

Photocatalytic Elimination of Phenol and 2,4 Dichlorophenoxyacetic Acid by Mg-Zn-Al Layered Double Hydroxides

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Introduction

In recent years, there has been an increasing demand for solutions to the multiple environmental problems associated with the use of toxic compounds. Amongst these, phenol and chlorinated phenols play a major role, because of their high toxicity, extensive use and weak retention in soil sediments. Many research efforts have been devoted to the elimination of these compounds, and studies on photocatalytic degradation are worth noticing [1]. Another branch corresponds to the development of suitable adsorbents to be used in the elimination of these compounds. Some of the adsorbents that have been studied include layered double hydroxides (LDHs) [2]. LDHs are a class of naturally occurring anionic clays. The basic structure of an LDH may be derived from partial isomorphic substitution of divalent cations in a brucite lattice by trivalent cations. Since an ample assortment of compounds with the basic LDH structure might be prepared, they are represented by the general formula: $[M^{II}_{(1-x)}M^{III}_x(OH)_2]A^{n-}_{x/n} \cdot mH_2O$. There has been considerable interest in the use of LDHs to remove negatively charged species from solution, due to their high uptake levels. This paper presents a study of the adsorption and photocatalytic degradation of phenol and 2,4-Dichlorophenoxyacetic acid (2,4-D) by Mg-Zn-Al layered double hydroxides, which appear as a promising alternative for the elimination of toxic substances from waste water. The main advantages of these materials are their easy preparation, low cost, and reusability. Mg-Al layered double hydroxides were also prepared and tested to determine the role of Zn^{2+} cations.

Materials and Methods

The layered double hydroxides containing Mg-Al and Mg-Zn-Al with different amounts of zinc were prepared by the coprecipitation at low supersaturation method at constant pH [3]. The adsorption capacity of calcined LDHs was determined by preparing 6 solutions of 2,4-D, with concentrations varying between 0.45 and 1.58 mmol L⁻¹, in 200 mL of distilled water. 0.1 g of the calcined solid was added. Aliquots were taken from solution every 30 min for 6 hours, and the remaining amount of 2,4-D was determined by UV-Vis spectroscopy. The adsorption of phenol by LDHs was negligible, and is thus not reported here. Photodegradation of 2,4-D was carried out by preparing a solution of 1.36 mmol L⁻¹ in distilled water. Four aliquots of 200 mL were taken, and 0.2 g of catalyst was added to each one. Solutions were irradiated with UV light for 1 to 9 hours. Photodegradation of phenol was carried out by preparing solutions of 0.42 mmol L⁻¹ in distilled water, and following the same procedure as described above, irradiating solutions with UV light for 1 to 5 hours.

Results and Discussion

X-ray diffraction patterns revealed pure hydrotalcite-like phase in all solids. Surface area values of calcined solids, determined by N₂ adsorption-desorption, were 230 ± 50 m² g⁻¹.

Furthermore, it was confirmed that the addition of zinc provokes the shift of the adsorption edge to longer wavelengths, and thus a decrease in the band gap energy, from 5.45 eV for MgAl to 3.85 eV for MgZnAl-15. However, this is still relatively high when compared to a semiconductor material such as anatase, which has band gap energy of 3.0-3.2 eV.

Adsorption of 2,4-D onto LDHs was effectively described by Langmuir adsorption isotherms. The adsorption capacity was largest for the sample with lowest zinc amount, MgZnAl-5. As the amount of zinc increases, the adsorption capacity gradually diminishes. Regarding the photocatalytic degradation of 2,4-D, in all cases over 90% of the contaminant was degraded after 9 hours. The best results were obtained for the sample with the lowest amount of zinc, which also had the largest adsorption capacity. However, photocatalysis and adsorption may proceed by two different mechanisms, as was suggested by analyzing concentration evolution as a function of time (Figure 1).

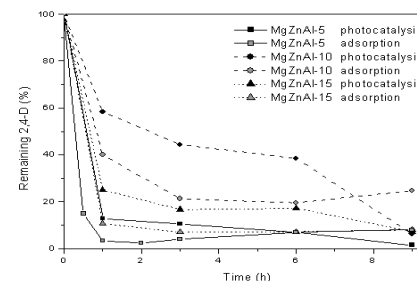


Figure 1. Photodegradation and adsorption of 2,4-D as a function of time.

For phenol photodegradation, a strong photocatalytic activity was evident for MgZnAl-5, degrading ca. 70% of phenol in 6 hours. A lineal plot of phenol photodegradation was developed, which adjusted well to a pseudo-first order kinetic behavior. Photodegradation of 2,4-D and phenol are better explained by the charge deficiencies presented by this kind of materials, than by their semiconducting properties, as experimental values are the opposite from what would be thus expected. A different hypothesis is thus proposed, that charge deficiencies in Al³⁺ act as an electron trap that is activated by UV light, stealing electrons from neighboring atoms and generating OH• free radicals, which in turn initiate the photodegradation processes. In this mechanism, zinc atoms in small amounts would act as impurities that might facilitate the generation of OH• groups.

Significance

Adsorption and photocatalytic activity was tested on herbicide 2,4-D, a representative molecule of an ample variety of contaminants. Elimination of over 90% can be achieved either way. Elimination of phenol by photodegradation was also attempted, degrading ~70% in 6 hours. Thus, LDHs appear as a promising catalyst for the photodegradation of contaminants in aqueous solutions.

References

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