

Tea (*Camellia sinensis*) Waste for the reduction of Malathion and Phorate in aqueous solutions

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Abstract— Diminution of Malathion and Phorate from aqueous solutions by tea waste biomass was examined in a batch experimental setup. Waste tea powder, obtained from University canteen, S.V. University, Tirupati, India has been used as an effective material for the reduction of Malathion and Phorate from aqueous solutions. Characterization of the adsorbent was studied using SEM micrograph and Fourier Transform Infrared spectral analysis. From the FTIR spectrum it is observed that the change in peak position at 3390 cm^{-1} in the spectrum of the Phorate and Malathion loaded tea powder indicates the binding of these pesticides with hydroxyl groups. The working solutions of the pesticides are in the range of $0.1\mu\text{g} - 1.0\mu\text{g}$ for Malathion and $0.05\mu\text{g} - 0.5\mu\text{g}$ for phorate. It was observed that percentage adsorption increased with pH of the liquid phase and reached an optimum value of 95 % for Malathion and 94 % for phorate at $\text{pH } 7.4 \pm 0.2$ and $\text{pH } 7.5 \pm 0.2$, respectively. The dosage of the adsorbent had showed considerable effect on the adsorption of Malathion and Phorate.

Keywords— Adsorption, Pesticides, Malathion, Phorate and Waste Tea Powder.

I. INTRODUCTION

A great number of pesticides are being used now to increase the crop productivity in modern agricultural practices. It is calculated that the productivity losses would double if the pesticides were put out of use [1]. Slow degradation of pesticides in the environment and extensive or inappropriate use by farmers can lead to environmental contamination of the water, soil, air, several types of crops and indirectly humans [2]. Pesticides have also been used in non-agricultural sectors such as wood preservation, disinfection or household uses. In spite of the several advantages, some pesticides can be toxic to humans and animals and their continuous application is causing serious problems of environmental and food contamination [3]. The wastewater discharged from pesticide factories is poisonous. It would kill aquatic organisms and threaten public health if it was discharged without proper disposal [4]. However, the use of pesticides requires great care and control as they can pollute the environment and harm human health [1]. There was a rapid global growth in the routine use of organophosphorous pesticides by the agricultural community during last half a century. Such practices have led to increasing concerns with respect to human, animal and insect health. In the last few decades organochlorine insecticides, (e.g. aldrin, lindane) have been progressively replaced by OP (Organo Phosphorous) pesticides (e.g. parathion, malathion) and insecticides based on derivatives of carbamic acid (e.g. carbaryl, aldicarb), both families showing decreased persistence in the environment but at a cost of higher acute toxicity. Organophosphorous compounds are neurotoxic and structurally similar to the nerve gases soman and sarin and operate by inhibiting the cholinesterase enzymes which are essential in modulating the central nervous system in both animals and insects. As acetylcholinesterase (AChE) promotes the hydrolysis of the natural neurotransmitter, acetylcholine (ACh), its inhibition terminates the propagation of nerve impulses [5].

Of late, hectic research based on adsorption phenomenon have done to reduce the pesticide contamination in drinking water. Activated carbon is a highly effective adsorbent but lack of cost effectivity prohibits its use in many countries including India. Intense research attention is now focused on cost effective, eco-friendly and easily available adsorbent particularly of biological origin. Different adsorbents such as agricultural byproducts, waste materials and microbial biomass have been utilized for removing different toxicants from wastewater. Malathion and Phorate are organophosphorus pesticides (Fig. 1 and Fig.2) of high selective toxicity are widely used in agriculture throughout the world [6].

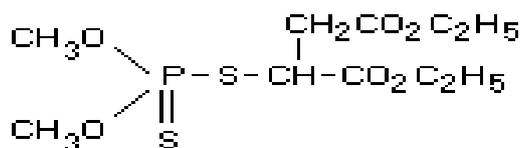


FIG. 1. STRUCTURE OF MALATHION

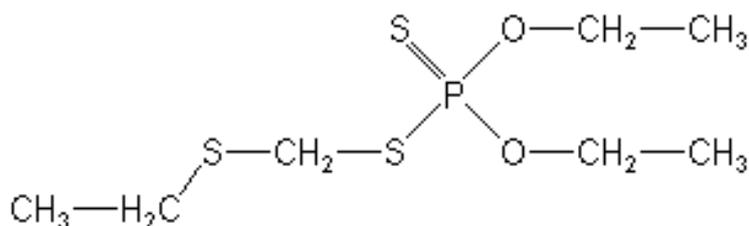


FIG. 2. STRUCTURE OF PHORATE

Malathion is suited for the control of sucking and chewing insects on fruits and vegetables and is also used to control mosquitoes, flies, household insects, animal parasites (ectoparasites), and head and body lice [7]. Phorate is used to control sucking and chewing insects, leafhoppers, leaf miners, mites, some nematodes, and rootworms. It is also used in pine forests and on root and field crops, including corn, cotton, coffee, some ornamental and herbaceous plants and bulbs [8]. To date adsorptive removal of organophosphorous pesticides from wastewater has not been studied in detail and only a few reports are available in this regard [9-14]. Materials investigated as adsorbents for pesticides includes: Charcoal from agro waste [15], straw [16], date and olive stones, wood chips/corn cob [17], lignocellulosic substrate from agro industry [18], bark [19], baggasse fly ash [20] and coal fly ash [21]. Tea powder is basically a waste after using it for the preparation of Tea. In India yearly production of tea is approximately 857000 tonnes which is 27.4% of total world production. The amount of dry tea produced from 100kg green tea leaves is 22 kg on average and approximately 18 kg tea is packed for the market. The other 4kg of dry tea material is wasted. With such a great production and consumption large quantities of tea wastes (From the Caff, Cafeteria, or tea –processing factory) are usually discarded into the environment without any treatment. Furthermore, additional amount of tea leaves enters the environment by defoliation and pruning annually [22]. Like other biomass residues tea waste represent an unused resource and pose increasing disposal problem. Based on these reasons it is being investigated strategically to evaluate their possible use as an energy source or in other value added application. The cell wall of waste tea consist of cellulose, lignin carbohydrate which have hydroxyl groups in their structures [23]. In the present study removal of Malathion and Phorate from water has been taken up by batch adsorption technique using waste tea powder as the adsorbent material.

II. MATERIAL AND METHOD

2.1 Chemicals and Instruments

Experiments were performed in triplicate and average values were used in the results. All the chemicals used were of analytical grade. Malathion (95.50%) and Phorate (93.20%) were obtained from Hyderabad Chemicals Limited, Hyderabad, India. Rhodamine B was obtained from S.d Fine – Chem limited, Mumbai, India. N-Bromosuccinimide was obtained from Hi Media Laboratories Pvt. Ltd. Mumbai, India.

The stock Malathion and Phorate solutions of 1000 $\mu\text{g mL}^{-1}$ were prepared by dissolving 0.813 μL and 0.856 μL of Malthion and Phorate in little amount of glacial acetic acid and made up the mark in 100 mL volumetric flask with double distilled water. The stock solutions were further diluted to obtain, solutions of various known concentrations of Malathion and Phorate. Standard base of 0.1 M NaOH and acid of 0.1 M HCl solutions were used for pH adjustment.

Elico LI120 pH meter was used for pH measurements. Magnetic stirrer (Remi Equipments Pvt. Ltd.) was used for stirring. After completion of each batch experiment the system was allowed to settle for 20-30 min and the supernatant was used for the determination of the concentration of Malathion and Phorate. UV-Visible spectrophotometer (SHIMADZU UV- 1800) was used to determine the concentration of Malathion and Phorate.

2.2 Preparation of the Biosorbent

Waste tea powder was collected from the S.V. University canteen and washed with tap water to remove the milk, dust and other impurities. The washed waste tea powder was air dried and grounded using Mortar and Pistle to form a powder. To avoid, the release of color by tea powder in to the aqueous solution during adsorption, it was treated with formaldehyde (Randall et al., 1976). For this 5mL of aqueous formaldehyde was added to 100mL of 0.1M H₂SO₄ and then 10 g of washed tea powder was added to this solution. The final mixture was stirred and heated at 50 OC for 24-48 h till the mixture became thick slurry. The slurry (treated tea powder) was washed with deionized water until the pH of the filtrate was more than 4.5. Finally the waste tea powder was air-dried and sieved. Particles in the range of 150-500 μm size were collected as the final adsorbent.

2.3 Experimental Methodology

Kinetic adsorption experiments were carried out to establish the effect of time on the adsorption process and to determine the rate of adsorption for Malathion and Phorate removal as affected by pH and contact time. Detailed experimental procedures were described as follows: 1) prepare 1 L solutions of different malathion and Phorate concentrations; 2) adjust initial pH; 3) Distribute 50 mL of solution to a series of 200 mL glass beakers 4) add a given amount of the waste tea powder (1 g/50mL) into the solution; 5) stirred well for about an hour to reach the equilibrium; 6) at the end of stirring separate the adsorbent and the supernatant was collected for determination of malathion and Phorate concentration.

2.4 Determination of Malathion and Phorate Concentration

An aliquot of sample solution containing $0.1\mu\text{g} - 1.0\mu\text{g}$ of malathion, $0.05\mu\text{g} - 0.5\mu\text{g}$ of phorate were transferred into a series of 25mL calibrated flasks, to which 1.5mL of NBS (0.01 %, w/v), 1mL of glacial acetic acid and 0.5mL of hydrochloric acid ($4\text{mol}\cdot\text{l}^{-1}$) were added successively; the solution was kept aside with occasional shaking for about 10 min at $30\text{ }^\circ\text{C}$ and then 0.7mL of rhodamine B solution (0.02%, w/v) was added and mixed thoroughly. The absorbance was measured at 550 nm against a reagent blank. A blank without pesticide (dye and NBS) and dye (devoid of pesticide and NBS) were prepared in similar manner and its absorbance was measured against distilled water. The decrease in absorbance corresponding to consumed oxidant, which reflects the pesticide concentration was obtained by subtracting the decrease in absorbance of the test solution (dye minus test) from that of the blank solution (dye minus blank). Calibration graph was prepared by plotting the decrease in absorbance of dye against amount of the pesticide [24].

III. RESULTS AND DISCUSSION

3.1 Scanning Electron micrograph

Characterization of the adsorbent was studied using SEM micrograph of biosorbent and depicted in the Figures 3.1a, 3.1b and 3.1c. These figures shows that the adsorbent have an irregular and porous surface after the sorption of malathion and phorate. The tea waste biomass was cellulose in nature – material containing tannin and lignin based organic compounds.

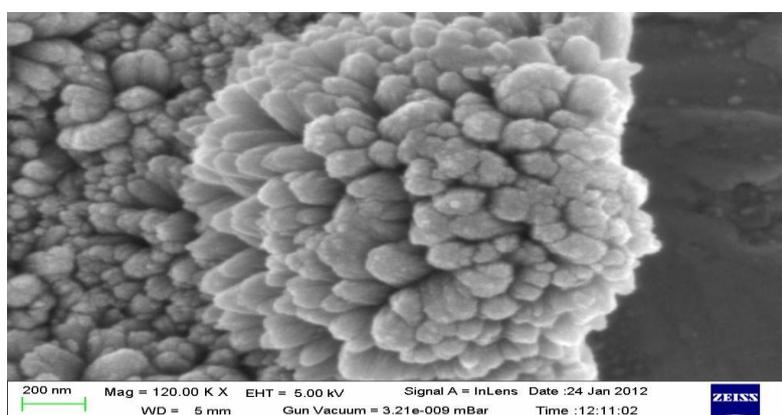


FIG. 3.1 A. SEM IMAGE OF WASTE TEA POWDER BIOMASS

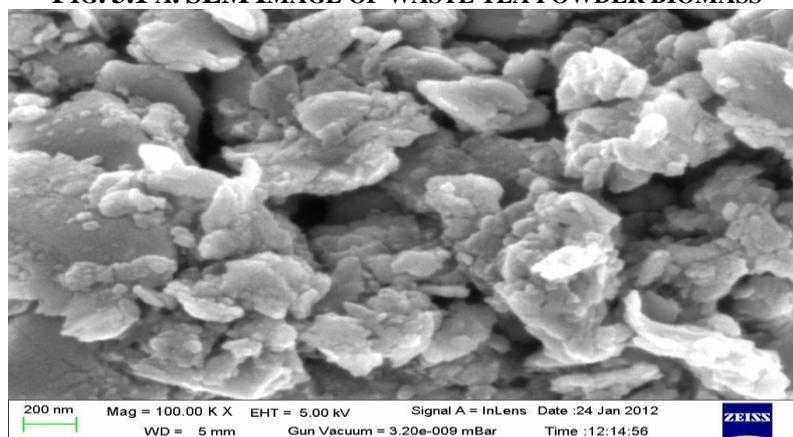


FIG. 3.1 B. SEM IMAGE OF MALATHION SORBED WASTE TEA POWDER BIOMASS

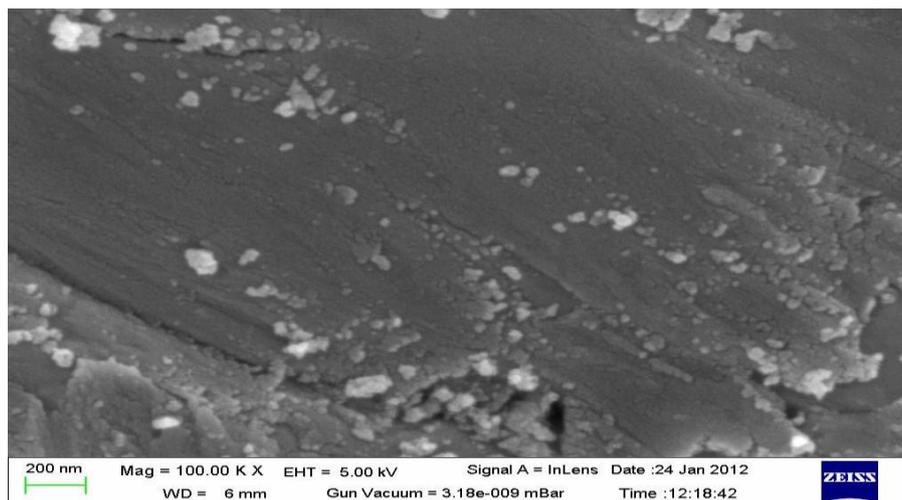


FIG. 3.1 C. SEM IMAGE OF PHORATE SORBED WASTE TEA POWDER BIOMASS

3.2 FT-IR (Fourier transform infrared) spectral analysis

FT-IR analysis was used to identify the characteristic functional groups on the surface of biosorbent and the spectra of biosorbent is shown in Fig.4 a. The FT-IR spectrum of tea powder biomass exhibited a broad peak at 3390 cm^{-1} which is indicative of the existence of macromolecular association (cellulose, pectin, etc.) and may denote the presence of both H-bonded amine and OH groups. The FT-IR spectrum exhibited characteristic main skeleton cellulose peak in the finger print region of $1000\text{--}1200\text{ cm}^{-1}$. The doublet peak appeared in the spectra at wave numbers $2854\text{--}2923\text{ cm}^{-1}$ is due to the asymmetric and symmetric stretch of aliphatic chains (--CH) respectively. The peak at 1621 cm^{-1} is assigned to the characteristic symmetrical stretching vibrations of carbonyl groups. The band at 1027 cm^{-1} regions is attributed to the asymmetric C-O-C stretching vibrations.

It appears from Fig. 4 b and 4 c that different functional groups on tea powder are responsible for biosorption of Phorate and Malathion. A change in peak position at 3390 cm^{-1} in the spectrum of the Phorate and Malathion loaded tea powder indicates the binding of these pesticides with hydroxyl groups. Further shift in the peak at 1621 cm^{-1} of tea powder on Phorate and Malathion biosorption indicating the binding of metal ions to carbonyl groups also. From these findings, it is presumed that Phorate and Malathion adsorbed mainly to the active groups such as hydroxyl groups (--OH) and carbonyl groups (C=O).

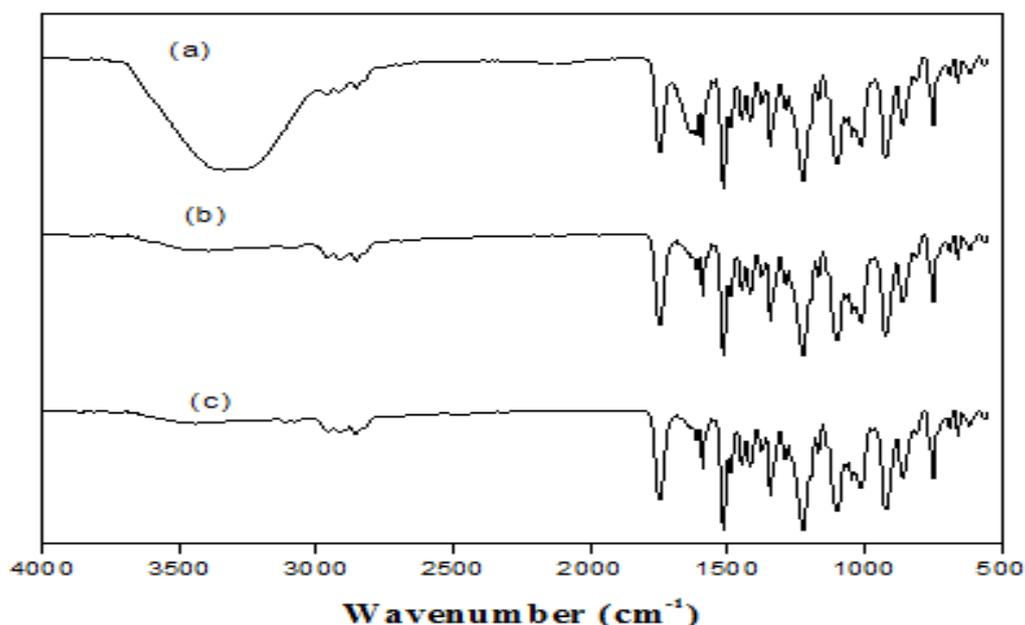


FIG. 4. FT-IR SPECTRA OF (A) TEA WASTE POWDER (B) PHORATE (C) MALATHION LOADED BIOSORBENT

3.3 Effect of pH

pH is a key controlling parameter in the bio-sorption process of toxic substances from aqueous solution because it affects the solubility of the ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. The effect of pH has been studied by plotting the curve between percentage removal of Malathion and Phorate versus pH as shown in the Figure 5. It was observed that percentage adsorption increased with pH of the liquid phase and reached an optimum value of 95 % and 94 % (removal) at $\text{pH } 7.4 \pm 0.2$ and $\text{pH } 7.5 \pm 0.2$, respectively. As the pH value became lower than 5, the acidic nature of the solution effected the sorption capacities of Malathion and phorate.

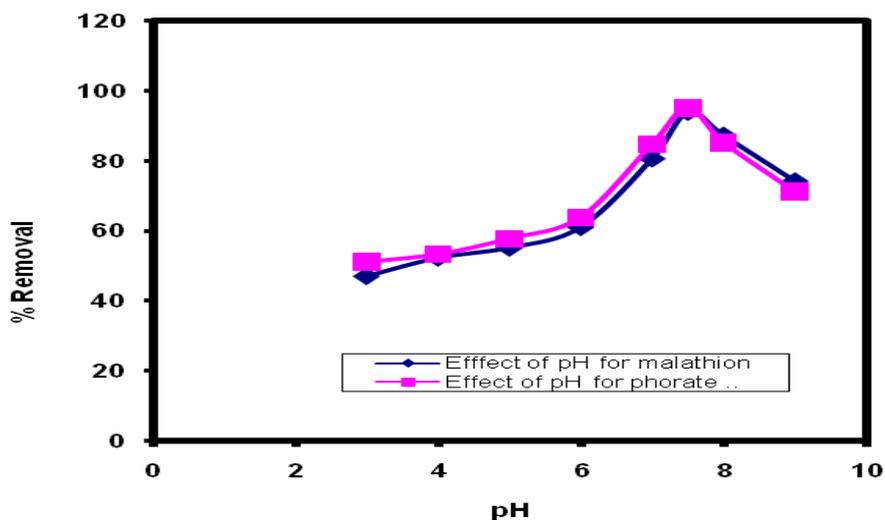


FIG. 5. EFFECT OF pH ON THE BIOSORPTION OF MALATHION AND PHORATE

3.4 Effect of adsorbent dose

The effect of sorbent dosage on the uptake of both Malathion and Phorate was represented in Figure 6, which shows that sorption efficiency increased as the dose of sorbate increases. These results may be due to the over lapping of adsorption sites as a result of adsorbent particle overcrowding and also more pores and surface area is available as binding sites. Higher dosage of the adsorbent, i.e 2.0 g /L, enhances the adsorption of the pesticides malathion and phorate in the present experiments.

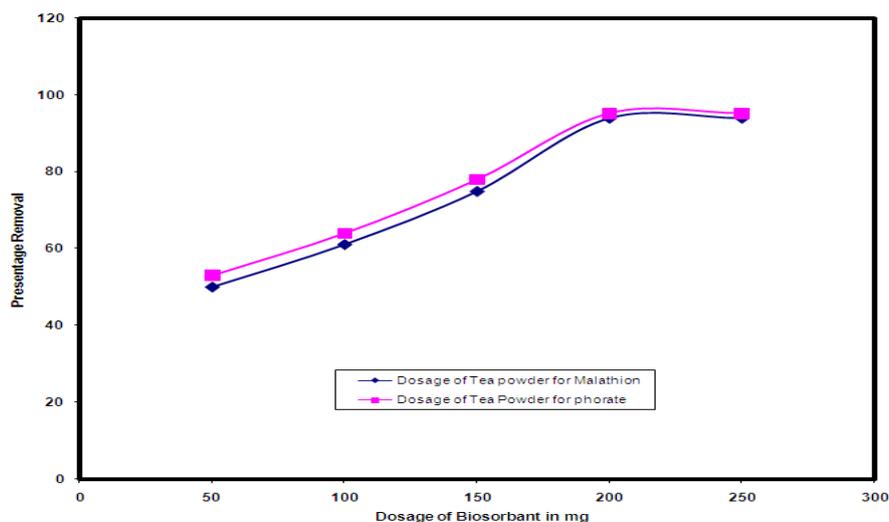


FIG. 6. EFFECT OF ADSORBENT DOSAGE ON THE BIOSORPTION OF MALATHION AND PHORATE

3.5 Equilibrium studies on Malathion and Phorate

Contact time is a fundamental parameter in all transfer phenomena of bio-sorption. Figure 7 shows that the 95 % and 94 % removal of Malathion and Phorate were obtained at 3 h. Hence, 3 h equilibrium time was considered in all the experiments. Tea waste biomass derived in present investigation has immense potential of Malathion and Phorate reduction from wastewater. Removal percentage of Malathion and Phorate from the liquid media was 95 and 94 % respectively at 2.0 g/L of initial adsorbate concentration, pH 7.4 and 7.5, equilibrium time 3 h respectively.

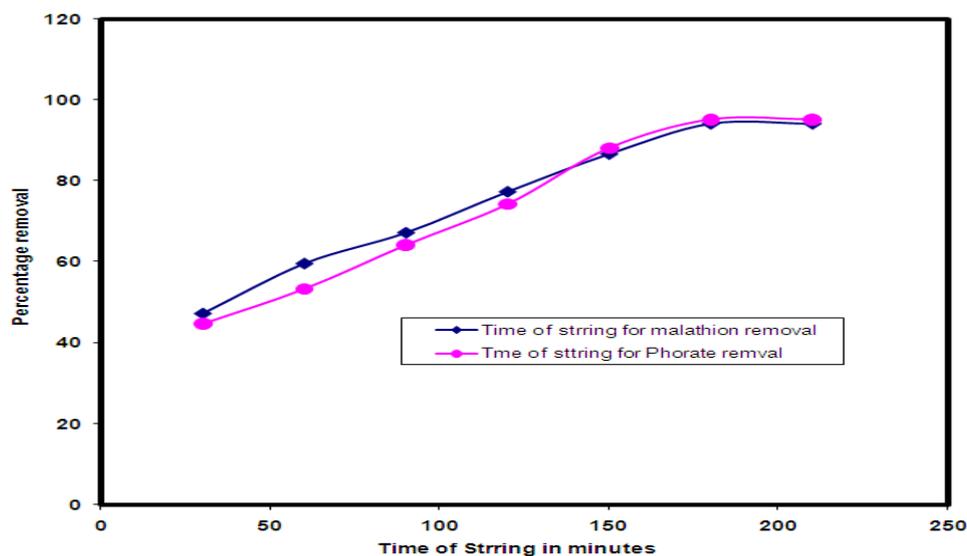


FIG.7. EFFECT OF TIME ON THE PERCENT REMOVAL OF MALATHION AND PHORATE

IV. CONCLUSION

Adsorptive properties of waste biomass largely depend on the source of biomass and treatments given to the adsorbent. The physical and chemical properties of the adsorbent such as surface area, surface functional groups, surface charge and particle size determines the adsorption characteristics of a material. The surface properties of the waste biomass can be improved by various thermal and chemical treatments given to the adsorbent prior to adsorption. However, this may incur cost and also lead to addition of other chemicals to the water. Pesticide properties such as mobility, hydrolysis and adsorption of a particular pesticide onto adsorbent. pH of the Solution, contact time and the mode of adsorbent–adsorbate contact are the main operating conditions which affects the adsorption capacity and the rate [25].

Tea waste acts a good adsorbent for the removal of toxic contaminants. From this present study it may be concluded that the usage of tea waste biomass instead of expensive adsorbents or conventional adsorbents is a good alternative for the uptake and reduction of the Malathion and phorate from aqueous solutions. Bio-sorption increases with increase in amount of adsorbent but become almost constant after certain dose of adsorbent. Tea waste used in the present work was not treated chemically or thermally. However results show that tea waste itself acts as a good adsorbent. If the tea waste is treated chemically it would become expensive and adds extra load of toxic chemicals into environmental medium. As the waste tea powder is available abundantly it can be used for the uptake and reduction of the selected pesticides which have higher toxicity and environmental importance.

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