Degradation of 2-Chlorophenol from Wastewater Using γ-Fe₂O₃ Nanoparticles

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Abstract:

In this study, magnetic nanoparticles $(\gamma - Fe_2O_3)$ were used for the degradation of 2-chlorophenol (CP) from wastewater. The size of these magnetic nanoparticles was measured using XRD and found to be about <50 nm. Experiments for the CP degradation by the γ -Fe₂O₃ nanoparticles from wastewater were carried out under ultrasound irradiation. Major influence factors on the degradation efficiency, such as, ultrasonic time, and initial pH value, were investigated. The results indicated that the γ -Fe₂O₃ nanoscale particles were very effective for the CP degradation. The degradation efficiency was 45% in 25 min under the ultrasonic irradiation. The effect of initial pH value showed that the degradation percent was improved by increasing the pH of solution. **Keywords:** Nanoparticle, 2-Chlorophenol, Ultrasound irradiation, Wastewater, Degradation.

1. INTRODUCTION

The degradation of aromatic pollutants such as phenol-like compounds in wastewater streams generated by different industrial activities such as pharmaceutical, petrochemical or chemical industries has emerged as an important concern due to the restrictive environmental laws and regulations. Phenol and phenol-like compounds show high toxicity for microorganisms, high chemical oxygen demand and poor biodegradability [1].

Many techniques have been applied for removal and degradation of phenolic compounds present in wastewater. These include adsorption, biodegradation, and extraction by liquid membrane and oxidation [2-8].

In recent years, nanoparticles of magnetic metals and oxides have attracted great interest due to their unique physical and chemical properties [9-11]. Especially, maghemite $(\gamma$ -Fe₂O₃) nanoparticles attracts great deal of interest due to their technological and fundamental importance, such as information storage, magnetic resonance imaging contrast agent, superparamagnetism, and macroscopic quantum tunnelling associated with size quantization and electronic quantum confinement effects [12-13].

The objective of this study was to investigate the feasibility of CP degradation by γ -Fe₂O₃ nanoparticles under ultrasonic irradiation. CP was selected as target substance because it has been extensively used throughout the world as wood preservative and general biocide, and was listed in the persistent organic pollutant by the United States Environmental Protection Agency [14].

2. EXPERIMENTAL

The nanoparticles (γ -Fe₂O₃) were prepared according to Ref. [15]. Briefly, anhydrous FeCl₃ (3.25 g) and FeCl₂.4H₂O (1.99 g) were separately dissolved in 20 mL deionized water, followed by the two iron salt solutions being mixed under vigorous stirring (800 rpm). Then, 30 mL of 25 w/w % aqueous ammonia was added to the solution. The color of bulk solution immediately changed from orange to black. The magnetic precipitates were washed twice with deionized water. The size of the nanoparticles was measured using X-ray diffraction.

CP solutions were prepared by adding CP into deionize water. 0.05 gram of the γ -Fe₂O₂ nanoparticles were added into 50 mL CP solution. Solution dispersed by ultrasonic irradiation for different times. It operated at a frequency of 20 KHz and a rated output power of 4.5 W. The temperature was maintained at 22-25°C by cycling water. The apparatus was open to air. Then, the absorbed metals on the surface of γ -Fe₂O₂ nanoparticles were separated by magnetic field (0.5 Tesla) and lastly the suspension was centrifuged for one hour at 3600 rpm. The concentration of residual CP in the solution was measured with gas chromatography (N2000, 0.25mm Ø×30 m, Agilent). The temperature regime of GC oven was as follows: (1) increasing from 40°C (holding time 3 min) to 150°C (holding time 1.5 min) at a rate of 20°C/min, (2) increasing to 280°C (holding time 5 min) at a rate of 30°C/min.

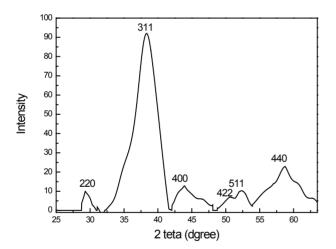


Figure 1: XRD patterns of maghemite nanoparticles

3. RESULTS AND DISCUSSION

The crystal structure of synthesized nanoparticles was investigated using XRD measurement (Cu K α

radiation, Philips, PW1800). The diffraction pattern matches well with the JCPDS file (e.g., No. 19-0629) of γ -Fe₂O₄, thus indicating the formation of γ -Fe₂O₂ with a cubic spinel crystalline structure (Figure 1). The crystallite size of γ -Fe₂O₂ nanoparticles was estimated using the Scherrer Equation (D= 0.9 λ / $(\beta \cos \theta)$, λ is the wavelength of the X-rays, θ is the scattering angle of the Bragg reflections, β is the full width at half maximum) [16]. The average crystallite size was calculated from XRD peak broadening using Scherrer's formula is 40 nm. The degradation percentage of CP as a function of ultrasonic irradiation time were investigated (Figure 2). High degradation efficiency was approximately 45% after 25 min of ultrasonic irradiation. It is due to size and surface area changing of nanoparticles. The short ultrasonic irradiation time suggests that the magnetic γ -Fe₂O₂ nanoparticles can have high adsorption efficiency to the CP degradation of from wastewater.

The effects of pH on degradation percentage of CP were investigated over the range of pH values from 2 to 9 in 25 min of ultrasonic irradiation. As shown in Figure 3, the degradation percentage is minimum at the initial pH of 2. The percentage of degradation is increased by increasing pH from 2 to 7, and then the degradation percentage is not significantly altered beyond pH of 7. It seems that hydroxyl radicals formed by ultrasonic irradiation plays an important role in the degradation of CP from wastewater using γ -Fe₂O₃ nanoparticles [17-18]. These hydroxyl radicals in alkali solutions are more than that of pH acidic solutions. The reaction between CP and iron surface sites (≡Fe) can be described as equilibrium reaction between sorbet and aqueous species [19-21]:

$$\equiv$$
 Fe + CP_e $\leftrightarrow \equiv$ Fe(CP)_s

hydroxyl radicals can probably attack the sorbet species as well as the aqueous species leading to the degradation and mineralization of CP.

HO + ≡ Fe(CP)_s → ≡ Fe + (CP by - products)_{solution} → Cl⁻ + CO₂ HO + CP_e → CP by - products → Cl⁻ + CO₂

Because of the highly existence of hydroxyl radicals

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in the alkali pH, the degradation efficiency of CP in the alkali pH was more than acidic pH.

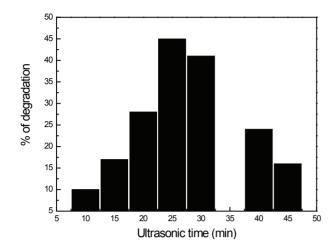


Figure 2: Percentage degradation of CP as a function of ultrasonic time

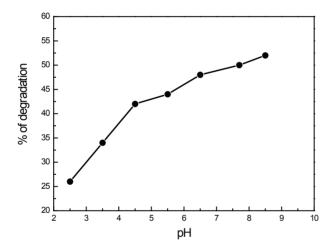


Figure 3: Effect of pH on the degradation of CP

4. CONCLUSION

It is conclusively evident from our studies that the use of γ -Fe₂O₃ nanoparticles for the degradation of CP is technically feasible, environmental-friendly, and economically attractive. Comparing to conventional separation, the advantages of adsorption followed by magnetic separation are attributed to its rapidness, efficiency, and simplicity. Degradation efficiency of CP by γ -Fe₂O₃ nanoparticles reached 45% within 25 min of ultrasonic time. The degradation efficiency was enhanced by increasing pH.

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