

Alginate-Encapsulated Gd-Ni Catalysts For Photocatalytic Degradation Of Theophylline In Aqueous Solution

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ABSTRACT

Pharmaceutical pollutants, including theophylline, a prevalent xanthine-based drug, present significant risks to aquatic ecosystems owing to their persistence and resistance to standard wastewater treatment methods. This study presents the synthesis of a novel gadolinium (Gd) and nickel (Ni) co-doped alginate bead catalyst through in situ co-precipitation and sol-gel techniques, with the objective of improving the photocatalytic degradation efficiency of theophylline in aqueous media. The Gd-Ni nanoparticles were effectively immobilized in alginate matrices, resulting in stable, magnetically separable beads that exhibit enhanced surface area and light absorption characteristics. Batch experiments were performed to evaluate the effects of critical operational parameters such as pH, catalyst dosage, and initial theophylline concentration on degradation performance under visible light irradiation. The optimized 7% Gd-doped Ni-alginate catalyst demonstrated an 84% removal efficiency within 240 minutes, showing enhanced activity relative to non-doped and single-metal-doped alternatives. The photocatalyst exhibited satisfactory reusability across three cycles, showing minimal activity loss. The findings suggest that Gd-Ni nanoparticle-embedded beads may serve as effective and sustainable photocatalysts for the removal of pharmaceutical contaminants from water.

Keywords : Gadolinium, nickel, photocatalytic, pharmaceutical, pollution, alginate.

1. INTRODUCTION

The unregulated discharge of pharmaceutical compounds into aquatic ecosystems has become a significant global issue. Theophylline, a methylxanthine drug commonly used for respiratory conditions like asthma and chronic obstructive pulmonary disease (COPD), is frequently found in surface waters and wastewater effluents due to its high solubility and resistance to biodegradation (Rivera-Utrilla et al., 2013; Verlicchi et al., 2015). The persistence of these compounds in the environment presents considerable ecotoxicological risks to aquatic organisms and may also affect human health via water reuse systems (Aus der Beek et al., 2016).

Traditional wastewater treatment methods, including biological degradation, sedimentation, and chemical oxidation, have been shown to be insufficient for the comprehensive removal of emerging contaminants such as theophylline (Luo et al., 2014). Advanced oxidation processes (AOPs), especially photocatalysis, have garnered significant attention as an effective and sustainable method for degrading persistent organic pollutants. is attributed to their capacity to produce highly reactive species, such as hydroxyl radicals, when exposed to light irradiation (Malato et al., 2009; Chong et al., 2010).

Transition metal-based catalysts, particularly nickel (Ni), exhibit significant photocatalytic activity due to their redox properties and capacity to enhance electron-hole separation (Rauf & Ashraf, 2009). Rare earth elements, such as

gadolinium (Gd), exhibit distinctive 4f-electron configurations that improve visible light absorption and electron transfer efficiency in semiconductor systems (Harini et al., 2022). The combination of Ni and Gd in a photocatalytic matrix can significantly enhance catalytic performance. The use of nanopowders in photocatalysis is associated with several limitations, such as inadequate recovery, particle agglomeration, and the potential for secondary pollution. Immobilizing nanoparticles in biopolymer-based beads, such as calcium alginate, provides a viable solution to these challenges, facilitating easy separation, enhancing reusability, and improving the dispersion of active sites (Hamidon et al., 2024). Alginate, a natural polysaccharide derived from brown seaweed, is extensively utilized for its gel-forming properties, environmental sustainability, and compatibility with metal ions (Kimling & Caruso, 2012).

This study presents the synthesis of a novel bead catalyst incorporating Gd-doped Ni nanoparticles, achieved through in situ co-precipitation and sol-gel methods, and subsequently encapsulated in calcium alginate matrices. The photocatalytic performance was assessed by degrading theophylline in an aqueous solution under UV light. The impact of operational parameters, including pH, catalyst dosage, and initial pollutant concentration, was systematically examined to enhance degradation efficiency. The reusability of the catalyst was evaluated through successive photocatalytic cycles. This study presents a novel approach to the design of efficient, recoverable, and environmentally friendly photocatalysts aimed at the removal of pharmaceutical contaminants from aquatic environments.

2. MATERIALS AND METHODS

2.1 Materials

Nickel (Ni) powder and gadolinium (Gd) powder (purity >99.5%) were procured from Macklin (China) and utilized without further processing. Sodium alginate powder was acquired from Sigma-Aldrich Laborchemikalien GmbH. Calcium chloride dihydrate (analytical reagent grade) was procured from Uchem. Theophylline anhydrous ($\geq 99\%$) from Sigma-Aldrich Laborchemikalien GmbH was utilized as a model pollutant. Epichlorohydrin and N,N-dimethylformamide (DMF) were acquired from Sigma-Aldrich. Hydrochloric acid (HCl) and sodium hydroxide pellets (NaOH) were procured from QReCTM. All compounds were of analytical quality and utilized without additional purification. Deionized water was utilized in the tests for the formulation of synthetic medicinal solutions, alginate and calcium chloride solutions, as well as for pH changes. pH modifications were executed utilizing 0.1 M HCl and 0.1 M NaOH solutions.

2.2 Preparation of catalyst

The entire procedure for synthesizing the bead catalyst has been refined and enhanced (Albarelli et al., 2009). 7% of gadolinium (Gd) was infused with nickel (Ni) in a DMF solution. The mixture was then dried on the hot plate and continually subjected to oven drying overnight at 378 K. The 7% Gd-Ni powder, Ni powder, and Gd powder were calcined at 823 K for 3 hours. A 3 wt.% calcium alginate solution was subsequently made by dissolving powdered alginate in deionized water and stirring for 2 hours. Thereafter, adhering to a 1:1 ratio, the powder generated from the calcination process was integrated and agitated for an additional 2 hours, subsequently allowing it to stand overnight. A combined solution was subsequently placed into a precipitation bath containing an aqueous CaCl_2 solution at a concentration of 0.5 M. Subsequently, the gel beads are subjected to cross-linking to render them insoluble in an acidic (low pH) aqueous solution. The wet alginate bead catalyst was subsequently cross-linked with epichlorohydrin using a modified method (Rocher et al., 2010). The next step entailed thoroughly rinsing the cross-linked alginate beads with deionized water to prepare them for photocatalytic testing. The bead was kept at a temperature of 4°C.

2.3 Photocatalytic reaction testing

The efficacy of the synthesized catalyst was assessed for its capacity to degrade theophylline concentrations in an aqueous solution by photocatalysis. The solution was subjected to visible light radiation exposure from an 8W/220V lamp, with temperature regulation and agitation maintained for 240 minutes. The light is emitted at a distance of 15 cm, situated between the lamp and the beaker containing 100 mL of theophylline solution with varying pH levels. The beaker has a capacity of 250 mL of liquid. The impact of catalyst dosage and the initial theophylline concentration was assessed during photocatalytic tests. A degradation sample was obtained, and the analyte concentrations were quantified using a UV-Vis spectrophotometer (Thomas Edison LSS-U2900 Double Beam). The quantification of

theophylline was conducted by examining their specific absorption bands at 273 nm. A 5 mL sample was obtained and then centrifuged at designated time intervals. The photodegradation rate on the catalyst at each time interval (adsorption quantity) was evaluated using Equation (1).

$$\text{Degradation (\%)} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

where C_0 signifies the initial concentration and C_t represents a changing concentration.

2.4 Recyclability of catalyst

The reusability of the photocatalyst was assessed by regenerating the bead catalysts via three consecutive adsorption-desorption cycles under optimum circumstances. Following each photocatalytic experiment, the pharmaceutical solution containing theophylline was magnetically isolated from the bead catalyst, and the supernatant was analyzed using a UV-Vis spectrophotometer (Thomas Edison U2900). The absorbance of theophylline was measured at 273 nm. Each cycle had a photodegradation period of 240 minutes. Subsequent to each cycle, the used catalyst beads were submerged in distilled water at pH 7 for 30 minutes to eliminate residual pollutants. The supernatant was analyzed until theophylline was undetectable, guaranteeing little carryover. The regenerated catalyst was subsequently stored at 4 °C until utilized in the following cycle. (Monroy et al., 2025).

3. RESULTS AND DISCUSSION

3.1 Performance study

Figure 1 presents the performance metrics of different catalysts in the photocatalytic degradation of theophylline, all conducted under uniform experimental parameters (pH = 7, catalyst dosage = 3 g/L, and initial theophylline concentration = 10 mg/L). Among all the catalysts tested, the 7 % Gd-Ni alginate bead demonstrated the highest removal efficiency at 84 %, followed by the Gd bead at 80 % and the Ni bead at 76%. In contrast, the plain alginate bead displayed a moderate removal rate of 55 %. In contrast, the associated metal powders, namely Ni, Gd, and 7 % Gd-Ni, exhibited notably reduced removal efficiencies, achieving removal rates of 34 %, 63 %, and 49 %, respectively. The improved photocatalytic performance of the 7 % Gd-Ni bead results from the synergistic effect of gadolinium and nickel co-doping, which facilitates effective charge separation and broadens light absorption into the visible spectrum. Gadolinium ions, characterized by unpaired f-electrons, are essential for the capture of photo-generated electrons. In contrast, nickel facilitates redox reactions and enhances the mobility of charge carriers. The incorporation of doped metals within a biopolymeric alginate matrix improves catalyst dispersion, mitigates agglomeration, and enhances interaction with the pollutant, thus increasing overall photocatalytic activity (Kanakaraju et al., 2017).

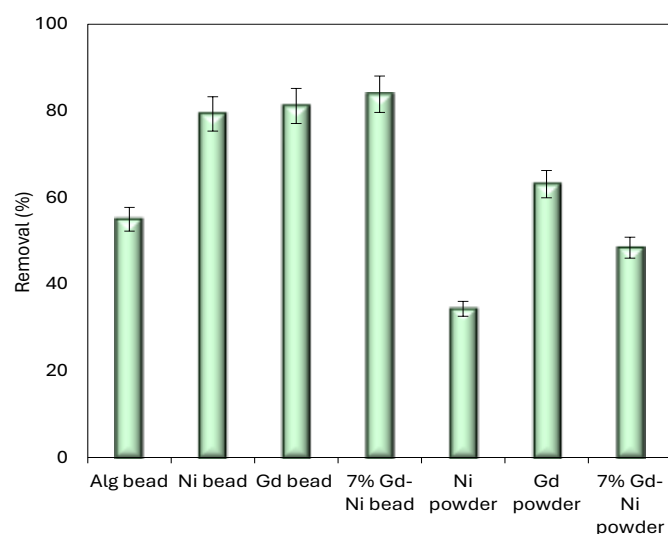


Fig. 1. Performance study of catalyst on theophylline removal [pH = 7, W = 3 g/L, C = 10 mg/L, t = 4 h, T = 303 K]

The observed low performance of the metal powders may be attributed to their restricted surface area, insufficient structural stability, and increased propensity for particle aggregation, which limits the availability of active sites and promotes electron-hole recombination (Manohara et al., 2021; Sohrabi et al., 2020). Alginate beads offer structural support and enhance the pre-concentration of pollutants at the catalyst surface through their inherent adsorption properties. This renders them especially efficient for heterogeneous photocatalysis in aqueous settings (Ullah et al., 2023).

3.2 Effect of pH

Using the photocatalyst at a fixed catalyst dosage of 9 g/L and an initial pollutant concentration of 10 mg/L, Figure 2 shows how pH affects theophylline removal efficiency. Between pH 3 and pH 11, there are notable differences in the photocatalytic performance. Neutral pH (pH 7) exhibits the best removal effectiveness (80 %), but basic pH (pH 9 and 11) and acidic pH (pH 3 and 5) exhibit noticeably lower removal rates. Efficiency sharply declines to roughly 13 % at pH 3, but it rises to 47 % at pH 5. The elimination efficiencies under alkaline circumstances are similar at pH 9 and pH 11, at roughly 66 % and 64 %, respectively. The optimal performance at neutral pH is due to the surface charge characteristics of the photocatalyst and the ionization behavior of theophylline. At pH 7, the photocatalyst surface and the target molecule likely demonstrate favorable electrostatic interactions, which enhance adsorption and subsequent degradation. In acidic conditions, particularly at pH 3, the protonation of functional groups on both the catalyst and theophylline molecules may lead to electrostatic repulsion or diminished availability of reactive oxygen species (ROS), consequently decreasing degradation efficiency (Menacherry et al., 2022). Under alkaline conditions, the increase in hydroxyl ion concentration theoretically promotes the generation of hydroxyl radicals.

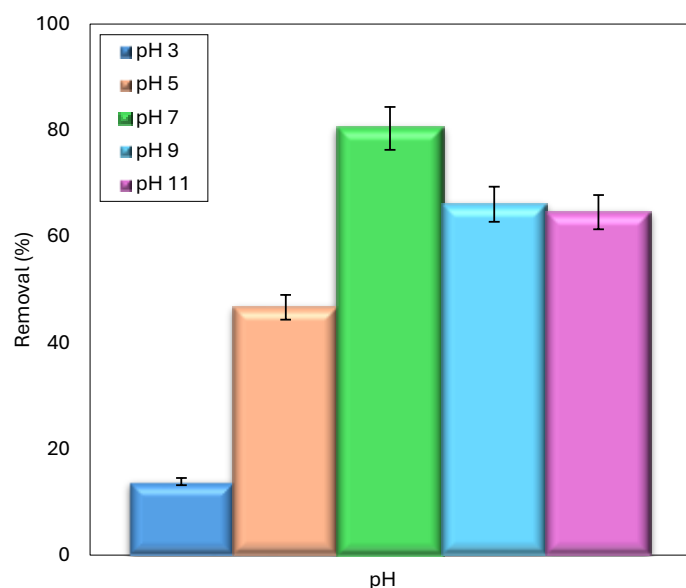


Fig. 2. Effect of pH on theophylline removal
[W = 9 g/L, C = 10 mg/L, t = 4 h, T = 303 K]

However, an excess of OH^- may function as radical scavengers or destabilize the catalyst structure, leading to a reduction in photocatalytic performance (Shinde et al., 2013). The pH-dependent behavior underscores the significance of surface chemistry in photocatalytic degradation. Alginate-based catalysts can experience conformational changes at extreme pH levels, which may influence the accessibility of active sites and the efficiency of mass transfer (Naseem et al., 2023). The zero-point charge (pH_{pzc}) of the catalyst is essential in defining the interaction between the catalyst and the pollutant. At pH levels close to the pH_{pzc} , electrostatic attraction prevails, enhancing both adsorption

and degradation processes.

3.3 Effect of catalyst dosage

Figure 3 illustrates the impact of catalyst dosage on the photocatalytic removal efficiency of theophylline at pH 7, with an initial concentration of 10 mg/L. The examined catalyst dosages were 3, 6, 9, 12, and 15 g/L. The findings indicate a distinct trend: removal efficiency improves with increasing catalyst dosage from 3 to 15 g/L, peaking at 3 g/L (84 %). Further increases in catalyst dosage beyond this point resulted in a gradual decline in efficiency, with removal decreasing to approximately 61 % at 15 g/L. The initial increase in degradation efficiency with higher catalyst dosage is due to enhanced availability of active sites and improved light absorption, which promote the generation of reactive oxygen species (ROS) like hydroxyl radicals ($\bullet\text{OH}$) and superoxide anions ($\bullet\text{O}_2^-$), responsible for the breakdown of theophylline molecules (Mamaghani et al., 2019; Fosso-Kankeu et al., 2020).

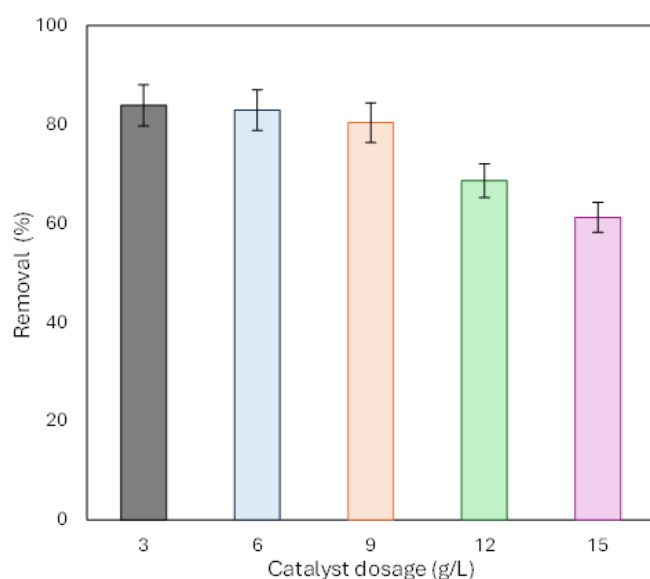


Fig. 3. Effect of catalyst dosage on theophylline removal [pH = 7, C = 10 mg/L, t = 4 h, T = 303 K]

At dosages exceeding 3 g/L, the decline in performance may result from excessive catalyst loading, leading to particle aggregation and increased turbidity in the solution. This effect diminishes light penetration and obstructs photon absorption by the photocatalyst, consequently restricting the activation of charge carriers (Mamaghani et al., 2019; Fosso-Kankeu et al., 2020; Sapawe, 2015; Cheah and Sum, 2022). Additionally, a highly concentrated catalyst suspension may elevate the likelihood of recombination between photogenerated electron-hole pairs, thereby reducing the generation of reactive oxygen species (ROS). Moreover, increased solid content may hinder the diffusion of pollutant molecules to the active sites, consequently diminishing the overall degradation rate (Mamaghani et al., 2019; Fosso-Kankeu et al., 2020; Sapawe, 2015; Cheah and Sum, 2022).

3.4 Effect of initial concentration

Figure 4 demonstrates the impact of the initial theophylline concentration on the photocatalytic degradation process, with a solution pH of 7 and a catalyst dosage of 3 g/L. The concentrations employed in this study were 10, 20, 30, 40, and 50 mg/L. The maximum degradation achieved was 84 % at a concentration of 20 mg/L. Theophylline clearance rates were observed at 75 %, 68 %, 59 %, and 47 % for initial concentrations of 20, 30, 40, and 50 mg/L, respectively. The graph demonstrates that a rise in the initial concentration of theophylline leads to a reduction in the percentage of elimination. This trend indicated that the formation of OH radicals on the surface catalyst was reduced due to the obstruction of active sites by tetracycline ions. At higher concentrations, a greater number of molecules adhered to the

catalyst's surface, which inhibited their reaction with catalytic sites or radicals due to a decreased availability of semiconductor molecules for excitation. The primary degradation occurs near the irradiated surface, where the irradiation intensity is considerably higher than on the opposite side (Saadati et al., 2016). As a result, increased tetracycline concentrations lead to reduced deterioration at greater distances from the light source or reaction zone, attributable to the attenuation of light penetration.

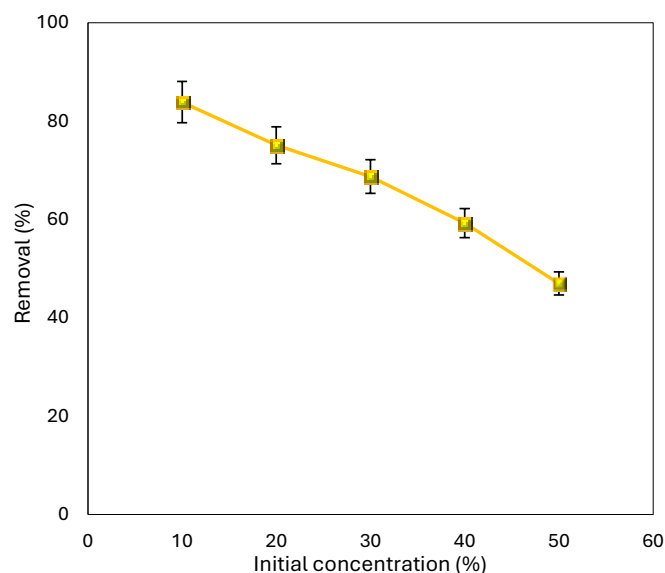


Fig. 4. Effect of initial concentration on theophylline removal
[pH = 7, W = 3 g/L, t = 4 h, T = 303 K]

An increase in the initial concentration of tetracycline requires a larger catalyst surface area for effective degradation. This may also arise from the transition from kinetic control at low doses to mass transfer limitations at higher concentrations. The temporal concentration of organic substrate in photocatalytic oxidation depends on photonic efficiency. At high substrate concentrations, photonic efficiency decreases, leading to saturation of the photocatalyst surface and subsequent catalytic deactivation (Saadati et al., 2016; Khairol et al., 2019). Additionally, an increase in substrate concentration may lead to the generation of intermediates that can adsorb onto the surface of the catalyst. The slow diffusion of produced intermediates from the catalyst surface can result in the deactivation of active sites on the photocatalyst, consequently reducing the degradation rate. At high concentrations, the buildup of intermediate products causes hydroxyl radicals to become the limiting reactant, leading to a decrease in degradation rate constants. (Cheah and Sum, 2022; Saadati et al., 2016).

3.5 Reusability study

Figure 5 presents the reusability performance of a 7% Gd-Ni bead catalyst across three consecutive cycles for the removal of theophylline from an aqueous solution under controlled conditions (pH = 7, catalyst dosage = 3 g/L, and an initial theophylline concentration of 10 mg/L). The initial run of the experiment achieved an 84 % success rate, followed by 83 % in the first cycle and 82 % in both the second and third cycles. The performance reduction is less than 5 %. The bar graph illustrates a progressive decrease in removal efficiency across successive reuse cycles. During the initial cycle, the catalyst demonstrated the highest removal efficiency, indicating robust initial activity. By the third cycle, a noticeable decrease in efficiency was observed, suggesting a reduction in catalytic activity likely attributable to surface fouling, blockage of active sites, or partial structural degradation of the catalyst. The catalyst exhibited sustained performance over three cycles, indicating its viability for practical applications with limited regeneration needs. The findings highlight the operational stability and reusability of the Gd-Ni bead catalyst in water treatment applications.

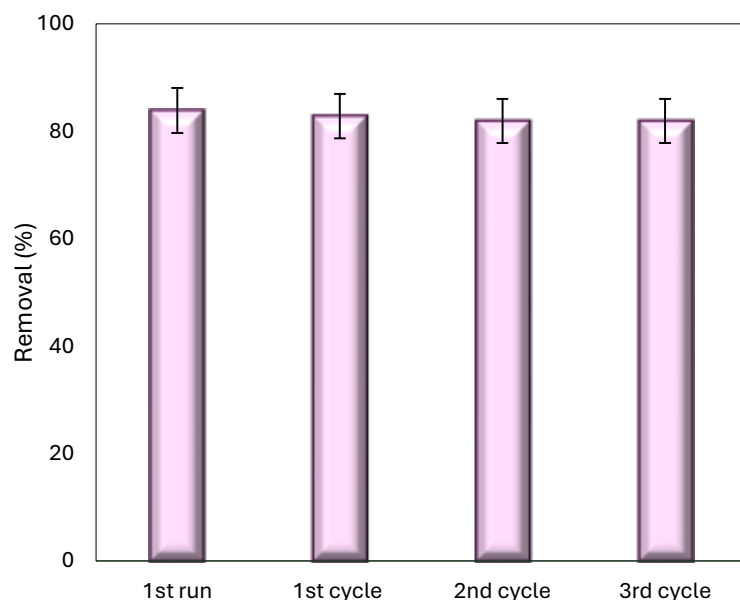


Fig. 5. Reusability of 7% Gd-Ni bead catalyst for three cycles
[pH = 7, W = 3 g/L, C = 10 mg/L, t = 4 h, T = 303 K]

4. CONCLUSION

This study demonstrates that the 7 % Gd-Ni bead catalyst shows superior effectiveness in the photocatalytic degradation of theophylline compared to individual metal beads, alginate beads, and powder catalysts. Under optimal conditions (pH 7, 3 g/L catalyst dosage, and 10 mg/L theophylline concentration), a maximum removal efficiency of 84 % was achieved within 240 minutes of UV irradiation. The 7 % Gd-Ni bead catalyst exhibited sufficient stability and notable reusability across three cycles, leading to a total efficiency reduction of under 5 %. The bead shape offers practical advantages over powder catalysts, including easier separation and the elimination of additional separation costs. The findings highlight the considerable efficacy of 7 % Gd-Ni beads as a viable photocatalyst for the elimination of theophylline from aqueous solutions.

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