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Heterogeneous Photocatalysis and its Potential Applications in Wastewater Treatment

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ABSTRACT

To increase the photocatalytic activity of AgCl for environmental applications, a simple precipitation–deposition technique was established for the synthesis of the CoFe2O4/AgCl complex. For that, the phase of the nanoparticles was identified by X-ray diffraction (XRD), and the morphology was investigated by scanning electron micrograph (SEM), The gap energies of $CoFe_2O_4$(CFO) and AgCl, evaluated from the UV-VIS diffusion reflectance, were found to be 1.46 eV and 3.20 eV, respectively. For the photodegradation of the orange acid dye, some operating parameters such as the mass ratio of $CoFe_2O_4$/ AgCl, the catalyst, the pH of the solution and initial AO61 concentration were optimized. 25%/75% mass ratio of CFO/ AgCl, catalyst dose of 1.25 g/L, pH ~ 6 and 50 mg/L initial concentration were found as optimal conditions for the degradation performance under visible light with an efficiency of 93% within only 240 min. Moreover, this hetero-system demonstrated effective oxidation by facilitating photo-electron transport with the deference potential.

Keyword: $CoFe_2O_4$; AgCl; Photodegradation; Dye; Visible irradiation.

1 Introduction

Semiconductor photocatalysis has been considered as a promising and green technology to remove harmful organic pollutants in water, especially some hazardous dyes. Among the plentiful semiconductor photocatalysts, cobalt ferrite $CoFe_2O_4$ (CFO) is a popular magnetic material with a high level of coercive strength and strong magnetization, CFO is also known for its optical proprieties with a bandgap of ~1.8 eV and an extended depletion width where the electron/hole (e-/h+) are separated [1]. Recently, it has been reported that nanostructured CFO was successfully used as a photocatalyst [2]. It is also combined with other photocatalytic semiconductors to enhance the photocatalytic performance, such as $MoS_2/CoFe_2O_4$ [3]. In this study, nanoparticles of (CFO) were synthesized by nitrate route, tested for the elimination of an anionic dye namely the Acid Orange 61 and enhanced its photocatalytic activity by the novel hetero-junction $CoFe_2O_4$/AgCl.

2 Experimental

CFO as elaborated from nitrates as precursors: for an amount of 15 g of CFO, a mass of 18.9861 g of $Co(NO_3)_2.6\ H_2O$) and 52.1796 g of $Fe(NO_3)_3.9H_2O$ were dissolved in 100 mL of distilled water. First, the mixture was treated to 100 °C to eliminate the water, followed by heating at 350 °C to remove the nitrates. Then, the powder was ground in an agate mortar and heated in an alumina boat according to the following program 500 °C (2 × 6 h) and 700 °C (2 × 4 h), interspersed with grindings, necessary to obtain a single phase. CFO/AgCl composites were prepared by precipitation-deposition route, to prepare 2g of CFO/AgCl = (25%/75%); 0.5g of CFO powder was dissolved with a 1.7778 g of $AgNO_3$ in 50 mL of distilled water under agitation (10 min) to ensure the mixture homogenization, then 0.6116 g of NaCl dissolved in 20 ml of distilled water was added dropwise into the above suspension under stirring for 30 min. Finally, the precipitate was filtered, thoroughly washed and treated at 80 °C (24 h) and 100 °C (6 h).

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3 Results and Discussion

3.1 Characterization of catalyst

The phase and structural form of the samples was identified using HighScore Plus. The crystal structure of CFO was found to be cubic spinel-type. The presence of (111), (220), (311), (400), (422), (511) and (440) miller indices in the XRD pattern of the CFO sample in Fig. 1,a is in accordance with cubic spinel structure of CFO with space group Fd-3m which is in agreement with JCPDS standard cards No. 01-077-0426 with no impurities . The XRD of AgCl agreed with JCPDS standard cards No. 31-1238 with lattice constant a = 5.5491 . Fig 1 shows also the XRD pattern of the hetero-junction CFO/AgCl with different ratios, as can be seen, there are changes in the structure of the samples in each ratio of hetero-junction.

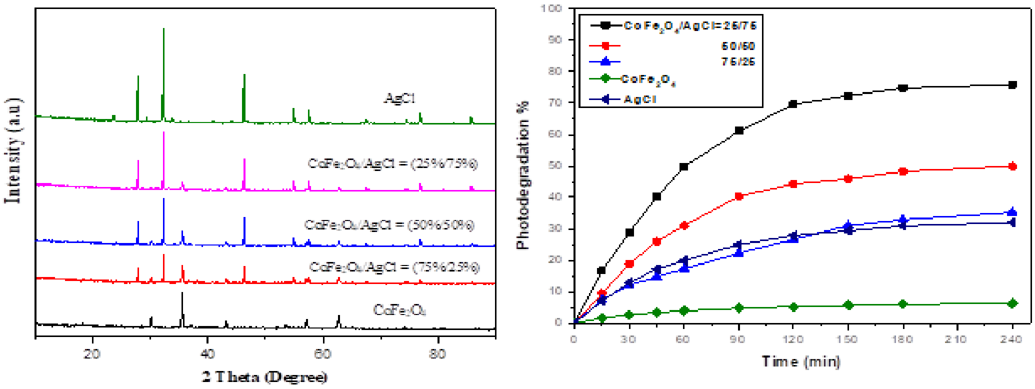

Fig1: a) The XRD pattern of $CoFe_2O_4$, AgCl and $CoFe_2O_4$/AgCl with different ratios, b)Influence of the mass ratios of hetero-system (CFO/AgCl) on photodegradation kinetics of AO61 (C_o = 50 mg/L, pH ~ 6, T =25°C).

3.2 Study of the photo-degradation of AO61 on the hetero-system CFO/AgCl

Batch photocatalytic degradation tests are carried out in order to observe the effect of certain operating parameters that can influence the CFO/AgCl hetero-system, such as the mass ratio of the hetero-system and the dose of the hetero-system. We can see in Fig. 1,b that the photocatalytic activity of the CFO/AgCl composite increased with the AgCl content, significant degradation of the AO61was recorded for the CFO/AgCl ratio (25/75) which reaches 75.86% during 4 h. This is due to the activation of the photocatalytic sites between both CFO and AgCl by sharing electrons under visible illumination which allowed the formation of radicals that participate in the degradation of AO61 . On the other hand, the photodegradation efficiency by the CFO/AgCl ratios (50/50) and (75/25) reaches 49.93% and 35.23% during 4 h respectively. They are low compared to the ratio (25/75). For AgCl and CFO as a separate photocatalyst, they can degrade only a small amount 31.99 % and 6.18% respectively after 4 hours.

4 Conclusions

In summary, CFO was synthesized by the nitrate route and then characterized by various methods such as XRD, and SEM. The gap energies of CFO and AgCl were evaluated from the UV-VIS diffusion reflectance and were found to be 1.46 eV and 3.20 eV, respectively. For the photodegradation of the orange acid dye, it was tested by CFO and enhanced using AgCl as a hetero-system. Some operating parameters such as the mass ratio of $CoFe_2O_4$/AgCl and catalyst dose, were optimized. 25%/75% mass ratio of $CoFe_2O_4$/ AgCl, catalyst dose of 1.25 g/L, pH ~ 6 and 50 mg/L initial concentration were found as optimal conditions for the degradation performance under visible light with an efficiency of 93% within only 240 min.

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