrid materials are a promising solution for the remediation of emerging pollutants in waters. In this work, we report on Gd-Ni functionalized alginate beads synthesis, use in the visible-light-driven TC photocatalytic degradation. The catalyst was fabricated via a facile and scalable preparation method of ionic gelation and tested under different operational conditions such as pH, initial TC concentration and catalyst dosage. Reusability study and kinetic analysis were studied at the optimum condition.

2. Methodology

2.1 Chemical and Materials

Nickel (Ni) powder of a purity above 99.5%, gadolinium (Gd) powder, and tetracycline hydrochloride were purchased from Macklin Biochemical Co., Ltd. (China). Dimethylformamide (DMF) was obtained from Sigma-Aldrich (USA). Sodium alginate and epichlorohydrin solution were from Sigma-Aldrich Laborchemikalien GmbH (Germany), and calcium chloride dihydrate (A.R. grade) was obtained from Uchem (China). Analytical grade hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from QReC™ (New Zealand). The reagents and chemicals employed in the present study are of AR grade and used as received without any additional purification. All of the solutions (synthetic tetracycline solutions, alginate stock solution, calcium chloride crosslinking

solutions and pH adjustment buffers were prepared by means of deionized water). The pH of the reaction mixture was adjusted as necessary with 0.1 M HCl and 0.1 M NaOH solutions.

2.2 Synthesis of Catalyst

The method used to prepare the bead catalyst was then optimized using information obtained from a modified process found in the literature [9]. First, 5% gadolinium (Gd) was doped with nickel (Ni) in a dimethylformamide (DMF) solution for impregnation. The mixture was initially dried on a hot plate, followed by the overnight drying in an oven at 378 K. The obtained Gd-Ni composite was calcined at 823 K for 3 h. In parallel, a 3 wt. % solution was prepared by dissolving alginate powder in deionized water with continuous agitation for 2 hours. The washed powders were mixed with the alginate solution in the mass ratio of 1:1 and stirred for another 2 h and left standing overnight to assist in achieving good dispersity. The product suspension was then dropped into a 0.5 M $CaCl_2$ aqueous solution to form a gel bead via ionic crosslinking. To increase the chemical stability of the beads in acid medium, they were additionally cross-linked by means of epichlorohydrin according to a literature protocol [10] with minor modifications. The as-synthesized catalyst beads were rinsed thoroughly with deionized water and saved at 4°C for future photocatalytic tests.

2.3 Photocatalytic Activity

The photocatalytic performance of the as-prepared catalyst was evaluated by degrading tetracycline in aqueous solution. The above reaction was then stirred and controlled at a constant temperature for 120 min under a UV lamp (8W, 220V). The UV source was 15cm above was a 250mL beaker, with 100mL of TC solution prepared at different pH. Catalyst dose and initial TC concentration effects were investigated in photocatalytic studies. After proved time, 5mL samples were withdrawn from the reaction mixtures. Determination of tetracycline the concentration of tetracycline was determined by a UV-Vis spectrophotometer (UV-1900) by measuring its characteristic absorption peak at 356 nm. The rate of photocatalytic degradation at each time point was calculated by the decrease in the A value as a function of time, as indicated according to Eq. (1), which describes the adsorption and decomposition of TC on the catalyst.

$$\text{Degradation (\%)} = (C_o - C_i)/C_o \times 100\% \quad (1)$$

where C_o represents the initial concentration and C_i denotes a variable concentration.

2.4 Reusability Analysis

Reusability of the photocatalyst was evaluated through the recovery of the bead catalyst for five consecutive adsorption-desorption cycles under the optimal conditions. After each photocatalytic reaction, the drug solution with TC was separated from the bead catalyst, and the supernatant was analyzed by a UV-Vis spectrometer (Thomas Edison U2900). The absorbance spectrum of TC was analyzed at 356 nm. The photodegradation time for each cycle was 120 min. At the end of each cycle, the used catalyst beads were soaked in distilled water with pH 7 for 30 min to remove any remaining contaminants. The supernatant was checked until the TC level was determined to be zero, ensuring a minimal amount of carryover. The regenerated catalyst was then stored at 4°C prior to use in the next cycle as stated in previous study [11].

3. Results and Discussion

3.1 Performance of Catalyst

Figure 1 shows removal efficiency of tetracycline by 3 types of catalyst via three distinct conditions, under dark, in photolysis and photocatalytic experiments. The 5% Gd-Ni bead catalysts showed much better photocatalytic activity than alginate bead, 5% Gd-Ni power with 81% TC removal. The maximum photoactivity was less than 60% for alginate bead, alginate is not a photoactive and is not very good light absorbing material [12]. Alginate beads are frequently used as a supporting matrix for inclusion of photocatalytic chemicals. The lowest removal in photocatalytic reaction was 36% by 5% Gd-Ni powder catalyst. The use of 5% Gd-Ni powder leads to the deposition of dense coatings, which effectively shade all the particles. This leads to non-uniform activation and suppresses the photocatalytic reactions [13].

Utilizing 5% Gd-Ni powder combined with alginate, which is confined within the bead, serves as a photocatalyst for photocatalytic processes, resulting in better performance. It is observed that the 5% Gd-Ni bead provides higher light penetration into the catalyst bead as well as uniform distribution throughout the catalyst bead. Therefore, homogeneous light exposure can significantly strengthen the photocatalysis efficiency [13]. On the other hand, both dark and photolysis show the low removal efficiency (usually less than 30%) which adsorption and direct photolysis cannot be used to remove tetracycline effectively. These findings emphasize the role of photocatalysis in the degradation pathway and demonstrated further advantages of bead form catalysts, particularly 5% Gd-Ni bead which is the most efficient form for TC photodegradation.

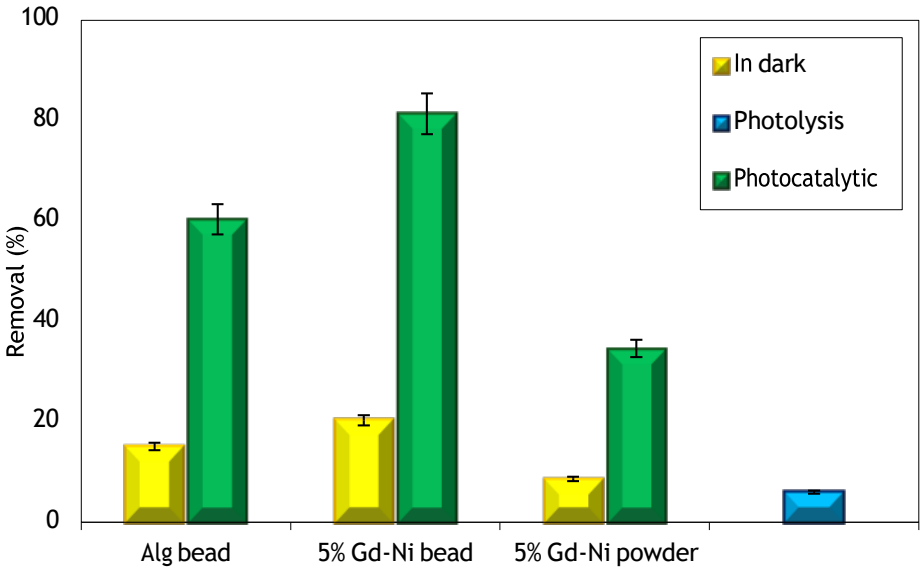


Fig. 1. Removal of TC using different catalysts in the dark condition, photolysis and photocatalytic

3.2 Effect of pH Solution

The effect of solution pH on photocatalytic degradation efficiency of TC, using 5% Gd-Ni functionalized alginate beads, was shown in Figure 2. The pH measurements were carried out at pH

3, 5, 7, 9 and 11. The efficiency of degradation was very pH-sensitive, and the highest degradation rate (81%) was at pH of 5. At pHs of 3, 7, 9, and 11, the removal rates were 70%, 76%, 74%, and 70%, respectively. The degradation rate increased from pH 3 to 5, which exhibits better photocatalytic activity under the slightly acid condition.

However, increase in pH beyond 5, led to a gradual reduction in the efficiency. The results suggest that pH 5 gives the optimum condition for TC degradation in the presence of 5% Gd-Ni beads. The discrepancy in photocatalytic activities with pH may be ascribed to the variation of the surface charge of the photocatalyst and ionization of TC. Changing the pH changed the electrical double layer on catalyst surface as well as redox potentials, thereby affecting the adsorption of organic solute and the generation of reactive species. Thus, pH plays a critical role in controlling the system reactivity and degradation rate [14,15].

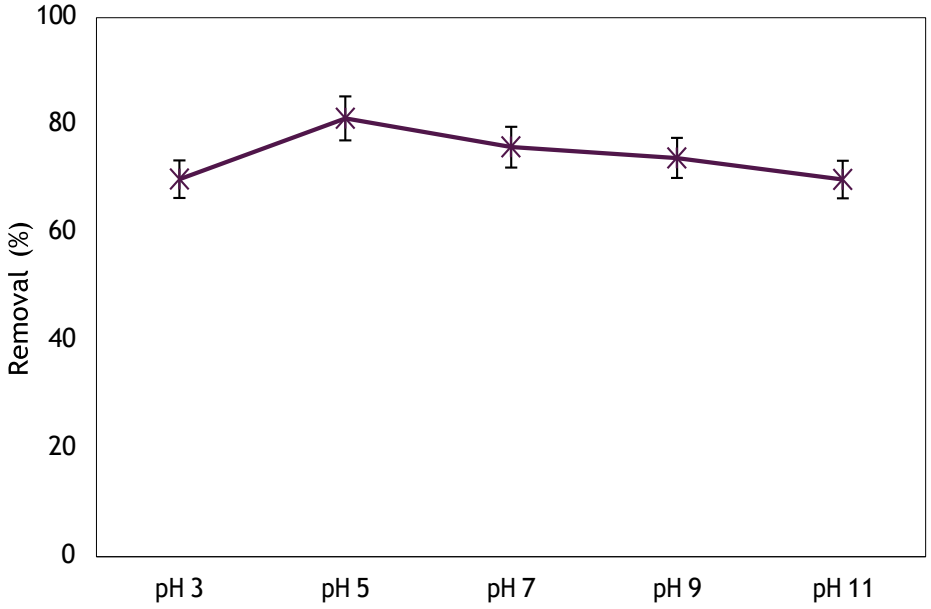


Fig. 2. Effect of pH solution on photodegradation of TC [W: 3g/L, C: 20mg/L, t: 120min]

3.2 Effect of Catalyst Dosage

The effect of Gd-Ni bead dosage on photocatalytic degradation efficiency of TC at pH 5 with the initial concentration of 20mg/L was shown in Figure 3, the dosage of catalyst solution ranging from 3g/L to 15g/L with the gap of 3g/L. The maximum degradation efficiency (81%) was achieved at the catalyst dosage of 3g/L, and the decrease efficiency reached 80%, 77%, 75% and 70% as the catalyst dosage increased to 6, 9, 12 and 15g/L. This data clearly shows that an increasing above the certain threshold value of the catalyst dose resulting on a decrease of a TC removal efficiency.

At first, higher degradation rate at high amount of catalyst is due to the presence of more available active site on the surface of the photocatalyst, which promotes more photon absorption and generation of reactive oxygen species (e.g., hydroxyl radicals and photo induced holes) [16-18]. However, at higher the dosage, the efficiency of degradation decreases, possibly because of the scattering effect. This is because the large amount of catalyst particles increases the turbidity of the suspension, which makes light cannot penetrate well. Furthermore, particle clustering at higher concentration can reduce the available surface area and thus diminish photocatalytic activity [19,20].

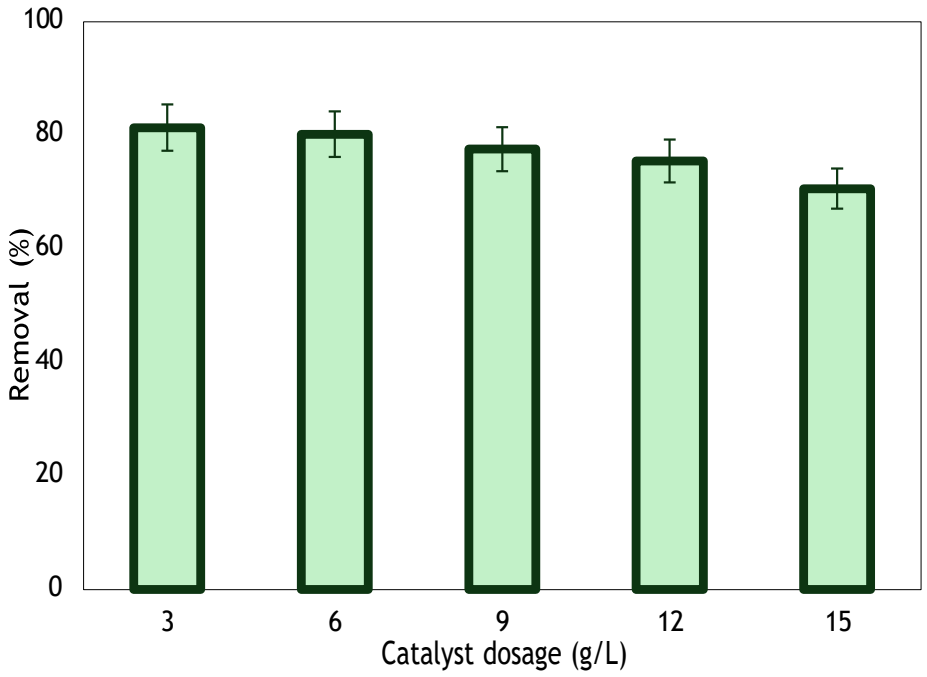


Fig. 1. Effect of catalyst dosage on photodegradation of TC [pH: 5, C: 20mg/L, t: 120min]

3.3 Effect of TC Initial Concentration

Figure 4 revealed the effect of initial TC concentration on photocatalytic degradation efficiency with a dose of 3g/L at pH 5 and the initial concentrations ranged between 20 - 100mg/L, and the optimal degradation efficiency (81%) was found at 20mg/L. The removal efficiency fell to 75%, 73%, 71%, and 64% as the initial concentration increased, indicating that the degradation efficiency was inversely proportional to the initial concentration of pollutants. This trend indicates that with higher initial concentrations, the surface coverage of the catalysts with TC molecules are saturated hampering the active sites and the production of hydroxyl radicals. The extra adsorbed molecules block the interactions with the photocatalytic-generated holes and radicals and the number of photons getting into the catalyst can be reduced by the light absorption, especially in the bulk solution [21]. In these cases, as the amount of light entering the high concentration region decreases, the activity decreases, because photocatalytic processes are essentially surface phenomena near the illuminated surface region.

Again, as the TC content rises a greater amount of catalyst will be need for efficient degradation. This trend may be a sign of kinetic limitation transforming into mass transfer limitation with the increase of pollution load. Photocatalytic degradation also relies on photonic efficiency, with a decrease occurs at high substrate concentrations that contribute to the saturation of the catalyst surface and site utilization [22]. Furthermore, the accumulation of intermediate degradation products at higher concentration could adhere to the catalyst surface, which could inhibit their transport and cover the active site. This in turn, controls the supply of hydroxyl radicals making them the rate-limiting species, and further reducing the degradation rate constants [20,21].

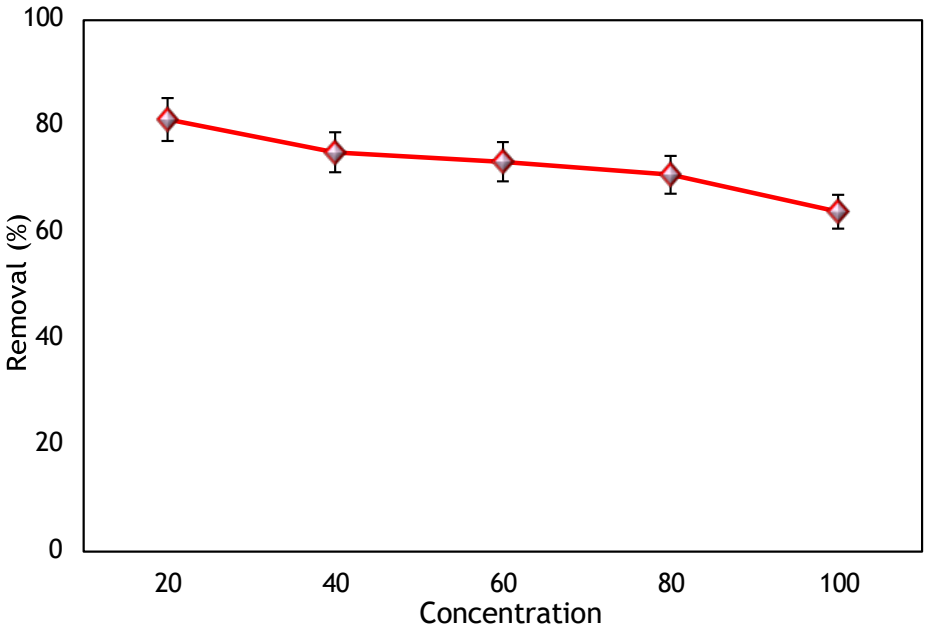


Fig. 2. Effect of catalyst dosage on photodegradation of TC [pH: 5, W: 3g/L, t: 120min]

3.4 Reusability of Photocatalyst

Reusability test of the 5% Gd-Ni bead catalyst for photodegradation of TC was performed under best condition (pH5, 3 g/L catalyst dosage, 20 mg/L of the initial concentration) and the data are shown in Figure 5. The initial concentration of TC was fixed at 20 mg/L according to the optimum parameters previously reported. The ultimate decay of each cycle for the fifth cycle is reduced from 81%, 81%, 68%, 65%, 60%, to 57%, respectively. The degradation trend in the cycles indicates good stability and low reusability at the extended periods of photocatalytic reaction with the difference between the first run and the last cycle is 24%.

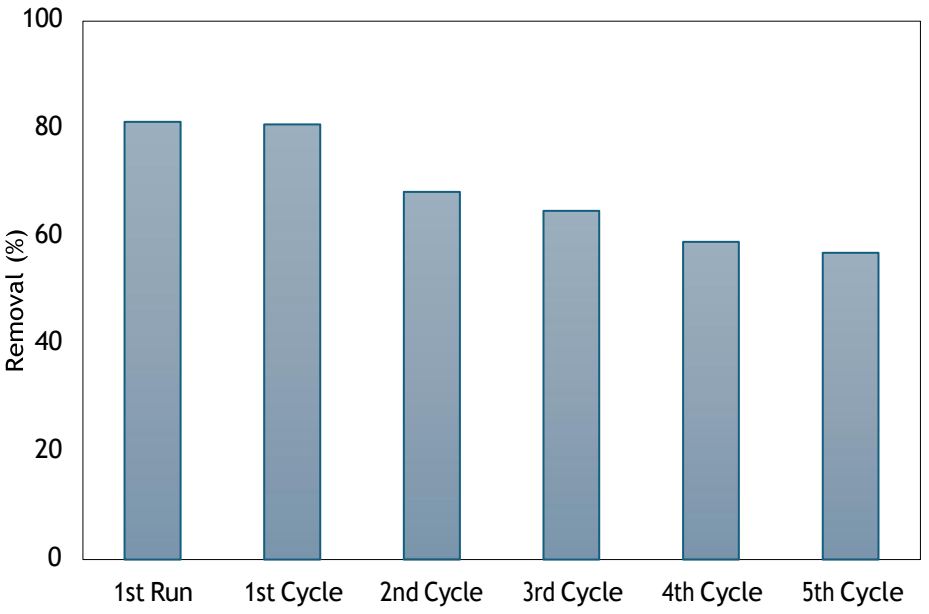


Fig. 3. Reusability of 5% Gd-Ni bead photocatalyst [pH: 5, C: 3g/L, C: 20 mg/L, t: 120min]

The induction of pH variation during the photocatalytic decomposition of tetracycline might significantly affect the stability of metal–alginate interactions. Under acidic conditions, the carboxyl groups of alginates may be protonated, thereby lessening their ability to bind to metal ions to ease the release of metal ions [23]. TC and its degradation products contain various functional groups capable of metal-ion chelation. These compounds may outcompete alginate for Gd^{3+} and Ni^{2+} complexes, resulting in increased leaching by ligand exchange processes [24].

3.5 Kinetic Analysis

The kinetics of tetracycline degradation was investigated by performing a series of experiments using different initial concentrations of TC (between 20 and 100 mg/L) under the previously optimized pH and catalyst dose conditions. Pseudo first order kinetics is used in many cases to describe the influence of the initial pollutant concentration on the rate of the photocatalytic degradation, which can be presented and interpreted in the framework of a modified Langmuir–Hinshelwood model that considers the presence of a solid–liquid interface. At lower concentrations, tetracycline degradation rates could be fitted using the simplified version of this model.

$$\ln C_t = -kt + \ln C_o \tag{2}$$

Where k is the pseudo first-order rate, C_o and C_t are the concentrations of the TC at initial and time t, respectively. The integration of Eq. (2) yields Eq. (3)

$$\ln(\frac{C_o}{C_t}) = kt \tag{3}$$

The linear part of the $\ln(C_0/C_t)$ yields out the apparent first-order rate constant. This was supplemented by Eq. (4) and Eq. (5), in which the r_0 was the initial degradation rate, K_R is often considered as a pseudo first order Langmuir-Hinshelwood type rate of coefficient while K_{LH} a pseudo-equilibrium constant correlated to monolayer adsorption.

$$r_0 = -\frac{dC}{dt} = \frac{K_R K_{LH} C_\&}{1 + K_{LH} C_\&} = K_{app} C_0 \tag{4}$$

$$\frac{1}{K_{app}} = \frac{1}{K_R K_{LH}} + \frac{C_\&}{K_R} \tag{5}$$

The straight lines of $\ln(C_o/C_t)$ versus time of degradation of TC using 5% Gd-Ni bead as photocatalyst are presented in Figure 6a shows that pseudo-first-order reaction kinetics. The apparent first-order rate constants (K_{app} as listed in Table 1 for 5%, Gd-Ni bead) are shown in the slope of these figures. Such results implicate large and positive effect of catalyst compositions on TC degradation performance.

More kinetic research has been performed by plotting $1/K_{app}$ with the initial concentration of tetracycline (C_o), as presented in Figure 6b the linear correlations have demonstrated the dependence of the photocatalytic degradation of tetracycline by 5% Gd-Ni bead with Langmuir–Hinshelwood model. According to the equation resulting from 5%Gd-Ni bead in Figure 6b, the

reaction rate constant K_R is 2.4426 mg L^{-1} min^{-1}, and the adsorption equilibrium constant K_{LH} is 0.0075 L mg^{-1}.

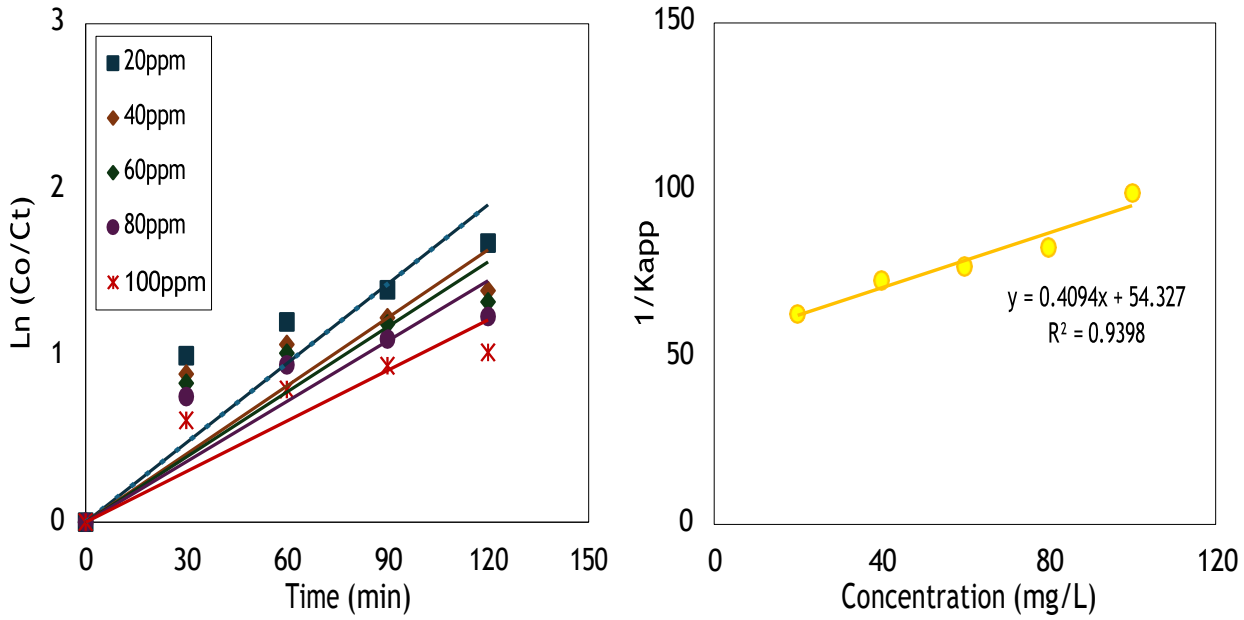


Fig. 4. (a) Photodegradation Kinetic of TC Using 5% Gd-Ni Bead at Different TC Concentration and (b) The relationship between $1/K_{app}$ and Initial Concentration

Table 1
The Parameters of Photodegradation at Different Concentration of TC Using 5% Gd-Ni bead

Initial concentration (mg/L)	Reaction rate, k (1/min)	Initial reaction rate, r_0 (mg/ L.min)	Degradation (%)
20	0.0159	0.318	81
40	0.0137	0.548	75
60	0.013	0.78	73
80	0.0121	0.968	71
100	0.0101	1.01	64

In general, values of K_R are higher than K_{LH} for the 5% Gd-Ni bead photocatalysts. This implies that the photocatalytic degradation of TC is not significantly controlled by the adsorption mechanism, also justified by Fatimah *et al*., [25]. According to Fauzi *et al*., [26], then the reaction step is the rate-controlling step for the entire photocatalytic process, and it is suggested that the degradation mainly occurs on catalyst surface, when K_R is higher than K_{LH}.

4. Conclusions

In summary, the efficiency of 5% Gd-Ni functionalized alginate beads as visible light driven photocatalysts for the degradation of TC in an aqueous medium was demonstrated in this work. The photocatalytic activity was systematically studied in relation to different operating parameters, such as pH, catalyst amount, and initial pollutant concentration. The results showed that maximum removal of up to 81% at initial TC concentration 20 mg/L was obtained at acid conditions (pH 5) using a catalyst dose of 3 g/L which suggested that 5% Gd-Ni bead has a potential to be employed as a

photocatalyst for antibiotic removal application from a wastewater treatment plant. The catalyst had comparatively good stability and slight reusability through five runs with a total decrease of 24%. In addition, the results emphasize the importance of optimizing the reaction conditions to maximize the photocatalytic efficiency. In addition, the photocatalytic degradation of TC with the 5% Gd-Ni bead catalysts fitted the Langmuir–Hinshelwood kinetic model, K_R (reaction rate constant) being greater than K_{LH} (adsorption equilibrium constant). This evidence indicates that surface reaction kinetics rather than adsorption is the primary factor in controlling the process, which highlights the efficiency of the surface-controlled photocatalytic degradation achieved by the 5% Gd-Ni bead catalyst. The present contribution opens new possibilities for the construction of recyclable photocatalytic systems for the removal of pharmaceutical pollutants and fosters the development of visible light-driven wastewater treatment technologies.

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