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Removal of Malathion Pesticide from polluted water using 4-HADTOT-HCAC Composite

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Abstract

Initially 4-HADTOT copolymer was synthesized by acid catalyzed condensation polymerization method using 4-Hydroxy Acetophenone (4-HA), Dithio Oxamide (DTO) and Trioxane(T) as starting materials. Activated carbon derived from Hibiscus *cannabinus* fruit shell (HCAC) was generated using known methods. The new composite material was obtained from 4-HADTOT and HCAC and it is abbreviated as 4-HADTOT-HCAC. The resulting composite was characterized by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy studies. Adsorption studies for removal of Malathion pesticide, a pollutant, were conducted in the laboratory. The optimum conditions like adsorbent doses, agitation time, initial concentration of pesticide and pH on adsorption of Malathion by 4 -HADTOT-HCAC composite were investigated. HPLC method was used to determine concentration of Malathion pesticide. At 300K temperature and pH 7, 99% of the pesticide was removed from Malathion solution (25 ml, 0.1 mg dm^{-3}). Thus 4-HADTOT-HCAC composite has been proved to be the new promising excellent material for water/ waste water treatment and can be used successfully in control of environmental pollution, with special reference to pesticides.

Keywords:-Copolymer, Activated carbon, composite material, malathion, pesticide pollutants, adsorption isotherm.

Introduction

World population is increasing at an enormous rate and is expected to reach seven billion by the end of year 2050. Population growth and the resultant development of large high-density urban populations together with global industrialization have placed major pressure on our environment, alarming environmental viability and food security potentially. This has resulted in global warming and the buildup of chemical and biological contaminants throughout the biosphere, but most notably in soils, sediments and various aquatic bodies.[1]

During the 20th century, the main significance of agricultural development all over the world was the increasing productivity per unit area of land used for crop production to feed the ever-increasing population. This was considerable accomplished through over utilization of natural resources such as water and plants and excessive use of fertilizers and pesticides.[2]

Nowadays, existing commercial sorbents including, activated carbon, zeolites, activated alumina, and silica gels play important roles in adsorptive separation and purification. However, innovative technological developments are needed in the new economy and under the stringent environmental regulations. Despite of very promising features of the newly developed composite structured sorbent materials, basically exploring and systematic investigations are needed on both synthesis methods and adsorption characteristic studies.[3]

4-HADTOT, a polymeric resinous material, contains high units of two functional groups, hydroxyl (ArOH) and amino (ArNH2), which are responsible for the reactivity of this polymer as an excellent powerful adsorptive capacity. Due to the highly reactive amino groups and carbonyl groups, polymer can be a new useful material for various purposes such as treatment of wastewater, ion-exchanger and functional matrixes.[4-7]

In recent years, polymer doped activated carbon composites have been studied increasingly as an alternative adsorbent in water treatment. Saifuddin et al. have studied a polymer based composite for the removal of pesticides from water.[8-12]

Malathion[*S*-1,2-bis(ethoxycarbonyl) ethyl *O,O*-dimethyl phosphorodithioate] is suspected to cause child leukemia, anemia, kidney failure and human birth defects, but still widely used pesticide in developing countries.[13-14] It is believed to be an agent in causing DNA abnormalities even at small doses.[15-16] There are reports of Malathion causing ***"deletions"*** in one section of the chromosome thereby inducing mutations in human beings.[17-19] Malathion can persist in the human body for at least two generations.[20-21]

The present investigation reports the synthesis of 4-HADTOT polymer, generation of new HCAC activated carbon, to develop new 4-

HADTOT-HCAC composite material, characterization followed by systematic study towards application of this new composite material for removal of ***Malathion Pesticide*** from contaminated water.

Materials and Methods

Chemicals

The entire chemicals used were procured from Merck, Mumbai, India and were of analytical or chemically pure grade. Deionized/distilled water was used throughout the investigation.

Synthesis of 4-HADTOT polymer

The polymer 4-HADTOT was synthesized by the polymerization reaction of 4-hydroxyacetophenone (0.6mol) and Dithio Oxamide (DTO) (0.3mol) with Trioxane (0.1mol) using hydrochloric acid as the reaction medium at 124±2ºc in an oil bath for 5 hrs under refluxed condition with occasional shaking. The reaction mixture was then cooled and the separated polymer out was washed with warm water followed by extraction with diethyl ether. The dried sample was then purified by dissolving in 10% aqueous NaOH and regenerated using 1: 1 (v/v) HCl/water with constant and rapid stirring to avoid lump formation. The process of re-precipitation was repeated twice. The polymer 4-HADTOT thus obtained was filtered, washed with hot water, dried in air, powered and kept in vacuum desicator over silica gel. The yield of the polymer was found to be 92 %.

Generation of Activated Carbon from the *Hibiscus cannabinus* fruit shell (HCAC)

The fruit shell of *Hibiscus cannabinus* species was collected from the local area. The fruit shell was cut into small pieces. It was washed with tap water to remove the sand particles and then treated with formaldehyde to avoid release any colour of fruit shell into aqueous solution. It was again washed several times with de-ionized water. Then it was allowed to sun dried for 6 days. After drying, the material was subjected to pyrolysis process for carbonization using muffle furnace at 800-9000ºC for about 7 to 8 hr so that volatile products were removed and residue was converted into a char. The char was then subjected to microwave activation in microwave oven. The input power of microwave equipment was set at 360 W for 30 min. The resulting activated carbon particles were grounded and sieved in 120-200 mm size. This activated carbon was then washed with double distilled water and dried at 105ºC for 3 hr.

Preparation of 4-HADTOT-HCAC composite

4-HADTOT polymer was dispersed in N-N Dimethylformamide using mechanical stirrer for 75 min at room temperature. Then HCAC was added and stirring was continued for 6 hrs. The temperature of the system was raised to 65°C and kept overnight so that the solvent was evaporated completely. Equimolar polymer-activated carbon composition was taken in the composite. The solid 4-HADTOT-HCAC composite was characterized by FTIR and SEM Studies. The morphological properties were investigated from SEM picture and thermal properties from TG analysis.

Results and Discussion

Characterization of 4-HADTOT-terpolymer

FTIR Analysis

Fig.1 represents FTIR spectrum of 4-HADTOT polymer with its characteristic bands. Band at 1547–1498 cm^{-1} is due to aromatic ring stretching. Appearance of band at 3130-3070 cm^{-1} is due to aromatic C-H stretching and 1304-932 cm^{-1} is due to aromatic C-H bending (in the plane). Bands at 770-735 cm^{-1} and 860-800 cm^{-1} is indicative of ortho and para substitution in aromatic ring. Very strong absorption band 3744cm^{-1} proves the presence of aromatic secondary amino linkage. Presence of ketonic group is evident by appearance of bands at 1615 cm^{-1}. Comparatively weak absorption band at 3618 cm^{-1} indicates the presence of CH_3 group (C-H stretching).

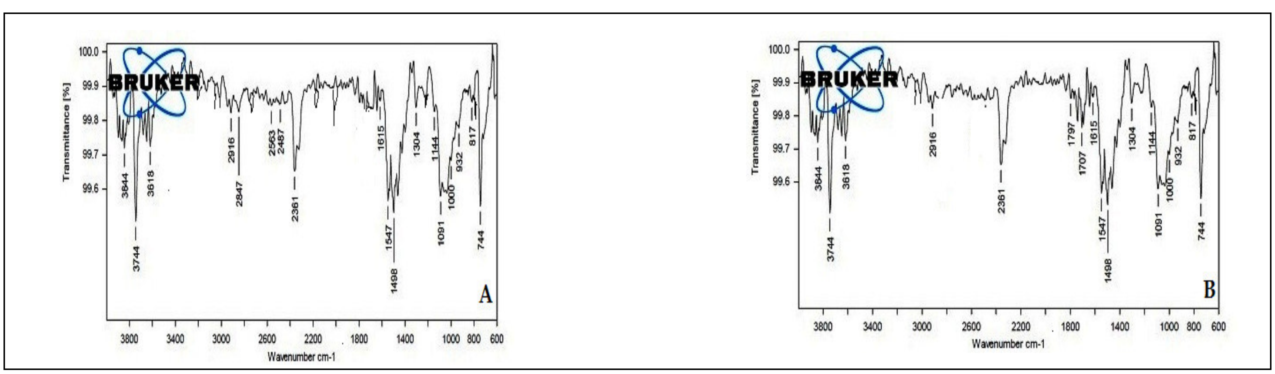

Fig.1 FTIR spectra of

A) 4-HADTOT-terpolymer **B) *4-HADTOT-HCAC Composite***

On the basis of physicochemical and spectral evidences the most probable structure has been proposed for *4-HADTOT*-terpolymer which is presented in fig.2

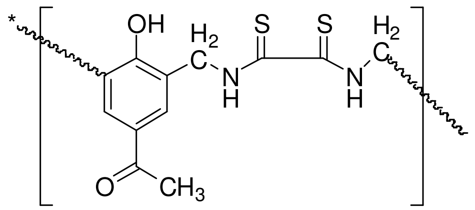

fig.2 . 4-HADTOT polymer

Characterisation of 4-HADTOT-HCAC Composite

FTIR Studies

Fig.1 represents the FTIR spectrum of 4-HADTOT-HCAC composite. It can be observed that both, the FTIR for 4-HADTOT terpolymer and 4-HADTOT-HCAC composite are almost similar. The noticeable difference is appearance of strong sharp absorption band at 1797 cm^{-1} which is indicative of C=O group (reactive oxygen functional groups). It proves the incorporation of HCAC (possessing C=O surface group) in the terpolymer matrix during composite formation.

SEM Analysis

SEM pictures of 4-HADTOT-HCAC composite are given in Fig.3. It is evident from the SEM pictures that the HCAC have been successfully incorporated in 4-HADTOT polymer matrix thus the synthesis of composite is fruitful. The SEM picture also proves highly porous nature possessing rod-plate like particle structure of the composite under investigation which is suggestive of very high surface area. Thus this composite material may be of great use as excellent absorbent.

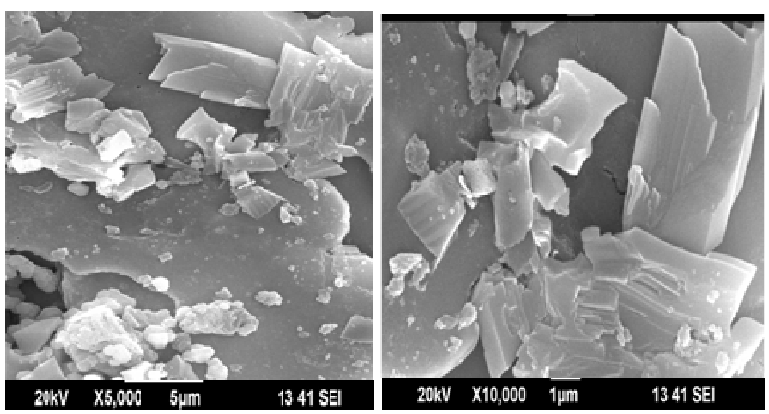

Fig.3 SEM Micrographs of 4-HADTOT-HCAC composite.

Adsorption Studies

Batch equilibration method has been employed to study adsorptive efficacy of 4-HADTOT-HCAC composite for removal of Malathion Pesticide from contaminated water. The data were found to be best fitted with Frundlich adsorption isotherm. At 300K temperature and pH 7, 99% of the pesticide was found to be removed from Malathion solution (25 ml, 0.1 mg dm^{-3}).

Conclusions

- The 4-HADTOT polymer was successfully prepared and characterized.
- The HCAC activated carbon could be successfully generated employing known methods.
- The composite material was successfully obtained from 4-HADTOT and HCAC and it has been characterized successfully.
- SEM studies proved highly porous morphological structure with very high surface area of the composite which indicates its suitability for various practical applications as an excellent adsorbent.
- 300K temperature, 7 pH, 5g adsorbent dose and 0.1 mg dm^{-3} adsorbate (Malathion Pesticide) concentration have been noticed to be the optimum conditions during this study.
- The composite material under present investigation in useful for successful removal (99%) of Malathion Pesticide from contaminated water, under above

mentioned optimum conditions, thus can be successfully used for water/wastewater treatment.

Scope for future work

There is a scope for further studies to test the practical applicability of this composite material for removal of other pesticides/water pollutants.

Acknowledgments

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