

Nucleophile Chemistry of Two-Component $\gamma\text{Al}_2\text{O}_3$ / ZSM5 Zeolite Nanocomposite Adsorbent for the Removal of the Insecticide Methamidophos

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ABSTRACT

In this work, $\gamma\text{Al}_2\text{O}_3$ nanoparticles were fabricated on the ZSM-5 zeolite via ultrasonic-assisted hydrothermal method. The morphology and structure of the as-fabricated $\gamma\text{Al}_2\text{O}_3$ /ZSM-5 nanocomposite adsorbent was fully characterized by SEM, EDAX and XRD, and FTIR analyses. Applying XRD analysis, the average particle size of $\gamma\text{Al}_2\text{O}_3$ /ZSM-5 was obtained to be 13.8 nm. The removal reactions of O, S-dimethyl phosphoramidithioate (methamidophos) organophosphorus insecticide have been evaluated via $\gamma\text{Al}_2\text{O}_3$ /ZSM-5 adsorbent at room temperature. The ³¹P NMR analysis outcomes demonstrated that 96.7% of methamidophos was removed by $\gamma\text{Al}_2\text{O}_3$ /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.

Keywords: $\gamma\text{Al}_2\text{O}_3$ /ZSM-5; Nanocomposite; Adsorbent; Methamidophos; Removal; ³¹P NMR

Introduction

Nanocomposite

A nanocomposite is a multi-phase solid material in which one of the phases has one, two or three sizes less than 100 nanometers (nm) or structures with nanometer-scale repeat spacing between the different phases make up the material. [1] Figure 1 The idea behind Nanocomposite is to use building blocks at the nanometer scale to design and create new materials with unprecedented flexibility and improved physical properties. In the broadest sense, this definition can include porous media, colloids, gels, and copolymers, but is generally understood to mean a solid combination of a bulk matrix and one or more nanoscale phases with specific properties different properties due to structural

and chemical differences. [2] The mechanical, electrical, thermal, optical, electrochemical and catalytic properties of nanocomposites will differ significantly from those of the component materials. Size limits for these effects have been suggested.

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].

Nanocompounds are found in nature, for example in the shell and bone structure of abalone. [4] The use of nanoparticle-rich

materials has long predated the understanding of the physical and chemical nature of these materials. Some researchers have investigated the origin of Maya Blue paint color depth and resistance to biological and acid corrosion, assuming it is due to a nanomolecular mechanism. Since the mid-1950s, nanoscale organic clays have been used to control the flow of polymeric solutions (e.g., as a viscosity agent in paints) or to form gels (e.g., as a thickener in cosmetics) products, maintaining the preparations in a homogenous form). By the 1970s, polymeric/clay composites were the subject of textbooks, although the term “nanocomposites” was not commonly used. [5] Mechanically, nanocomposites are distinguished from conventional composite materials by the exceptionally high surface-to-volume ratio of the reinforcement phase and/or its exceptionally high aspect ratio. Reinforcing materials may include particles (e.g.,

minerals), sheets (e.g., exfoliated clay piles) or fibers (e.g., carbon nanotubes or electromolecular fibers). [6] The area of interface between the matrix and the reinforcing phase(s) is generally an order of magnitude larger than that of conventional composite materials. [7] The properties of the base material are significantly affected in the vicinity of the reinforcement. Some scientists know that with polymer nanomaterials, the properties are related to local chemistry, degree of thermoset hardening, mobility of polymer chains, structure of polymer chains, and degree of chain order polymer or crystallinity can both vary significantly and continuously from the interface to the matrix’s large component reinforcement. This huge amount of reinforcement surface means that a relatively small amount of nanoscale reinforcement can have an observable impact on the large-scale properties of the composite [8] Figure 2.

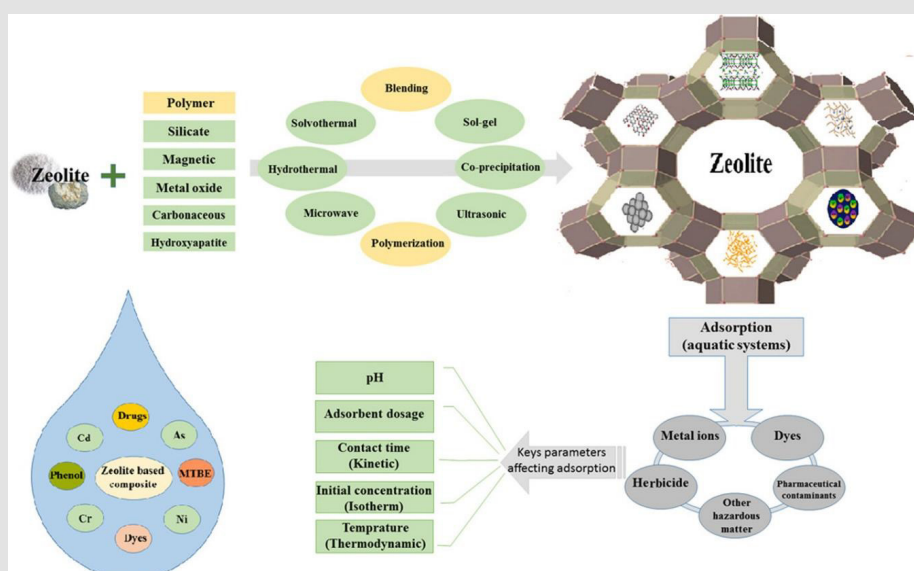


Figure 1: Graphical abstract Zeolite-based composites for the adsorption of toxic matters from water [1].

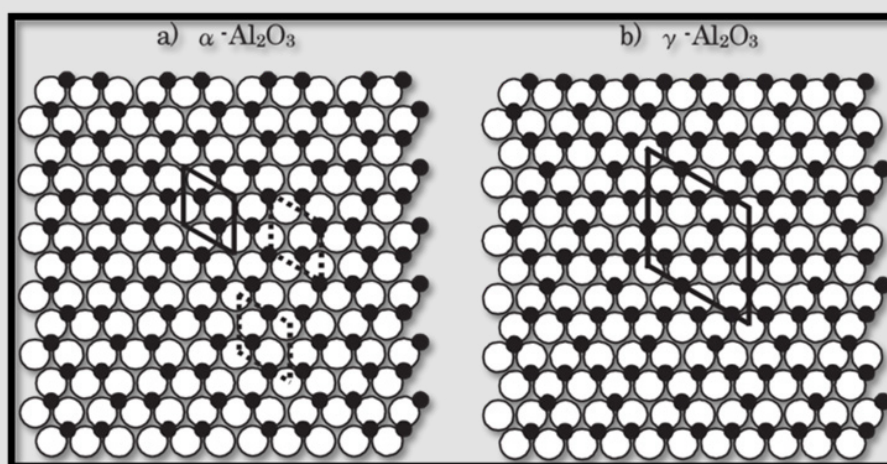


Figure 2: Model structures of α - Al_2O_3 (0001) and γ - Al_2O_3 (111).

Zeolite

Zeolites are a group of crystalline materials consisting of uniformly sized pores and tunneling systems. When purifying VOCs and hydrocarbons, we use hydrophobic synthetic zeolites. As contaminated air passes through the material, the hydrocarbons are absorbed. The material can adsorb a certain amount of hydrocarbons before having to be regenerated. [9,10] a smaller stream of hot air is then directed through the material so that the hydrocarbons release from the zeolite at a higher concentration. This allows for more cost-effective incineration. One of its strong points is that it is non-flammable, i.e., it can withstand very high temperatures. [11] This means we can also purify volatile hydrocarbons such as vulcanized fumes, plastic fumes and styrene, all of which require very high temperatures in the regeneration process. The high temperature resistance and structure of the material also allow

the zeolite to be completely regenerated, meaning that VOCs are completely liberated from the zeolite upon heating. This means that the system maintains a high purification rate year after year, and the equipment needs to be replaced, providing long life and little maintenance. [12] Our system has over 99% availability and a lifespan of more than 25 years. Combining the benefits of zeolite with our 30 years of air filtration experience gives our customers a customized and extremely durable system with low running 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] Figure 3.

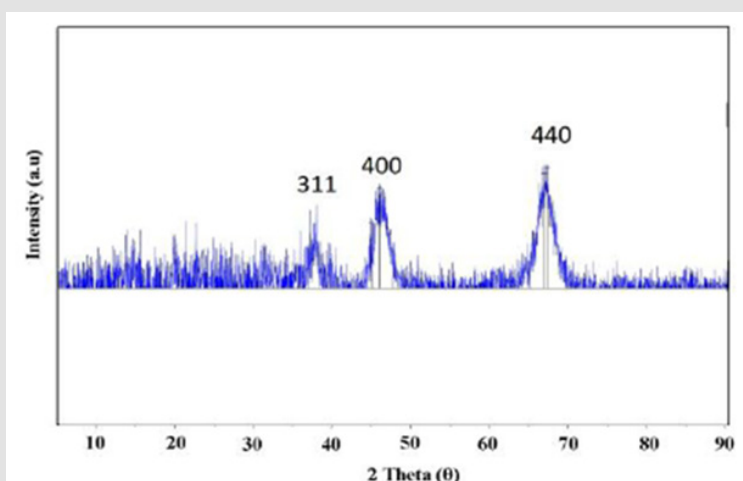


Figure 3: XRD patterns of synthesized γ - Al_2O_3 .

Ion Exchange

The mesh structure allows clinoptilolite to act as an ion exchanger and as a selective adsorbent. The adsorption and exchange of ions depends on their charge and size. The closer the ion size is to the incident mesh size of the clinoptilolite, the easier it

is to capture and retain [15]. Entry pore diameter is approximately 4 angstroms, 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.

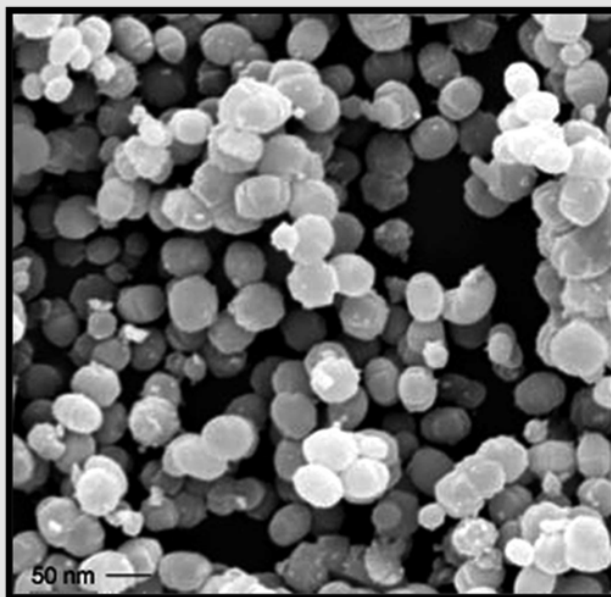


Figure 4: SEM micrograph of nano-sized ZSM-5 zeolite.

What Exactly is Ion Exchange?

Ion exchange describes a specific chemical process in which unwanted dissolved ions in water and wastewater - like nitrate, fluoride, sulfate, and arsenic - are exchanged for other ions with a similar charge. Ions are atoms or molecules containing a total number of electrons that are not equal to the total number of protons.

There are two different groups of ions:

- Positively charged cations
- Negatively charged anions

We have Michael Faraday to thank for these names, which he devised based on cations' attraction to cathodes and anions' attraction to anodes in a galvanic device.

Removing Ionic Contaminants

This attraction is used to remove dissolved ionic contaminants from water. The exchange process occurs between a solid (resin or a zeolite) and a liquid (water). In the process, the less desired compounds are swapped for those that are considered more desirable. These desirable ions are loaded onto the resin material. These resins can be used alone or in concert to remove ionic contaminants from water. In the exchange of cations during water treatment, positively charged ions that come into contact with the ion exchange resin are exchanged with positively charged

ions available on the resin surface, usually sodium. In the anion exchange process, negatively charged ions are exchanged with negatively charged ions on the resin surface, usually chloride. Various contaminants - including nitrate, fluoride, sulfate, and arsenic - can all be removed by anion exchange. Compared to other technologies, including continuous electrodeionization (CEDI), chromatography, ultrafiltration, and biological treatments, ion exchange is particularly suitable when trying to remove a specific low concentration pollutant, for example, removing boron from well water.

Recharging Resins

Resin materials have a finite exchange capacity. Each of the individual exchange sites will become full with prolonged use. When unable to exchange ions any longer, the resin must be recharged or regenerated to restore it to its initial condition. The substances used for this can include sodium chloride, as well as hydrochloric acid, sulfuric acid, or sodium hydroxide. The primary substance remaining from the process is called "spent regenerant." It contains not only all of the ions removed, but also any extra regenerant ions, and will also have a high level of total dissolved solids. Regenerant can be treated in a municipal wastewater facility, but discharges may require monitoring. The efficacy of ion exchange for water treatment can be limited by mineral scaling, surface clogging, and other issues that contribute to resin fouling. Pretreatment processes such as filtration or addition of chemicals can help reduce or prevent these issues.

Exchange Resins Market

The global market for ion exchange resins, which was estimated at \$1.54 billion in 2014, was projected in 2016 to be \$2.46 billion by 2022, a compound annual growth rate of roughly 6%, according to Statistics MRC, a Maryland-based market research firm. Their analysts see increased nuclear power demand and stringent environmental regulations driving the market. This is particularly seen in the power generation and wastewater treatment markets.

Ion Exchange in Drinking Water Treatment

Recently ion exchange resins have been increasingly used to produce drinking water. Specialized resins have been designed to treat various contaminants of concern, including boron, perchlorate, and uranium. There are many resins designed for these purposes, such as strong base/strong anion resin, which is used to remove nitrates and perchlorate. Ion exchange is used extensively in water softening, where it's considered a solid, proven technology.

Food Processing

Adsorption and ion exchange, both used in food processing, are similar in design and sometimes in their operating cycles. Ion exchange can be used for wine, fruit juice, and whey demineralization, and cane sugar decolorization. In whey demineralization, ion exchange is used to recover and convert lactose and mineral salts into more valuable substances for use in products such as baby food and pharmaceuticals. In fruit juice decolorization, ion exchange is used to decolorize must from grapes, for instance, and is also used for demineralization in wineries.

Is Ion Exchange Right for Your Needs?

Although ion exchange and biological treatment are widely recognized as the two leading technologies for denitrification, ion exchange is typically used to treat for nitrates in groundwater, while biological treatment is typically used to treat surface water. Ion exchange can also be used in the removal of arsenic and other metalloids and metals. Other viable alternatives, including membrane separation, may be more efficient, but also come with a higher cost.

Conclusion

This work undertakes the investigation of the removal reactions of methamidophos as an organophosphorus insecticide on the $\gamma\text{Al}_2\text{O}_3/\text{ZSM-5}$ zeolite nanocomposite. The impact of solvent type (methanol, acetonitrile and n-heptane) on the removal potential of nanocomposite was studied. The synthesized samples were identified by SEM, EDAX and XRD, and FTIR techniques. The

^{31}P NMR results demonstrated that about 96.7% of methamidophos was removed in the presence of above nanocomposite 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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