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Adsorption of toxic carbamate pesticide oxamyl from liquid phase by newly synthesized and characterized graphene quantum dots nanomaterials

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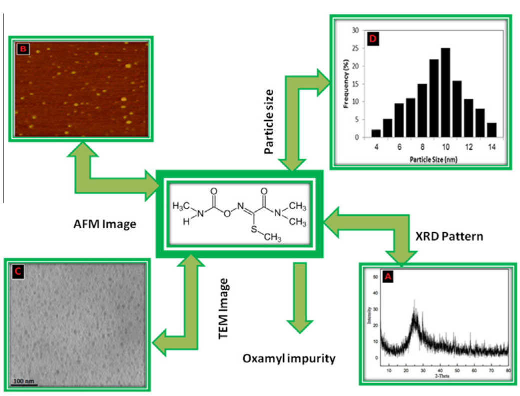
GRAPHICAL ABSTRACT

Morphological and anatomical property of the synthesized graphene quantum dot nanomaterials and chemical structure of oxamyl impurity.



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ABSTRACT

Graphene quantum dots have been synthesized using the microwave-assisted hydrothermal route. The surface textural and morphological structure of synthesized adsorbent i.e. graphene quantum dots was analyzed using various analytical techniques such as X-ray diffraction, Transmission electron Microscopy, Atomic Force Microscopy and N_2 adsorption-desorption instrumental techniques. The application of graphene quantum dots as an adsorbent for the removal of noxious pesticide compound i.e. oxamyl from aqueous solutions was well investigated and elucidated. The impact of several effective parameters such as effect of agitation speed, pH, adsorbent dose, contact time, temperature and initial concentration on sorption efficiency was studied and optimized using batch adsorption experiments. The optimized pH for maximum oxamyl adsorption was found to be 8.0 and for the maximum adsorption rates the adsorbent dose of 0.6 g was found to be optimum to carry out the adsorption with in less than 25 min of contact time. From the results obtained, it is clear that for all contact times, an increase in oxamyl concentration resulted in increase in the percent oxamyl removal. The adsorption equilibrium and

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kinetic data were well fitted and found to be in good agreement with the Langmuir isotherm and pseudo-second-order kinetic model.

1. Introduction

The use of large quantities of pesticides in agriculture practices is one of the main causes of soil pollution. Soil acts like an active filter, where chemical compounds are degraded by physical, chemical, and biological processes [1]. Both the accumulation of pesticides in the soil and their dispersion in the environment depend chiefly on the characteristics and overall functioning of the ecosystem. The concentration of these contaminants usually found in continental waters is quite low (in the range of μg^{-1} or less) and very often may be broken down, or degraded, by the action of sunlight, hydrolysis or micro-organisms [2,3].

Oxamyl (*N*,*N*-dimethylcarbamoyloxyimino-2-(methylthio)acetamide) is a main carbamoyl oxime insecticide nematicide which is extensively used in India for controlling the growth of nematodes in vegetable crops. It is a colorless crystalline solid with a melting point of 100–102 °C changing to a dimorphic form with a melting point of 108–110 °C. It has a slightly sulphur like odour and has a specific gravity of 0.97 (25°/4°). Due to its high water solubility product (K_{sp} = 280 gL^{-1}) and low soil sorption coefficient value (K_{oc} = 25), it is defined as an extremely noxious compound having an acute oral lethal dose (LD_{50} = 3.1 mg kg^{-1} for male rat). It possesses severe detrimental and toxicological effects on the prevailing flora and fauna of the particular ecosystem as well as in living beings. If it enters the biological cycle of the human, it inhibits the acetylcholinesterase by the rapid carbamylation of its active site [4,5]. It is somewhat less toxic for the fishes living in that particular aquatic ecosystem and it induces a concentration dependent increase in genomic DNA damage. Several other side effects include Malaise, osteoporosis, excessive sweating, nausea, abdominal pain, and Miosis with unclear vision [6–8].

Graphene quantum dots (GQDs), which are a new member of the carbon nanomaterial family, have attracted considerable scientific attention due to their unique, excellent physical and chemical properties. Owing to better quantum confinement, more edge defects, high aqueous solubility, strong photoluminescence (PL) emission, desirable fluorescence properties and low cytotoxicity, GQDs have been developed for applications in various fields, such as photocatalysis [7], biosensing [8] and chemiluminescence analysis [9].

GQDs can be prepared using two strategies, including the top-down method and the bottom-up growth process. Most top-down methods include cutting graphene oxide (GO) by a hydrothermal method [10] and graphitic exfoliation by an electrochemical route [11].

In the present work, the adsorption characteristics of oxamyl were investigated using GQDs as an adsorbent. The adsorption isotherms, thermodynamics, and kinetics of the adsorbent were measured. Equilibrium, thermodynamic and kinetic parameters were calculated to determine the adsorption mechanism. The GQDs has several properties such as high surface area, high stability, and low cost. Hence this material plays an important role in adsorption study for removal of noxious oxamyl compound.

2. Materials and methods

2.1. Raw materials

In this study, chemicals i.e. citric acid, tetrahydrofuran (THF), oxamyl, HCl and NaOH were purchased from Sigma–Aldrich Ltd. Stock solution and all working solutions were prepared with deionized water. All reagents used in the study were of analytical grade. Prior use, all glassware was cleaned with dilute nitric acid and repeatedly washed with deionized water.

2.2. Synthesis of GQDs

The citric acid was heated by convectional microwave oven a certain power (800 W) for 20 min to complete the pre-processing of precursor. After cooling to room temperature, the sample was dissolved by tetrahydrofuran (THF). After ultrasonic treatment for 2 h, the mixture was transferred into Teflon-lined stainless steel autoclave and heated at 150 °C for 6 h. After the hydrothermal reaction, samples were washed dried in vacuum at 100 °C for 1 h.

2.3. Characterization and analyses

X-ray powder diffraction (XRD) patterns were measured by a Japan Rigaku D/max-3C using Cu Ka radiation. Atomic force microscopy (AFM) images were obtained by tapping-mode on a Nanoscope IIIa (Digital Instruments) with NSC15 tips (silicon cantilever, Mikro Masch). The particle size was measured using Transmission Electron Microscope (TEM) (Zeiss EM-900). The Brunauer–Emmett–Teller (BET) was analyzed by nitrogen adsorption instrument in an ASAP2020 surface area. UV–vis and photoluminescence studies were performed using TEC Avaspec 2048 Spectrophotometer (excitation source = Xenon arc lamp 450 W).

2.4. Batch experiments

Batch mode adsorption studies for oxamyl have been carried out to investigate the effect of different parameters such as agitation speed, adsorbate concentration, adsorbent dose, temperature and pH. Solution containing 20 ml adsorbate and 0.6 g adsorbent was taken in 250 ml capacity conical flask and agitated at 200 rpm in water bath shaker at predetermined time intervals. The adsorbate solution was centrifuged at (3000 rpm) for (5 min). The initial and final Oxamyl concentrations remaining in solutions were analyzed by using the aid of a two dimensional Gas Chromatography (GC∗GC).

Adsorption efficiency was expressed as a percentage of adsorbed Oxamyl compared to initial Oxamyl concentration, whereas adsorption capacity was expressed as amount of Oxamyl adsorbed per mass unit of GQDs using the following equations, respectively:

$$q\ (mg/g) = \frac{(C_i - C)V}{C_i} \tag{1}$$

$$\text{Oxamyl removal efficiency}(\%) = \frac{C_i - C}{C_i} \times 100 \tag{2}$$

where C_i and C are the initial and residual concentrations of Oxamyl in mg/L, q is the adsorption capacity in mg/g, V is the volume of Oxamyl solution in L, and m is the adsorbent mass in g.