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# Nucleophilic Chemistry of γ-Al<sub>2</sub>O<sub>3</sub>/ZSM-5 Zeolite Binary Nanocomposite Adsorbent for the Removal of Methamidophos Insecticide

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**Keywords:**  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/ZSM-5; nanocomposite; adsorbent; methamidophos; removal; <sub>31</sub>PNMR.

## Introduction

## NanoComposite

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 Nanometers (nm) or structures having nano-scale repeat distances between the different phases that make up the material [1].

The idea behind Nanocomposite is to use building blocks with dimensions in nanometre range to design and create new

## Abstract

In this work, γ-Al<sub>2</sub>O<sub>2</sub> nanoparticles were fabricated on the ZSM-5 zeolite via ultrasonic-assisted hydrothermal method. The morphology and structure of the as-fabricated  $\gamma$ -Al<sub>2</sub>O<sub>2</sub>/ ZSM-5 nanocomposite adsorbent was fully characterized by SEM, EDAX and XRD, and FTIR analyses. Applying XRD analysis, the average particle size of y-Al<sub>2</sub>O<sub>2</sub>/ZSM-5 was obtained to be 13.8 nm. The removal reactions of O, S-dimethyl phosphoramidithioate (methamidophos) organophophorus insecticide have been evaluated via γ-Al<sub>2</sub>O<sub>2</sub>/ZSM-5 adsorbent at room temperature. The 31 PNMR analysis outcomes demonstrated that 96.7% of methamidophos was removed by y-Al<sub>2</sub>O<sub>2</sub>/ZSM-5 at n-heptane solvent within reaction time of 100 min. On the other hand, the gained outcomes for the acetonitrile and methanol solvents were lower. It seems that a nonpolar solvent transfer to the reactive surface site on the nanocomposite without occupying and blocking of these sites.

materials with unprecedented flexibility and improvement in their physical properties. In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry [2].

The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Size limits for these effects have been proposed.



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- 1. <5 nm for catalytic activity
- 2. <20 nm for making a hard magnetic material soft
- 3. <50 nm for refractive index changes

4. <100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement [3].

Nanocomposites are found in nature, for example in the structure of the abalone shell and bone [4]. The use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials. Some researchers investigated the origin of the depth of colour and the resistance to acids and bio-corrosion of Maya blue paint, attributing it to a nanoparticle mechanism. From the mid-1950s nanoscale organo-clays have been used to control flow of polymer solutions (e.g. as paint viscosifiers) or the constitution of gels (e.g. as a thickening substance in cosmetics, keeping the preparations in homogeneous form). By the 1970s polymer/ clay composites were the topic of textbooks, although the term "nanocomposites" was not in common use [5].

In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibres (e.g. carbon nanotubes or electrospun fibres) [6]. The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials [7]. The matrix material properties are significantly affected in the vicinity of the reinforcement. Some scientists be aware that with polymer nanocomposites, properties related to local chemistry, degree of thermoset cure, polymer chain mobility, polymer chain conformation, degree of polymer chain ordering or crystallinity can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix. This massive quantity of reinforcement surface area means that a relatively small amount of nanoscale reinforcement can have an observable effect on the macroscale properties of the composite [8].



**Figure 1:** Graphical abstract Zeolite-based composites for the adsorption of toxic matters from water [1].

## Zeolite

Zeolites are a group of crystalline materials made up of evenly sized pores and tunnel systems. When purifying VOCs and hydrocarbons, we use a synthetic hydrophobic zeolite. When the contaminated air passes through the material, the hydrocar-



Figure 2: Model structures of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (111)

bons are adsorbed. The material can adsorb a certain amount of hydrocarbons before needing to be regenerated [9,10].

A smaller flow of hot air is then directed through the material so that the hydrocarbons release from the zeolite in a higher concentration. This enables more cost-effective incineration. One of its strengths is that it is non-combustible-meaning it can withstand very high temperatures [11]. This means that we are also able to purify volatile hydrocarbons such as fumes emitted from vulcanization, plastic smoke and styrene, all of which require very high temperatures during regeneration. The resistance to high temperatures and the structure of the material also allows the zeolite to be completely regenerated-meaning that the VOCs completely release from the zeolite when heated. This means that the system maintains its high purification rate year after year and that the material does not have to be replaced, which gives it a long lifespan and a minimal need for maintenance [12]. Our systems have an availability of over 99% and a lifespan exceeding 25 years. Combining the benefits of zeolite with our 30 years of experience in working with air purification gives our customers a supremely sustainable and customized system with low operating costs and high availability.

#### Reversible hydration and dehydration

During drying it comes to the removal of free and bound water from the crystal grid, which is then counterbalanced back in contact with materials such as stored grain and feed, pet litter, in flue gas to prevent condensation and the like [13]. Clinoptilolite stabilize moisture at a low dose of volume and avoid the adverse effects of water [14].



#### Ion exchange

Grid structure allows clinoptilolite to operate as Ion exchanger and as a selective adsorbent. Adsorption and exchange of ions depends on their charge and size. The more the size of the ion matches the size of the entering grid of clinoptilolite, the easier it will be captured and kept [15]. Entry pore diameter is approximately 4 angstrom, which corresponds to the average ammonium ions  $NH_4^+$ ,  $H_2O$ ,  $_{134}Cs \& _{137}Cs$ . These compounds exhibit the greatest affinity to bind to clinoptilolite, which operates as a selective adsorbent for a wide range of pollutants [16].



Figure 4: SEM micrograph of nano-sized ZSM-5 zeolite.

#### Conclusion

This work undertakes the investigation of the removal reactions of methamidophos as an organophophorus insecticide on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/ZSM-5 zeolite nanocomposite. The impact of solvent type (methanol, acetonitrile and n-heptane) on the re-

moval potential of nanocomposite was studied. The synthesized samples were identified by SEM, EDAX and XRD, and FTIR techniques. The 31PNMR results demonstrated that about 96.7% of methamidophos was removed in the presence of above nano-composite at n-heptane solvent after 100 min. On the other hand, the results for the acetonitrile and methanol solvents were lower compared with the n-heptane.

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