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Comparative study of malathion removal from aqueous solution by agricultural and commercial adsorbents

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ABSTRACT

Massive use of an insecticide such as malathion has caused a setback to the environment and also has increased potential risk to human health as it is an endocrine disruptor chemical. This work was carried out to study the removal of malathion from aqueous solution using adsorbents, such as rice husk (RH) activated rice husk (ARH) and commercially available powdered activated carbon (PAC). The effect of system variables such as pH, contact time, initial concentration and adsorbent dose were investigated in a batch process. The adsorption equilibria of the system at constant temperature were modeled by Langmuir, Freundlich and Temkin isotherms. Langmuir model showed excellent correlation with experimental data. For kinetic study, the adsorption process fitted the pseudo-second order model. Maximum malathion removal efficiency of 53, 87 and 94% were obtained with RH, ARH and PAC, respectively, under optimum conditions.

1. Introduction

Pollution is the biggest problem of modern world which is boosting day by day and impinging our environment system immensely. One of them is contamination of water due to various contaminants originating from human use [1]. The rapid and indiscriminate use of pesticides in modern agriculture practices for social betterment such as to chop crop losses, enhance yield and meet rising food need has become a matter of social accountability now [2]. It gives rise to concerns at local, regional, national and global scales because of the facts that pesticides residue are ingested by human with foodstuff, drinking water and are being bio accumulated in blood, mother milk, tissues etc. [3–5]. It contributes to symbolic human symptomatic illnesses, both acute and chronic [6–8]. The effluent discharged without treatment into surface water such as rivers, lakes cause environmental damage such as polluting ground, surface and drinking water [9]. Among different pesticides, organophosphorous pesticides contribute 73% poisoning among all agriculture pesticides reported by Poison Information Center in National School of Occupational Health, Ahmadabad, India [1].

Malathion (Diethyl dimethoxythiophosphorylthio succinate) which is a broad spectrum, highly toxic organophosphorous insecticide, registered in 1956, is abundantly used in agriculture, industrial and public health field to kill insects, ants, aphids, bagworm, beetle, cotton leaf worm, mosquito, lice etc. by inhibiting Cholinesterase enzyme [10]. Malathion is rapidly and effectively absorbed by all routes including the gastrointestinal tract, skin, mucous membrane and lungs and causes blurred vision, excessive salivation, headache, giddiness, nausea and vomiting due to active metabolite malaoxon (metabolic product from malathion) which is 61 times more toxic than malathion [11,12]. It affects nervous system, immune system, adrenal glands, liver and also carcinogenic in nature [13]. Apart from this it is toxic to birds, fishes other aquatic invertebrates and honey bees too [14,15]. According to a survey, Kanpur in northern India has high presence of malathion (29.84 $\mu g\ L^{-1}$), which is higher than the water quality standards of the ground water [16].

The removal of malathion from natural water, therefore, has become a matter of grave concern. Although many treatment processes have been proposed for the removal of environmental contaminants from aqueous solutions, adsorption is considered to be one of the prominent techniques due to its effectiveness, reliability, low cost, ease of application, equipment handling and eco-friendly nature [17–20]. The PAC has been widely used as adsorbent for the removal of a number of pollutants from aqueous solutions owing to its highly developed surface properties [21]. Due to high cost of PAC, the present work was aimed to explore new inexpensive material, the RH and ARH for adsorption of malathion in place of PAC. The objectives of this work were to

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evaluate the effect of various process parameters on the adsorption of malathion onto ARH, RH, PAC and to study the applicability of various adsorption isotherms, such as, Langmuir, Freundlich and Temkin models. The experimental data was also explored to establish the proper kinetics of the process.

2. Materials and method

2.1. Reagent and solution

All the reagents used in this study are of analytical grade. All glasswares used were of Borosil. Distilled water was used for making the synthetic samples. Technical grade malathion of 95% purity was obtained from Sigma–Aldrich and used as such without further purification. Ethyl alcohol, potassium hydroxide, nitric acid and ammonium metavanadate were procured from S.D. Fine Chemicals. Standard base of 0.1 M NaOH and acid 0.1 M HCl solutions were used for pH adjustment.

2.2. Preparation of adsorbent

The RH, a natural adsorbent, was collected from agricultural field of Institute of Agriculture Sciences, Banaras Hindu University, Varanasi, and the commercial grade PAC was procured from local manufacturer. RH was washed several times with water and dried in sunlight. To remove the moisture content, it was further dried in an oven at 110 °C for 24 h. Dried RH was grounded and sieved to 250 μm mesh size and treated with KOH to remove cellulosic material and to oxidize the adhering organic material [22]. It was again washed with distilled water and dried in hot air oven at 110 °C overnight. ARH was prepared by heating in an electric furnace at 850 °C for 2 h in absence of air and stored in airtight plastic bottles.

2.3. Instrumentation

Adjustment of solution pH was done using a digital pH meter (LI 120, Elico India), calibrated using buffer solutions (pH 4.0, 7.0 and 9.2). Adsorbent was dried and made moisture free by drying in an oven (S.M. Scientific Instruments Pvt. Ltd., New Delhi). Adsorption studies were conducted in a water bath (Remi) with temperature controller. Fourier transform infrared spectral analysis of the adsorbent before and after adsorption was done using NICHOLET 5700 spectrophotometer (Thermo electron). Infrared spectroscopy (FTIR) was used to detect the surface functional groups of adsorbents which are responsible for adsorption. For this sample was mixed with a dry alkali halide (KBr), which is transparent in the mid-infrared region (4000–400 cm^{-1}) and made into a 1 cm disk. Infrared radiation was passed through the sample and the spectrum was obtained by determining the fraction absorbed at a particular energy. This analysis relates the surface of the adsorbent to the modes of the vibrations of functional groups present on it, responsible for the adsorption. Mineral identification and crystallinity of the adsorbent were tested by X-Ray Diffraction studies. Pattern was recorded by a Philips 1710 X-ray diffractometer with a Cu Kα target of radiation wavelength 1.542 Å operating at 40 kV and 40 mA. Peaks signify whether the sample is crystalline or amorphous, sharp peaks indicate crystalline nature and amorphous nature is shown by the broad peaks. The Brunauer–Emmett–Teller (BET) surface area of the adsorbent was investigated by N_2 adsorption–desorption method using Micromeritics ASAP 2020, V302G single port. Nitrogen was used as the cold bath (77 K). Malathion concentration was determined using a UV-visible spectrophotometer (model SL-210).

2.4. Estimation of malathion in solution

Stock solution of malathion was made according to standard methods. Working samples were made by adding required stock solution to the predetermined quantity of distilled water. The experiments were performed with a stock solution of 1000 mg L^{-1} concentration. Determination of malathion in water was done by simple and well established method in which decomposition of malathion occurred in the presence of alcoholic KOH and ethyl alcohol which gives dimethyl di-thio-phosphate. This mixture gives yellow color on reaction with ammonium meta vanadate. The color absorbance was measured at 560 nm [10].

2.5. Batch adsorption studies

Malathion adsorption using RH, ARH and PAC as adsorbents was conducted in batch experiments. In all sets of experiments, fixed concentration of malathion (10 mg L^{-1}) was agitated with varying adsorbent doses for different time periods. The effects of process conditions, pH (2–8), contact time (30–150 min) and initial concentration (10–50 mg L^{-1}) were evaluated for all adsorbents. Malathion concentration was estimated using UV spectrophotometer at 560 nm wavelength by following the procedure prescribed above.

The amount of malathion adsorbed (mg g^{-1}) at any time was computed using the following equation:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where q_e is malathion concentration in adsorbent (mg g^{-1}), V the volume of the solution (mL), C_i and C_e the initial and equilibrium solution concentrations (mg L^{-1}) and m the mass of adsorbent (g).

2.6. Kinetics and equilibrium adsorption modeling

Batch experiments were conducted at different initial concentrations ranging between 10 and 50 mg L^{-1} taken in each 100 ml conical flasks. The solution along with the adsorbent was agitated at 30 °C at 110 rpm for a definite time period keeping initial pH at 6.0. After required equilibrium time, the samples were withdrawn and analyzed. The data were fitted to Langmuir, Freundlich and Temkin isotherms to find the best fitted isotherm.

The kinetic study was done for the adsorbents RH, ARH and PAC in order to estimate the equilibrium time of adsorption and the best fitted kinetic model (Pseudo 1st or 2nd Order). Different concentrations of malathion spiked in synthetic water sample (100 mL) were taken in the conical flask and adsorbents doses of 3, 2, 5 g L^{-1} of ARH, PAC, RH, respectively, were added to it. The mixtures at temperature 30 °C were agitated at 110 rpm at pH 6.0 for 150 min for ARH and RH and 120 min for PAC. Samples were withdrawn and the concentrations were analyzed.

3. Results and discussion

3.1. Adsorbent characterization

The characterization of physical and chemical surface properties of adsorbents is one of the most important issues in an

Table 1
Characteristics of rice husk.

Surface area ($m^2 g^{-1}$)	649.08
Bulk density (g mL^{-1})	0.3410
Moisture content (%)	8.25
Ash content (%)	18.39
Volatile matter (%)	42.80
Fixed carbon (%)	30.56