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Ni-Nanoparticle Beads: An Advanced Nano-Catalyst for Efficient Photocatalytic Degradation of Pharmaceuticals

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ABSTRACT

The increasing demand for pharmaceuticals, essential for promoting human health and maintaining quality of life, is contributing to environmental degradation. Pharmaceuticals are found in various sources, including industrial wastewater, urban agricultural runoff, and hospital effluent. Their improper disposal leads to environmental pollution, posing significant risks to both living and non-target organisms. Photocatalysis using semiconductor nanoparticles is a clean, efficient, and environmentally friendly method for degrading pharmaceuticals, due to the presence of potent oxidizing species. This study investigates the degradation of two pharmaceutical chemicals, aspirin and theophylline, in an aqueous solution using alginate, a naturally occurring polymer derived from brown seaweeds. This research advances the development of efficient photocatalytic technologies for environmental remediation and water treatment, aiming to improve water quality and public health. The Ni nanoparticle bead catalyst was produced using the sol-gel process following established procedures. The photocatalytic activity was evaluated by examining the effects of pH levels (4, 5, 6, 7, and 8), catalyst doses (10, 20, 30, 40, 50, and 60 g/L), and initial concentrations (10, 20, 30, 40, and 50 mg/L) over a one-hour irradiation period. Aspirin concentration was measured using a UV-Vis spectrophotometer at 229 nm, and theophylline concentration at 273 nm. The study identifies the optimal conditions for the removal of aspirin and theophylline as a pH of 5, a catalyst dosage of 40 g/L, and an initial concentration of 10 mg/L. Under these conditions, the Ni nanoparticle bead photocatalyst achieved 89% removal of theophylline and 86% removal of aspirin.

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1. Introduction

Presently, the growing human need for pharmaceuticals is leading to a surge in consumption, consequently leading to environmental deterioration. Pharmaceuticals are vital for preserving and upholding human health, as they have a pivotal function in enhancing the standard of life and mitigating disorders [1]. Currently, the pharmaceutical industry utilizes over 3000 chemicals as medical compounds, producing hundreds of tons annually. The pharmaceutical substances present in the aquatic ecosystem originate from several sources, including domestic sewage, medical waste, pharmaceutical manufacturing industries, and animal farms [2]. Researchers have discovered pharmaceutical residues in almost all environmental matrices on every continent. This includes many water sources, including lakes, rivers, streams, estuaries, seas, groundwater, wastewater treatment plant effluent and influents, and sludge [3]. Water sources in several large countries across multiple continents have been found to contain pharmaceuticals at varying concentrations [4].

These pollutants typically infiltrate the environment through both treated and untreated industrial wastewater, urban agriculture runoff, and hospital effluent. Hospitals contribute significantly to the release of pharmaceuticals into the environment through the excretion of drugs by patients and the improper disposal of unnecessary medications [5]. Additionally, the unregulated disposal of industrial pharmaceutical waste is a significant factor in causing harm to the environment [6]. Their presence in the environment has the capacity to pose a threat to living beings and diverse non-target creatures [7,8]. Nevertheless, the complete understanding of the effects of these pharmaceuticals on human health and marine species is still lacking because of their ability to accumulate in living organisms and their long-lasting presence in the environment [9]. Pharmaceutical substances possess innate bioactivity and persistence, allowing them to retain their medicinal effectiveness. Upon being released into the environment, certain medications undergo rapid degradation, while others remain intact [10,11]. While biodegradation does decrease the levels of these substances in the water they are released into, the byproducts of their breakdown remain and cannot be effectively eliminated using typical biological and chemical treatment methods [12].

Photocatalysis using semiconductor nanoparticles is a clean and popular method for degrading pharmaceuticals. This innovative approach is highly efficient, environmentally friendly, and utilizes highly oxidizing species like hydroxyl radicals (•OH) to break down organic molecules into less harmful substances such as water, carbon dioxide, and short-chain organics [13-16]. Unlike processes like the Fenton reaction and ozonation, photocatalysis mineralizes organic molecules without the need for additional reagents [17]. Photocatalysis involves exposing a photocatalyst to light, generating charge carriers that facilitate the breakdown of pollutants. This method's high efficiency and minimal environmental impact make it a promising solution for treating inorganic compounds [18]. Upon exposure to light, the photo-excited electrons (e^-) and holes (h^+) produce highly reactive oxygen species (ROS) such as hydroxyl radicals (•OH) and superoxide radicals ($O2•^-$) on the surface of the semiconductor. These ROS are responsible for the oxidation of medicinal compounds [19]. Furthermore, sulfate radicals ($SO4•^-$) have been progressively utilized for applications in environmental photocatalysis [20]. Over the last ten years, a variety of nano-enabled photocatalysts have been employed to break down diverse pharmaceuticals using ultraviolet (UV) and visible light exposure. The crucial variables that influence the photocatalytic treatment and performance encompass the light source, pH level, dose or concentration of photocatalyst, optimal reaction time for degradation, and concentration of pollutant [21].

Alginate, a natural polymer derived from brown seaweed, is the salt of alginic acid and is widely used as an entrapment component. It is an inexpensive, non-toxic, and highly effective polymeric matrix [22]. The carboxylic groups in alginate enhance the adsorption of metal ions, making it a suitable material for creating durable hydrogels that can support catalysts [23]. The choice of calcium alginate gel in this investigation is due to its efficacy, affordability, ease of preparation, and porous structure that allows rapid diffusion of metal ions [22,24]. Additionally, researchers have explored using calcium alginate (Ca-Alg) beads with immobilized titanium dioxide (TiO_2) for degrading methylene blue [25]. Their findings indicate that recycled TiO_2–Ca-Alg beads improve the degradation process, as the beads become rougher with repeated use, enhancing their effectiveness.

Nickel (Ni) nanoparticle beads are selected for the degradation of pharmaceutical products in photocatalysis due to their high catalytic activity, cost-effectiveness, and magnetic properties. These beads facilitate efficient breakdown of complex molecules and are more economical than noble metals like platinum or gold. Their magnetic nature allows for easy recovery and reuse, which is essential for sustainable and cost-effective operations. Ni nanoparticles are chemically stable and durable, ensuring consistent performance over time and under various environmental conditions. Compared to other nanomaterials, Ni nanoparticles provide several advantages [26,27]. They absorb visible light more effectively than TiO_2, making them suitable for natural sunlight-driven processes. While noble metals are highly effective, Ni offers a more affordable alternative without compromising much on catalytic performance. Ni nanoparticles can also be easily functionalized or combined with other materials to enhance their properties, providing versatility in their application [26]. Overall, their combination of efficiency, affordability, and practical benefits makes them an excellent choice for photocatalytic degradation of pharmaceutical pollutants.

In conclusion, this study explores the degradation of aspirin and theophylline in water using a photocatalytic approach. It investigates the impact of pH, catalyst dosage, and initial concentration on the photocatalytic reaction, deepening understanding of the breakdown of pharmaceutical compounds. This research is vital for advancing photocatalytic technology to effectively remove pharmaceutical contaminants from water systems. The primary goal is to develop an efficient and eco-friendly method for eliminating these pollutants. By using photocatalysts to break down the compounds, the study advances photocatalytic technologies for environmental cleanup and water treatment. Ultimately, this work aims to improve water quality and promote public health.

2. Methodology

2.1 General Procedure and Methodology

The research methodology flow is illustrated in the diagram in Figure 1.

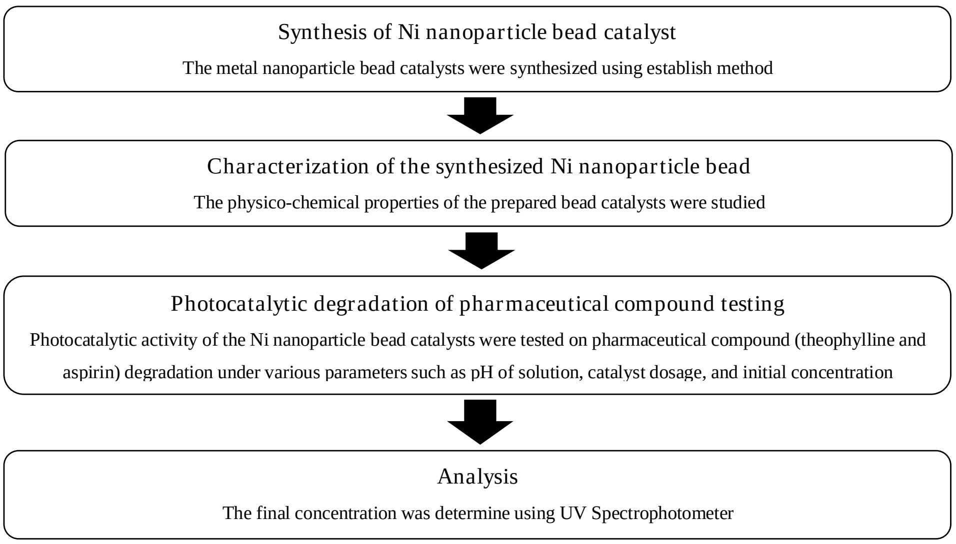

Fig. 1. Research flow chart diagram

2.2 Materials and Chemical

The nickel (Ni) nanoparticle powder was acquired from Macklin, China with a purity level exceeding 99.5%. The powder was used in its original form without any modifications. The ingredients used include alginate powdered from Sigma-Aldrich Laborchemikalien GmbH, calcium chloride dihydrate of A.R. grade from Uchem, epichlorohydrin solution, aspirin powder from Chemiz, and theophylline anhydrous with a minimum purity of 99% from Sigma-Aldrich Laborchemikalien GmbH. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were acquired from QReCTM. All the reagents were of analytical quality and were utilized without any further processing. Deionized water was utilized to prepare solutions, including synthetic medicinal compounds, alginate solution, calcium chloride solution, and pH solution. Adjustments to pH were made using 0.1 M HCl and 0.1 M NaOH solutions.

2.3 Alginate Bead Catalyst Preparation

The entire procedure of preparing the bead catalyst was updated and enhanced [25]. The 3 wt% calcium alginate solution was made by dissolving the powdered alginate in deionized water, stirring for 4 hours, and allowing it to stand overnight. Subsequently, a solution containing 3 wt% of alginate was injected into a precipitation bath, which is composed of an aqueous $CaCl_2$ solution with a concentration of 0.5 M. Subsequently, the gel beads are cross-linked 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 technique [28]. The last stage of the alginate bead was thoroughly washing the cross-linked alginate beads with deionized water, rendering them prepared for photocatalytic testing.

2.4 Photocatalytic Testing

The photocatalytic efficacy of the produced Ni nanoparticle bead catalyst was assessed for the decomposition of theophylline and aspirin concentrations in an aqueous solution. The solution was exposed to radiation using a Philips Lifemax TLD 18W/54 lamp as the light source, while maintaining a steady temperature and stirring for a duration of 60 minutes. The light originates from 15 cm between the lamp and the beaker containing 100 mL of medicinal solution with varying pH levels ranging from 4 to 8. The beaker has a capacity of 250 mL. The impact of catalyst dosage and the starting concentration of theophylline and aspirin were also assessed in photocatalytic tests. A degradation sample was obtained and the quantity of analytes in the sample was determined using a UV-Vis spectrophotometer (UV 1900). Theophylline and aspirin were quantified using their characteristic absorption bands at 273 nm and 229 nm, respectively. A 5 mL sample was collected and then subjected to centrifugation at defined time intervals. The rate of photodegradation on the Ni nanoparticle bead catalyst at each time (degradation quantity) was determined by applying Eq. (1).

$$Degradation\ (\%) = \frac{C_o - C_i}{C_o} \times 100\% \tag{1}$$

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

3. Results

3.1 Photocatalytic Reaction

Figure 2 displays the results of performance research that examined the effectiveness of several catalysts in removing a pharmaceutical component. Ni nanoparticle bead catalysts have superior removal efficiency compared to alginate bead catalysts and Ni nanoparticle powder catalysts, achieving removal rates of 60% and 63% for aspirin and theophylline, respectively. The efficacy of the alginate bead in photocatalytic reactions is minimal because alginate itself does not exhibit inherent photocatalytic capabilities and is not effective in absorbing light [29]. Alginate beads commonly serve as a support matrix for incorporating photocatalytic compounds. When using Ni nanoparticle powder, it forms compact layers that effectively block light from reaching all the particles. This results in unequal activation and reduces the photocatalytic reactions. By utilizing the nickel nanoparticle powder trapped within the bead as a photocatalyst for photocatalytic reactions, enhanced performance can be achieved. Ni nanoparticle bead facilitates enhanced light penetration and even dispersion across the catalyst bead. Therefore, achieving equal exposure to light can significantly boost the efficiency of photocatalysis [30].

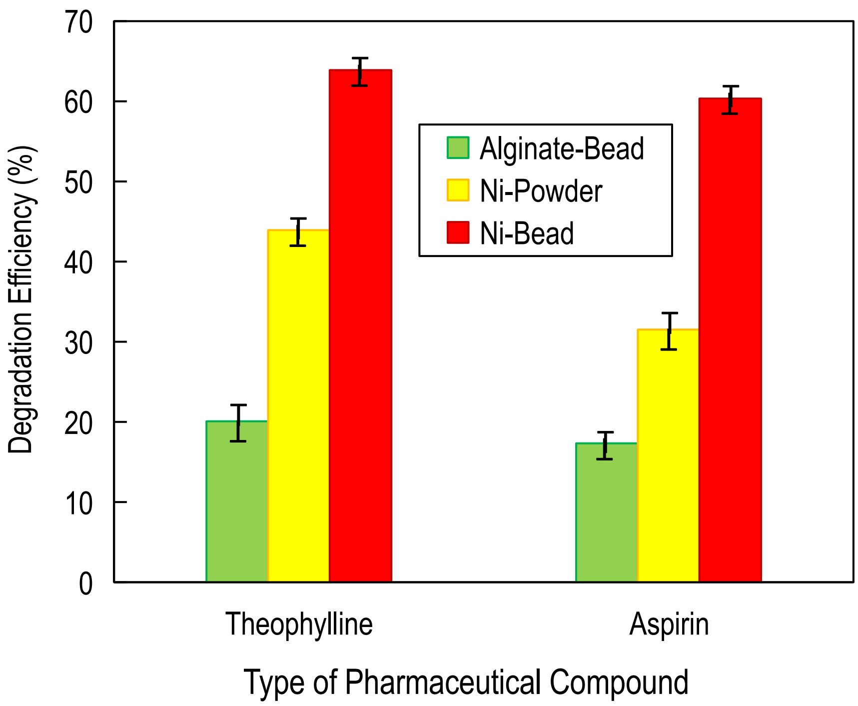

Fig. 2. Performance study using different types of catalyst and pharmaceutical compound

3.1.1 The effect of pH

Figure 3 illustrates the impact of pH on the degradation of pharmaceutical compounds in an aqueous solution. The pH values of the solution under examination were 4, 5, 6, 7, and 8. Theophylline experienced a degradation rate of 63% whereas aspirin had a degradation rate of 60% when utilizing Ni nanoparticle bead as a photocatalyst. When utilizing alginate beads, theophylline experienced a degradation rate of 20%, while aspirin experienced a degradation rate of 17%. The degradation employing Ni nanoparticle powder resulted in the highest clearance rates of 43% for theophylline and 31% for aspirin. The pH performance analysis indicates that the most effective pH for removing this medicinal ingredient is 5. The minimum percentage of the pharmaceutical ingredient that is eliminated when a pH of 8 is used in the photocatalytic reaction. The study determined that the ideal pH for effectively removing both theophylline and aspirin was found to be 5.

The pH of the solution is essential for the production of hydroxyl radicals during the process of photocatalytic degradation. OH- ions can enhance the abundance of hydroxyl radicals. Radicals are highly reactive substances that can accelerate the decomposition and degradation rate of pharmaceutical compounds [30]. The process of photocatalysis happens when the charge of the •OH radical is transferred to a medicinal component. The degradation percentage of the medicinal component rose when the pH was changed from 4 to 5. The presence of a higher number of photocatalysts with a negative charge in the solution leads to an increased production of hydroxyl radicals [31]. Photocatalysts function most effectively in capturing the necessary energy to boost their photocatalytic efficacy at an optimal pH of 5. Nevertheless, the photocatalyst's capacity to absorb the equivalent energy diminishes when the pH rises to 6, 7, and 8. When exposed to an alkaline solution, aspirin and theophylline acquire a negative charge, leading to a repulsive reaction with the photocatalyst [31]. It has been demonstrated that an increase in pH can result in a decrease in removal efficiency.

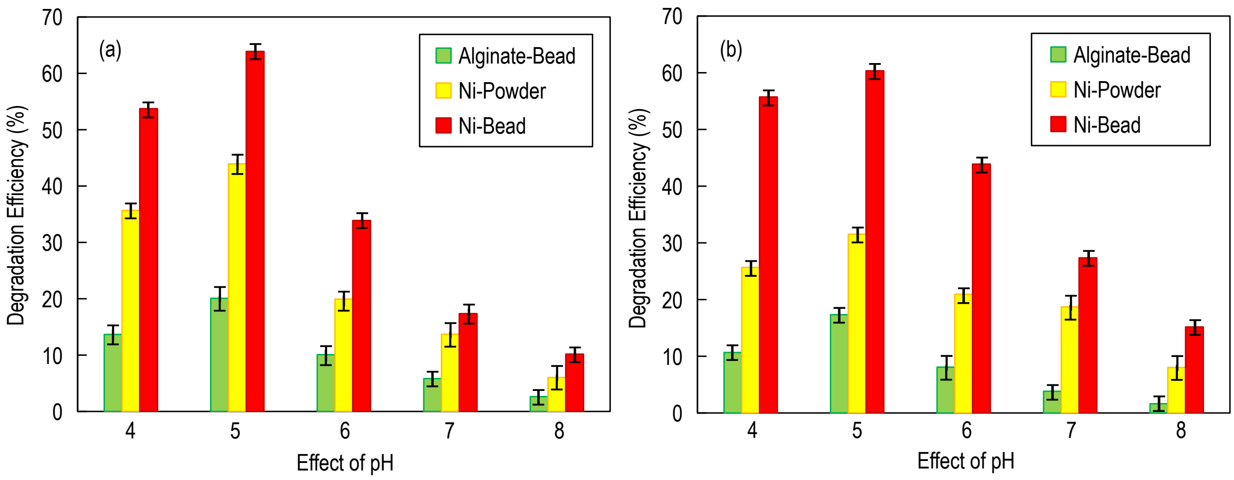

Fig. 3. Effect of pH (a) removal of theophylline (b) removal of aspirin

3.1.2 The effect of catalyst dosage

Figure 4 demonstrates the impact of the dosage of Ni nanoparticle bead, Ni nanoparticle powder, and alginate bead on the effectiveness of the photocatalytic degradation process. The catalyst dosage being studied ranged from 10 to 60 g/L, with increments of 10 g/L. The maximum degradation of aspirin and theophylline occurred when the catalyst dosage was set at 40 g/L. The alginate bead had the highest theophylline proportion at 40%, followed by the Ni nanoparticle powder at 65%, and the Ni nanoparticle bead at 89 %. The degradation rates for aspirin were 30%, 55%, and 86% when using alginate bead, Ni nanoparticle powder, and Ni nanoparticle bead, respectively. The performance trend of the catalyst dosage exhibits a rising degradation till reaching a dosage of 40 g/L. However, further increasing the concentration leads to a decrease in the elimination of the medicinal ingredient in the aqueous solution. The ideal catalyst dosage employed in the photocatalytic reaction of the medicinal molecule is 40 g/L.

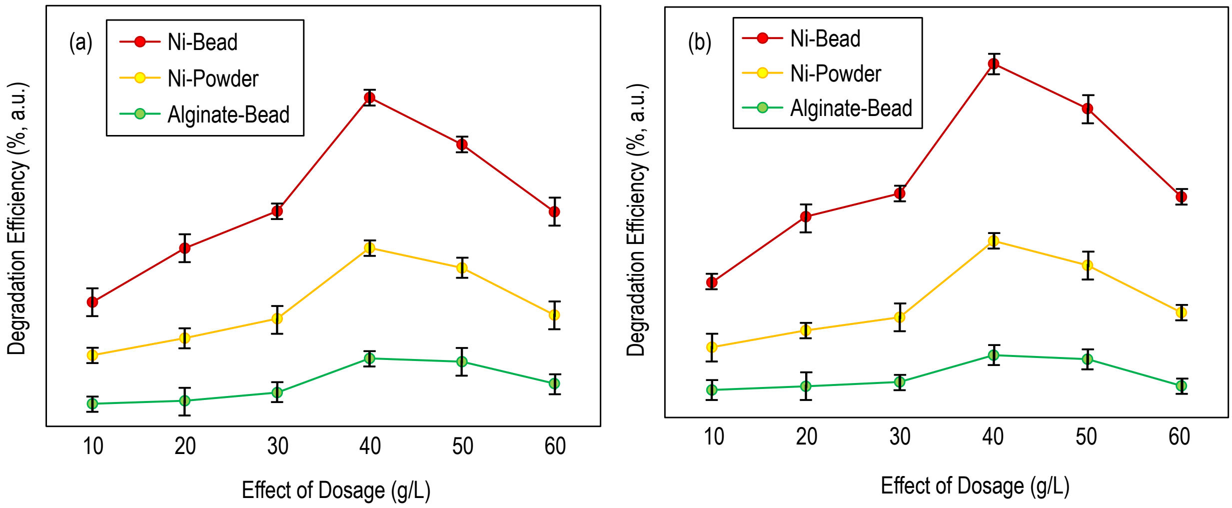

Fig. 4. Effect of catalyst dosage (a) removal of theophylline (b) removal of aspirin

It showed that the degradation escalated as the mass of the catalyst rose until it reached the state of equilibrium. The degradation was probably induced by an increase in the quantity of active sites with a greater concentration of catalyst, leading to a larger absorption of photons and pharmaceutical chemical molecules [32,33]. Enhancing photon absorption can lead to an elevated production of OH hydroxyl radicals and irradiation positive holes. However, when the catalyst dose exceeds a specific threshold, the larger concentration of particles leads to increased turbidity in the suspension. This turbidity obstructs the passage of light and impairs the process of photodegradation since the number of photons absorbed is lowered [34,35]. The photocatalytic activity may decrease in some situations when an excessive quantity of photocatalyst is employed during the process [33,36].

3.1.3 The effect of initial concentration

Figure 5 demonstrated the impact of the initial concentration of the pharmaceutical ingredient on the process of photocatalytic degradation. The pharmaceutical ingredient being studied had beginning concentrations of 10, 20, 30, 40, and 50 mg/L. The maximum degradation achieved was 40%, 65%, and 89% when a concentration of 10 mg/L of theophylline was employed for the alginate bead, Ni nanoparticle powder, and Ni nanoparticle bead catalyst, respectively. Conversely, the alginate bead, Ni nanoparticle powder, and Ni nanoparticle bead catalyst achieved removal rates of 30%, 65%, and 86% correspondingly for aspirin at a starting concentration of 10 mg/L. Increasing the initial concentration of a pharmaceutical ingredient will result in a decrease in its degradation by photocatalytic reaction, as indicated by the trend. The most effective starting concentration for the photocatalytic reaction of the pharmaceutical ingredient is 10 mg/L.

The level of pollutants is a critical factor that affects both the efficiency and speed of degradation. Generally, the pace at which degradation occurs increases as the concentration of the substrate rises, especially in cases of low contamination levels. This phenomenon can be explained by the presence of a large number of empty spaces and highly reactive particles that promote the interaction with impurities in situations where the concentration of the substance being reacted is low. However, the efficiency decreases as the concentration exceeds the optimal state due to insufficient hydroxyl radical presence [34]. In contrast, if there is a higher concentration of impurities, the contaminants will absorb the photons before they can reach the catalyst's surface. Therefore, the existence of pollutants causes a decrease in the efficiency of photocatalysis as a result of light absorption [37-39].

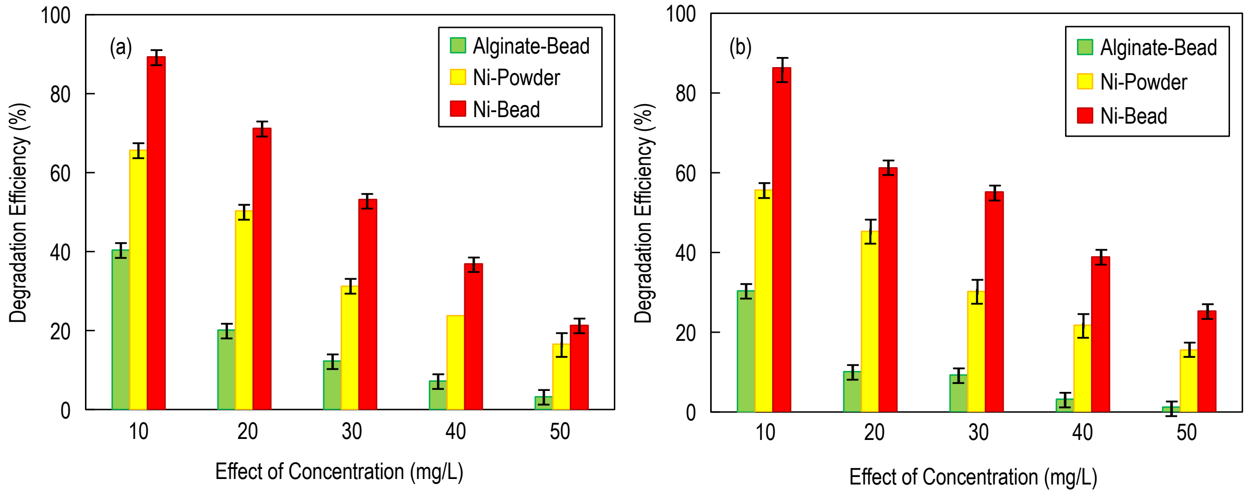

Fig. 5. Effect of initial concentration of pharmaceutical compound (a) removal of theophylline (b) removal of aspirin

4. Conclusions

In this study, the efficiency of the Ni nanoparticle bead on photocatalytic degradation of pharmaceutical compound in aqueous solution of different variable was investigated. Ni nanoparticle bead shows the better performance in removal of pharmaceutical compound compared to Ni nanoparticle powder and alginate bead. The pH influences the photo-degradation percentage of aspirin and theophylline significantly, in which the optimum pH was obtained at 5. The degradation increases with catalyst mass, leading to larger absorption of photons and pharmaceutical molecules however when excessive photocatalyst usage may decrease activity. The optimal catalyst dosage was obtained 40 g/L. Pollution levels have an impact on the efficiency and rate of degradation. Greater concentrations result in faster breakdown; however, efficiency declines due to inadequate hydroxyl radical present. An optimal initial concentration is 10 mg/L. The optimum degradation was obtained at one hour of irradiation for theophylline and aspirin were 89% and 86% respectively when Ni nanoparticle bead was applied as a photocatalyst. Consequently, it can be concluded that the photocatalytic process using Ni nanoparticle bead has a relatively high potential of pharmaceutical compound removal from aqueous solution and can be used as a convenient method for easy operation and has a low cost for the operational scale.

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