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Graphene based adsorbents for various pesticides

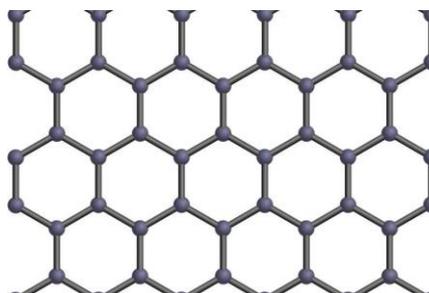
Monika and Mandeep

Abstract

This paper presents the function and application of graphene and its derivatives in various fields. Graphene applications in pesticides remediation is major field of research. Structural properties of graphene make it a useful material for all of the above applications. The adsorption properties of graphene make it a commendable material in surface chemistry. Thus, graphene based materials provide a huge thrust to the pollutant absorbent industry and semiconductor devices. Based on the application of graphene in controlling different pollutants by utilizing its adsorbent properties, this work stresses upon the useful applications of graphene in the context of adsorption of pesticides.

Keywords: Graphene, adsorption, pesticides

Introduction



To dimension graphene

World civilization leads to major changes in lifestyle and livelihood; at the same time, it also brings many issues which cause health problems and environmental concerns. In the present scenario, the major factors responsible for pollution worldwide are the industrial revolution, urbanization and population expansion. All these contribute in the pollution to water, soil and air. Industries are causing release of different pollutants, which are organic as well as inorganic. Eco-environments and the human health are affected by the major pollutants, including toxic gases (NO_x , SO_x , CO , NH_3), heavy metals, organics and bio-toxics. Some of the pollutants are biodegradable and some are not. The removal of non-biodegradable pollutants becomes a burden on our environment and is a major health concern.

Especially in surface chemistry, various contaminants can be removed from air and water systems. Since the industrial revolution, rapid developments in industrialization, population expansion, and urbanization have largely contributed to the severe pollution to air, water and soil. A vast number of pollutants, discharged from industrial processes and households annually, have caused significant effects on the environment and human life.

Applications of Graphene Pesticides

Pesticides are a diverse group of chemical compounds, which are used to eliminate pests in agriculture and households. However, their widespread use, as well as their high toxicity, generates risks to humans and the environment. Graphene, a new member of the carbon

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nanomaterial family, having two dimensional layers of sp^2 -bonded carbon, has sparked considerable research attention. Graphene and modified graphene materials have been widely employed for the treatment of pesticide-contaminated water. Mahpishanian *et al.* (2015) ^[1] synthesized silica coated magnetic micro-particles with functionalized graphene oxide and used them as adsorbents for the treatment of organophosphorus pesticides, including methyl parathion, fenitrothion, methidathion, ethion, methyl azinphos and coumaphos. Results indicated that the synthesized functionalized graphene oxide had great adsorptive ability and can be applied for the extraction of organophosphorus pesticides in different matrices. This may be due to the existence of a large delocalized π -electron system on the surface of graphene oxide which plays the main role in π -stacking interactions with the aromatic rings of organophosphorus pesticides or their electronegative atoms (P, N and S).

Li *et al.* (2015) ^[2] synthesized graphene-based magnetic nanoparticles and used them as adsorbents for the extraction of trace carbamate pesticides, metolcarb, baygon, methiocarb, carbofuran and isoprocarb in tomatoes. Graphene based nanoparticles showed better extraction efficiencies for the carbamate pesticides due to the contribution of the iron-containing magnetic nanoparticles to the adsorption capacity of the nanocomposites. Besides, the graphene based magnetic nanoparticles could be reused for more than 20 times without obvious decrease of the adsorption capacity. Shi *et al.* (2014) ^[3] synthesized graphene based adsorbent materials and used them for solid phase extraction of the carbamate pesticides, pirimicarb, baygon, carbaryl, isoprocarb, baycarb and diethofencarb. Graphene proved to be a good adsorbent for the solid phase extraction enrichment and purification of the six carbamate pesticides due to its large surface area and strong adsorption ability. The above-mentioned reports show that the graphene based nanoparticles can be used as simple and efficient adsorbents for trace carbamate pesticides. Ma *et al.* (2014) ^[4] developed the graphene reinforced hollow fibre liquid phase microextraction method, combined with high performance liquid chromatography, for the determination of some carbamate pesticides, metolcarb, carbaryl, isoprocarb, and diethofencarb in fruit samples. Graphene reinforced hollow fibre liquid phase microextraction combined with high performance liquid chromatography is a simple and cost effective technique. This method exhibits good precision, high sensitivity and low limits of detection because of the unique properties of graphene and the inherent advantageous features of the hollow fibre liquid phase microextraction. Graphene-modified TiO₂ nanotube arrays (Zhou & Fang, 2015) were synthesized and used for micro-solid phase extraction for the treatment of carbamate pesticides, including metolcarb, carbaryl, isoprocarb and diethofencarb. The factors affecting the enrichment efficiency of the micro-solid phase extraction procedure were optimized, and included sample pH, elution solvents, salting-out effect, adsorption time and desorption time. The results showed that the graphene-modified TiO₂ nanotube arrays were successfully used as effective adsorbents in micro-solid phase extraction of carbamate pesticides in water samples. Zhang *et al.* (2015) ^[3] prepared a new form of cellulose/graphene composite. The composite particles contain high adsorption power and are used for the adsorption of triazine pesticides, including simeton,

simazine, atrazine, cyprazine, ametryn and prometryn. The Langmuir isotherm model describes the adsorption process better and thermodynamic parameters show that adsorption is spontaneous, favourable, and endothermic in nature. Luo *et al.* (2015) used the magnetic graphene for the adsorption organochlorine pesticide residues in tobacco. In this case, the magnetic graphene was used as a modified quick, easy, cheap, effective, rugged and safe adsorbent. Montesinos *et al.* (2014) synthesized a cotton supported graphene as an extraction material, and used it for the extraction of multiclass pesticides from environmental water. The advantages of this extraction method are the simplicity of implementation, rapidity, and low consumption of sorbent per extraction.

Herbicides

Tang and co-workers (2012) reported that the electrodeposition and photoreduction processes could be used to design Ag nanoparticles and reduced graphene oxide co-decorated TiO₂ nanotube arrays. It was found that the ternary catalyst exhibited almost 100% photocatalytic removal efficiency of a typical herbicide 2,4-dichlorophenoxyacetic acid from water under simulated solar light irradiation. The photodegradation rate towards 2,4-dichlorophenoxyacetic acid over Ag nanoparticles and reduced graphene oxide co-decorated TiO₂ nanotube arrays was 11.3 times that over bare TiO₂ nanotubes arrays. Graphene oxide based solid phase extraction, combined with electro membrane extraction, was developed for ultra-preconcentration and determination of chlorophenoxy acid herbicides in environmental samples (Tabani *et al.*, 2013) ^[6]. Capillary electrophoresis was used in the method. This method reveals great potential of graphene as a reliable sorbent material in solid phase extraction. The newly reported technique has advantages compared to electro membrane extraction and solid phase extraction methods alone. Sha-Sha *et al.* (2013) reported that the graphene-based magnetic solid phase extraction, coupled with dispersive liquid-liquid microextraction, was developed to extract five chloroacetanilide herbicides, including alachlor, acetochlor, metolachlor, butachlor and pretilachlor, from water and green tea samples, followed by gas chromatography-flame ionization detection. Under optimum conditions, it was found that linearity was obtained in the range of 0.1 – 50.0 $\mu\text{g L}^{-1}$ for all the five herbicides with good correlation coefficients. The limits of detection ranged from 0.01 to 0.03 $\mu\text{g L}^{-1}$. The method has advantages, such as simplicity, high sensitivity and low cost. The results indicated that the method is suitable for the extraction and determination of the five chloroacetanilide herbicides in water and green tea samples. Tang *et al.* (2013) prepared the magnetic TiO₂-graphene hybrid photocatalyst and used it as a high-performance and recyclable platform for the efficient photocatalytic removal of herbicides from water. The results indicated almost 100% photocatalytic removal efficiency of the typical herbicide 2,4-dichlorophenoxyacetic acid from water under simulated solar light irradiation. In addition, the catalyst can be rapidly recovered with highly stable photocatalytic performance. After 8 successive cycles, the removal efficiency of 2,4-dichlorophenoxyacetic acid maintained 97.7%. Hence the designed photocatalyst should be a general and competent platform for the removal of organic herbicide and insecticide pollutants.

Conclusion

From the graphene based study, it has been concluded that the adsorbent properties of graphene can be exploited for the controlling of different pollutants, which cannot be controlled by different controlling agents. Its special properties will help in control of secondary pollutants which are non-degradable. Graphene and its derivatives can be further modified by use of different synthetic methods for control of various pollutants.

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