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Effect of Fe Doping on Zeolite Bead Nanoparticles for Enhanced Photocatalytic Removal of Phenol

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***Abstract*— This study focused on developing innovative bead catalysts of Fe doping with zeolite nanoparticles utilizing photocatalysis technology to address challenges posed by phenolic compounds. The photocatalytic efficiency of the magnetic zeolite bead catalyst for phenol degradation was evaluated under luminescent conditions. A comprehensive analysis was conducted to examine the influence of pH, catalyst dosage, and initial phenol concentration on degradation performance. The results suggest that these magnetic bead catalysts are highly effective in photodegrading phenol and can be efficiently recovered and reused multiple times during treatment at pH 5, 40 g L^{-1} of bead dosage and 20 mg L^{-1} of initial concentration of phenol. The application of magnetic zeolite bead catalysts for wastewater recovery proved to be fast, cost-effective, sustainable, and environmentally friendly. In conclusion, the development of magnetic zeolite bead catalysts presents a promising new solution for wastewater treatment challenges.**

Keywords— ***magnetic zeolite bead catalyst; phenol; photocatalytic degradation; visible light irradiation; wastewater treatment***

I. INTRODUCTION

Water, the essence of life, forms the foundation of Earth's ecosystems. However, the rising demands of an expanding population, combined with human activities and industrial processes, have led to a substantial increase in wastewater generation containing various inorganic and organic pollutants [1]. The deterioration of water quality affects ecosystems, communities, and industries alike. The world's limited freshwater resources are becoming increasingly polluted due to the continuous discharge of untreated or insufficiently treated wastewater into reservoirs, lakes, rivers, and coastal areas. Annually, an estimated 2 to 3 billion people face water shortages lasting at least one month, posing serious threats to their survival, particularly in terms of food and energy security. By 2050, the number of urban residents affected by water scarcity is expected to triple, rising from 930 million in 2016 to 1.7–2.4 billion. Additionally, prolonged and extreme droughts are becoming more frequent, exerting immense pressure on habitats and causing significant declines in wildlife populations. This growing pollution presents a serious threat to public health, with over one-third of the global population currently deprived of access to clean water and adequate sanitation [2]. Untreated industrial effluents discharged into water bodies not only endanger human health but also cause significant environmental harm. According to the World Health Organization (WHO), water pollution impacts millions globally, with predictions suggesting this crisis could affect 3.7 billion people by 2025 [3].

Phenolic compounds pose a significant threat due to their ability to accumulate in the body over time, persist in the circulatory system, and cause harm to both humans and livestock. The U.S. Environmental Protection Agency

(USEPA) classifies phenol as one of the most highly toxic substances [4]. Humans are particularly susceptible to phenolic compounds, as many can easily penetrate the skin and are readily absorbed by the digestive system [5]. Once these substances enter the bloodstream, they undergo metabolic processes that can produce reactive intermediates, such as quinone moieties, which form covalent bonds with proteins in the body and may have harmful effects.

Phenol concentrations in wastewater can range from 10 to 300 mg L^{-1}, with extremely polluted effluents reaching levels as high as 4.5 g L^{-1}. Additionally, the chlorination of phenol-containing water during disinfection can lead to the formation of toxic polychlorinated phenols. Phenol and its derivatives are toxic or lethal to fish at concentrations of 5 to 25 mg L^{-1} and may also pose carcinogenic risks. Even at much lower concentrations, such as 2 g L^{-1}, phenols impart an unpleasant medicinal taste and odor to water. The World Health Organization recommends a maximum safe phenol concentration of 1 g L^{-1} in drinking water [6].

Advanced oxidation processes have recently gained significant traction for wastewater treatment. These processes generate highly reactive species, such as hydroxyl radicals (•OH), which can react with a wide range of organic compounds through electrophilic addition to double bonds or electron-transfer reactions. The resulting intermediates can further interact with dissolved molecular oxygen, enhancing degradation efficiency and converting contaminants into less toxic or non-toxic compounds [7-14]. Among these methods, heterogeneous photocatalytic degradation has garnered particular attention for its ability to completely mineralize organic compounds into CO_2, H_2O, and inorganic ions.

A variety of technology-driven solutions are being explored today to address environmental challenges. Zeolites, a class of microporous materials with crystalline structures, have proven to be highly effective adsorbents for wastewater treatment. Their distinctive features, such as a high surface area, exchangeable cations, and a negatively charged framework, make them well-suited for adsorption-based remediation processes [15]. Furthermore, combining photocatalysis with adsorption techniques offers a synergistic approach to wastewater treatment, utilizing the photoactive properties of materials to degrade organic pollutants under light exposure [16]. Adsorption is widely regarded as an effective complement to photocatalysis, offering exceptional efficiency and ease of operation. Adsorbents increase the contact surface area between themselves and pollutants, while photocatalysts actively degrade the pollutants they encounter. As a result, combining these two methods can substantially enhance degradation efficiency. Since photocatalytic reactions primarily occur on semiconductor surfaces, the adsorption of contaminants onto a material's surface plays a crucial role in determining the overall efficiency of photodegradation.

Magnetic nanoparticles combined with zeolite enable exceptional pollutant removal through photocatalytic processes. The large surface area of a substance can enhance its affinity for hydroxyl groups, leading to the formation of hydroxyl radicals, which are often the primary oxidants responsible for contaminant degradation. Zeolite coated with magnetic nanoparticles results in nanocomposites with a low bandgap and small particle size. The lower bandgap of the magnetic nanoparticles contributes to a higher recombination rate. Additionally, Fe_3O_4 can act as an electron acceptor and transporter, promoting charge carrier dissociation and accelerating the photocatalytic process. Therefore, incorporating Fe_3O_4 into zeolite nanoparticles represents a significant advancement in photocatalytic mechanisms. This study focused on using zeolite integrated with iron magnetic nanoparticles as a photocatalyst, taking advantage of their unique properties for removing pollutants from water. These catalysts feature a large surface area and were modified to enhance their reactivity and efficiency in eliminating specific compounds. They were also designed to exhibit redox-active properties. The catalytic activity of the beads is influenced by factors such as their chemical composition, size, porosity, crystalline structure, and degree of crystallization.

A promising solution to these challenges lies in the development of innovative bead catalysts utilizing photocatalysis-adsorption technology. Recent advancements in magnetic zeolite bead catalysts and nanomaterials offer significant potential, particularly for water treatment applications. Due to their high permeability and extensive surface area, nanoparticles within magnetic zeolite bead catalysts facilitate rapid reactions. These nanoparticles can also be functionalized with various groups to enhance their reactivity or selectivity toward specific molecules. The strategies for designing magnetic zeolite beads have improved the structure and framework of the iron particles, thereby boosting the catalyst's efficiency and accelerating the degradation of phenol in water.

II. METHOD

The precursor solution was prepared by dissolving the powdered catalyst in 3% wt of alginate solution to form a viscous solution and well-mixed. The prepared solution is then pumped by using a syringe into a precipitation bath (non-solvent) that consists of 0.5M aqueous $CaCl_2$. The wet beads formed then cross-linked with epichlorohydrin solution and the reaction take place. Initially, magnetic zeolite bead catalyst was immersed in three successive ethanol/water baths (60% v/v ethanol, 400 mL each) for 2 hours each to replace the water in the beads with ethanol. The beads were then transferred to 400 mL of an ethanol/water solution (60% v/v ethanol) containing epichlorohydrin (6.109 g). A 1 mol/L NaOH solution was gradually added to adjust the pH to approximately 13. The crosslinking reaction was carried out for 4 hours. Subsequently, the beads were rinsed in three consecutive baths of distilled water (600 mL each for 2 hours). In the final bath, concentrated HNO_3 solution (53.7% w/w) was added to neutralize the mixture, bringing the pH to around 7.

The photocatalytic degradation of phenolic contaminants in phenol solutions has been utilized to assess the photocatalytic

activity of the magnetic zeolite bead catalyst. The research's photocatalytic reactions had been conducted in the presence of visible light. The study examined the influence of various factors, including solution pH (3, 5, 7, 9, 11), bead catalyst dosage (20.0, 40.0, 6.00, 8.00, 100.0 g L^{-1}), and initial concentrations of diclofenac and phenol (20, 40, 60, 80, 100 mg L^{-1}). These experiments were carried out under visible light conditions using the magnetic zeolite bead catalyst. To get the appropriate pH, 0.1 M NaOH or/and 0.1 M HCl solution was added to the sample mixture. Pour around 2.0 g L^{-1} (wet weight) of bead into a beaker with 100 mL of sample solution (20 mg L^{-1}). A magnetic stirrer was used to gently swirl the liquid continuously for 120 minutes. The sample solution was subjected to an irradiation source, a fluorescent light, with a 15 cm height restriction separating the solution and the illumination source. Samples have been taken on periodically shortly after the photocatalysis process has been completed and the concentration is assessed using a UV-Vis spectrophotometer.

III. RESULTS AND DISCUSSION

The photodegradation performance of the manufactured magnetic zeolite bead catalyst was evaluated by studying the degradation of phenol in a water-based solution. Key variables, includin the effect of pH on the solution (Figure 1), catalyst dosage (Figure 2), and initial pollutant concentration (Figure 3), were analyzed to determine the degradation rate. Batch sorption tests were conducted at room temperature over a two-hour exposure period.

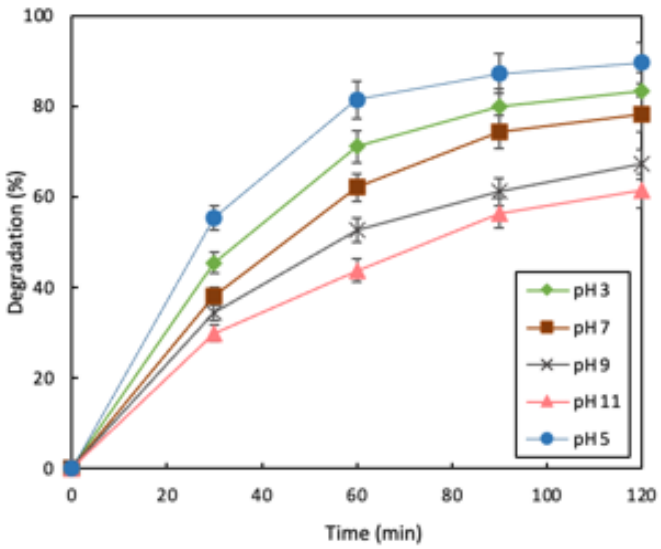

FIGURE 1. Effect of pH solution for magnetic zeolite beads catalyst [pH = X; W = 2.0 g L^{-1}; C = 20 mg L^{-1}; t = 2 h; T= 303.15 K]

The pH of the solution significantly influences the rate of pollutant degradation through photodegradation. Semiconductor oxides often exhibit amphoteric behavior, and since reactions occur on the active surface sites of the semiconductor, pH largely affects the surface charge characteristics of the magnetic zeolite bead catalysts. In this study, the highest phenol degradation rate for the magnetic zeolite bead catalyst was observed at pH 5, achieving a maximum degradation efficiency of 89.67%. These results are consistent with Ahmad et al.'s pH study [17], which reported a decline in degradation rates as pH increased from 5 to 11.

The improved performance at pH 5 is attributed to a higher generation of hydroxyl radicals (HO•) in acidic to moderately acidic conditions. As the pH increased, oxyhydroxides such as Fe(OH) and $FeOH^+$ formed on the catalyst's surface, leading to a gradual decline in degradation efficiency. The significant drop in performance at pH 11 is attributed to the reduced oxidizing ability of HO•, which forms inactive ferrous ions (FeO_2^+) at high pH levels [18]. Additionally, in alkaline environments, hydrogen peroxide dissociates more readily, causing both hydroxyl radicals and hydrogen peroxide to degrade rapidly, further reducing effectiveness.

Determining the optimal catalyst dosage is a crucial step in achieving maximum efficiency in the photocatalytic process. The effect of magnetic zeolite bead catalyst dosage on phenol photodegradation is illustrated in Figure 4. The results show that phenol photodegradation increased significantly as the catalyst dosage was raised, reaching its peak efficiency at a dosage of 4.0 g L^{-1}, where the maximum photodegradation rate was 95.98%. Beyond this saturation point, further increases in catalyst dosage had no significant impact on phenol degradation, as the photocatalytic reactions reached equilibrium under the given conditions.

This phenomenon can be explained by the reduction in the photon adsorption coefficient once the catalyst dosage exceeds a certain threshold (the saturation phase). At this stage, an excessive catalyst load may create a light-shielding effect, reducing the surface area exposed to photons and thereby limiting further photocatalytic activity. Ahmad et al. [17] similarly observed that both performance and degradation rates increase with catalyst dosage up to an optimal point, after which additional catalyst offers no further benefits.

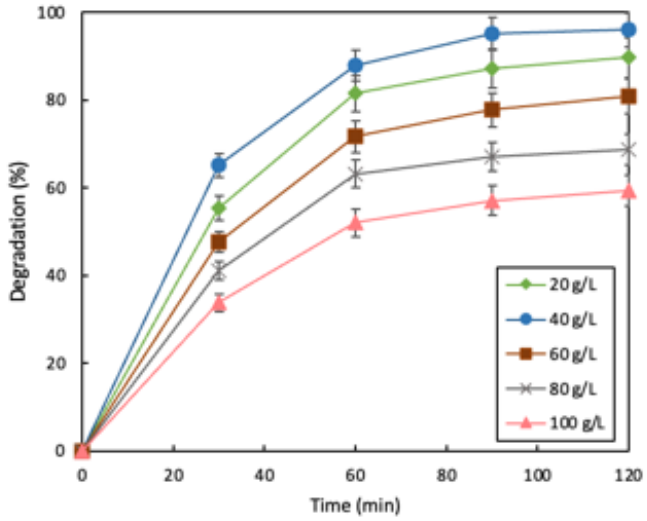

FIGURE 2. Effect of catalyst dosage for magnetic zeolite beads catalyst [pH = 5; W = X; C= 20 mg L^{-1}; t = 2 h; T = 303.15 K]

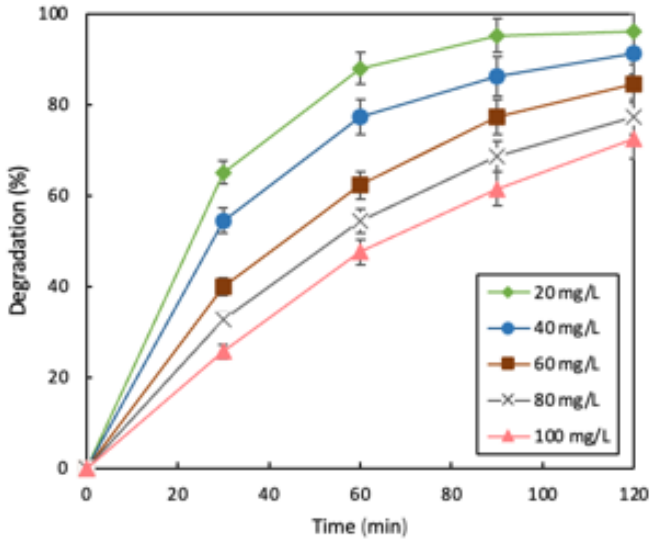

FIGURE 3. Effect of initial concentration for magnetic zeolite beads catalyst pH = 5; W = 6.0 g L-1; C = X; t = 2 h; T = 303.15 K]

The rate and efficiency of a pollutant's photocatalytic degradation depend on the type, concentration, and presence of additional substances in the water. The relationship between the initial pollutant concentration and the photocatalytic activity of the magnetic zeolite bead catalyst was examined by studying phenol adsorption on its surface. After two hours of exposure to radiation, the magnetic zeolite bead catalyst achieved a high degradation rate, reaching 95.98% at a concentration of 20 mg L^{-1}.

Research shows that phenol photodegradation decreases as the initial concentration of the reactant increases, primarily due to a shortage of active sites on the catalyst bead surfaces. When the initial reactant concentration is higher, the pollutant occupies more of these active sites, reducing the availability for further reactions and limiting oxidant production. Since the amount of magnetic zeolite bead catalyst was fixed in this experiment, the number of hydroxyl radicals generated in the system remained constant. Consequently, the decrease in degradation rate with higher pollutant concentrations was attributed to the insufficient hydroxyl radical concentration relative to the large number of pollutant molecules. This finding aligns with Ahmad et al. [17], who reported a similar decline in degradation rates as the initial pollutant concentration increased.

The optimal conditions for phenol degradation were achieved at pH 5, with a catalyst dosage of 40.0 g L^{-1} and an initial pollutant concentration of 20 mg L^{-1}. The factors influencing this outcome included the generation of hydroxyl radicals, which, in excessive amounts, reduced the catalyst's ability to decompose pollutants. Similarly, higher contaminant concentrations led to competition for photons and active reaction sites on the photocatalyst's surface, inhibiting oxidant production and slowing the photodegradation rate.

The results highlighted that the catalyst beads possessed a larger surface area and pore volume, enhancing their capability to degrade harmful substances effectively. The chemical interaction between the negatively charged carboxyl groups in alginate and the encapsulated catalyst beads demonstrated the potential for selective adsorption of organic molecules based on intrinsic charge carriers. This interaction also facilitated efficient separation techniques, showcasing the potential for these beads to achieve an advanced level of photocatalytic pollutant reduction.

IV. CONCLUSIONS

The developed magnetic zeolite bead catalyst demonstrates exceptional photocatalytic efficiency for phenol degradation, achieving maximum photodegradation rates within a two-hour exposure period. Under optimal conditions—such as pH, catalyst dosage, and initial solution concentration—the pollutant's degradation can potentially be achieved in an even shorter time frame. Modifications to the magnetic zeolite bead catalyst have notably enhanced its pore size, stiffness, hydrophilicity, chemical resilience, and biocompatibility. The findings indicate that these magnetic bead catalysts exhibit excellent efficiency in photodegrading phenol and can be effectively recovered and reused multiple times under optimal conditions of pH 5, a bead dosage of 40 g L^{-1}, and an initial phenol concentration of 20 mg L^{-1} with 95.98% of phenol

degradation. Moreover, this photocatalytic process generates environmentally friendly byproducts, primarily converting pollutants into carbon dioxide and water. Overall, this study highlights how the use of magnetic zeolite bead catalysts offers a novel and highly effective approach to addressing the challenges of wastewater treatment.

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