

Natural Sorbent's Bio-Sorption Efficiency for Liquid Phase Scavenging of Pesticides from Wastewater

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Abstract

The removal of pesticides from waste water is a major concern of today and poses a great threat to the human and environmental health hence this research study aimed at assessing the efficiency of the used tea residue as a low-cost bio-adsorbent for the treatment of waste water containing pesticides. Therefore, to carry out the intended research project, initially the adsorbent was activated in order to increase its efficiency or adsorption capacity. Moreover, batch experiments were conducted with three pesticides (2,4-D, Carbaryl and Imidacloprid) at variable parameters (pH, contact time, adsorbent dose and initial concentration) and the effects of these variables on the adsorption capacity was assessed.

UV-spectroscopy was put into service for obtaining the concentrations of pesticide after the contact between the adsorbate (pesticide) and adsorbent (activated tea residue) while the characterization of the adsorbent was performed using the FTIR spectroscopy. The non-activated tea-residue removed suitable amounts of pesticides from aqueous solution but the activation process enhanced the natural adsorbent's efficiency. The optimum adsorbent dose for the removal of all two pesticides (2,4-D and imidacloprid) was same, that is 10mg while, the optimum adsorbent dose for carbaryl was 30mg. Whereas, the optimal pH and pesticide concentration varied for all three pesticide. Firstly, large amount of 2,4-D was removed at acidic pH with 10 ppb pesticide concentration, secondly, carbaryl at basic pH with 1ppb and lastly, imidacloprid at neutral pH with 1 ppb. Under optimal conditions the activated tea residue removed 99.99% of 2,4-D, 99.5% of carbaryl and 99.7% of imidacloprid.

Keywords: Wastewater; Activated bio sorbent; Adsorption; Pesticides

1. Introduction

Eco-toxicity due to contaminated water sources effect on living organisms has become a main concern for the last few decades. Due to rapid industrialization and substantial urbanization, the waste effluents get discharge directly in river water causing pollution to environment. The main sources of water contamination are industrialization, agricultural activities and other environmental changes. Few hundred of organic pollutants have been found that polluting water resources. Organic pollutants are very dangerous because of their carcinogenic nature and various side effects (Yang, 2011). Therefore improving and preserving water quality is essential. Surface and ground water at many places of the world is polluted and unfit for drinking purposes. The global population is projected to reach to 9.3 billion by 2050 (United Nations, 2011c) and the world may face fresh water scarcity. Therefore, the removal of toxic organic pollutants from water is essential (Khan et al., 2012). Pakistan is an agrarian country and the economy mainly depends on agricultural activities. In order to enhance the crop yield and quality various pesticides are used in large amounts. Lack of awareness has resulted into improper use and application of pesticides which has caused severe harm to the aquatic as well as terrestrial ecosystems. The run off containing large amount of pesticides

from the crop fields eventually ends up into rivers, streams as well as it seeps down and pollutes the ground water. All of this is affecting the human health as well because most of the pesticides are categorized as carcinogens. 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 (Nuruzzaman et al., 2016; Abhilash and Singh, 2009). Through overuse and misuse there is considerable waste, adding to the cost and contributing to the adverse environmental and health consequences. The removal of pesticides from water is one of the major environmental concerns today. In past few years presence of pesticide residue in the ground water resources has grown significantly and has become an intensive issue of discussion.

Adsorption is a well-known equilibrium separation process and an effective method for water decontamination application. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility, and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances (Ahmad et al., 2010). However pollutants can be frequently removed by adsorption on an active-solid surface. In 1940 activated carbon was used for the first time as an adsorbent for wastewater treatment, but activated carbon is expensive and cannot be used at large amount. This situation compelled scientists toward the development of low cost adsorbents i.e. alternatives of activated carbon. Many techniques are used for wastewater treatment such as reverse osmosis, coagulation and ion exchange but among all adsorption seem most suitable because of its simplicity and cost effectiveness. Biosorption is potentially an attractive technology for treatment of waste water for retaining heavy metal from dilute solution. Biosorption has been suggested as cheaper, more effective and minimization of chemical and biological sludge. Many natural bio sorbents are present in our environment which has the capacity to remove pesticides from wastewater. Naturally occurring adsorbents are low cost adsorbent material as compared to the commercially available ones. Most of the bio-adsorbents are used without any activation or treatment for water purification. These include rice husk (Ajmal et al., 2003; Akhtar et al., 2010; Ye et al., 2010; Kumar et al., 2006; El-Shafey, 2007) bamboo husk (Kannan and Veemaraj, 2009), walnut (Kazemipour et al., 2008), banana peel (Gupta et al., 2009a, b; Anwar et al., 2010) and coffee husk (Utomo and Hunter, 2006). The plant based bio-adsorbents are lignocellulosic biomass. These materials are considered as low cost due to their wider availability and abundance in nature (Malik et al., 2015). These used materials have been found to remove various organic pollutants ranging from 80 to 99.9%. The materials are waste products from industries and act as natural adsorbents. These adsorbents are easily available, economic, and show high adsorption efficiency, and thus are more effective in the removal of pesticides. Tea residue can be a low cost bio-adsorbent for organic pollutants in waste-water due to its abundance and availability. The efficiency of used tea residue can be increased by the process of activation for the removal of organic contaminants from water bodies (Ahluwalia, 2005; Wasewar et al., 2009). In addition tea waste is alternative as an adsorbent for its abundance in nature, non-toxicity and bio-degradability. The purpose of the present study was to investigate the adsorption behaviour of the pesticide 2-4 D, carbaryl and imidacloprid at the activated tea waste from aqueous solutions and thus the possibility to remove all these pesticide from waters polluted by it. The objective of this study to investigate the adsorption properties of raw and activated tea residue as bio-sorbent. This study was performed to utilize the tea waste as a low cost natural adsorbent with respect to various parameters such as different doses, contact time and pH.

2. Materials and Methods

The adsorbates used were 2,4-D (2,4-Dichlorophenoxyacetic acid), Carbaryl and Imidacloprid and the activating chemical, was orthophosphoric acid. The adsorbent was collected in a plastic container randomly from domestic sources and Fatima Jinnah Women University's main cafeteria, as its availability, handling and transportation were easy.

2.1. Preparation of Adsorbent

The used tea residue was washed and boiled repeatedly with distilled water and filtered it, till it was apparently dry. After that the residue was placed in a hot air oven for almost 4 hours at 100°C for drying it completely whereas, one sample was sun-dried that is used as non-activated tea residue (NATR) adsorbent. After properly drying it, orthophosphoric acid was added to the washed and dried tea residue and it was heated and stirred at 800 rpm with 80°C for 2 hours. The pre-activated tea residue was then filtered-out overnight and the residue looked like a sludge-like

material. The sludge-like pre-activated tea residue was washed with distilled water until the filtrate became colorless. Approximately after 12 to 14 washings it became colorless. It was then left to be filtered-out until it became apparently dry (Ahmaruzzaman and Gayatri, 2010).

After drying the tea residue was placed in a muffle furnace at 500°C for 2 hours. After calcinations, the tea residue became completely activated and it was then finely grounded. Its final form was like a fine black powder. The fine black powder was then placed in a desiccators and ready to use as activated tea residue (ATR) adsorbent.

2.2. Batch Adsorption Experiment

The activated and non-activated tea residue were applied as bio-sorbent to synthetic wastewater samples containing varied types of pesticides from different classes (2,4-D, Carbaryl, Imidacloprid) during series of batch experiment under variable parameters of pH, Initial concentration and adsorbent dose at a constant shaking speed of 100 rpm.

2.3. Preparation of Spiked Wastewater containing 2,4-D, Carbaryl and Imidacloprid

A stock solution of 2,4-D was prepared containing 0.027g of 2,4-D, 0.21g of carbaryl and 0.25g of imidacloprid in 100ml of distilled water which were heated and stirred for few minutes to ensure complete dissolution. Moreover, for the first series of batch experiment three working solutions of three different concentrations were prepared using the stock solution. However, working solutions of five different concentrations of each pesticide were prepared using the stock solution to get the calibration curve data.

2.4. Batch as a function of Initial Concentration

The pH and adsorbent dose were kept constant and initial concentration of adsorbate solution varied. Varying initial concentrations (10ppb, 30ppb, 50ppb for 2,4-D and 1ppb, 3ppb, 5ppb for Carbaryl and Imidacloprid) of adsorbate solution were prepared and the originally it was an acidic solution and this pH was kept constant. ATR (activated tea residue) as adsorbent was added to the adsorbate solution and placed in a shaker (Lab companion SK-300). The aliquot was drawn at regular time interval of 5 minutes for 1 hour. Each aliquot was passed through filter paper (Whatman 40). Each filtrate was run on UV-VIS spectrophotometer (UV-1601, SHIMADZU) at a wavelength corresponding to maximum absorbance (λ max) that was 201nm for 2,4-D, 221nm for carbaryl and 249nm for imidacloprid. The concentration adsorbed was determined from the calibration curve constructed with standard stock solution.

2.5. Batch as a function of pH

100ml of adsorbate solution with initial concentrations (10ppb, 30ppb, 50ppb for 2,4-D and 1ppb, 3ppb, 5ppb for Carbaryl and Imidacloprid) were prepared in volumetric flasks, separately along with adsorbent weight (50mg). The initial pH was acidic therefore, for further batch experiments basic and neutral pH were adjusted and changed using a dilute HCL (1M) and NaOH 1M solution with the help of a pH meter (inoLab pH 720). The beakers containing the solutions were placed in a shaker at 100rpm. Each filtrate was run on UV-VIS spectrophotometer (UV-1601, SHIMADZU) at a wavelength corresponding to maximum absorbance (λ max) that was 201nm for 2,4-D, 221nm for carbaryl and 249nm for imidacloprid. The concentration adsorbed was determined from the calibration curve constructed with standard stock solution.

2.6. Batch as a function of Adsorbent Dose

100ml of adsorbate solution was prepared using initial concentrations (10ppb, 30ppb, 50ppb for 2,4-D and 1ppb, 3ppb, 5ppb for Carbaryl and Imidacloprid) of the adsorbate solution and varying weight of adsorbent (10, 30, 50mg) were applied as adsorbent dose. The solutions were placed in shaker at 100rpm. Each filtrate was run on UV-VIS spectrophotometer (UV-1601, SHIMADZU) at a wavelength corresponding to maximum absorbance (λ max) that was 201nm for 2,4-D, 221nm for carbaryl and 249 nm for imidacloprid. The concentration adsorbed was determined from the calibration curve constructed with standard stock solution. Mass balance equation is used to express q_e . According to the equation q_e is adsorbate concentration adsorbed on adsorbent at equilibrium, C_i is initial concentration of adsorbate in solution (mg/L or ppm) and C_e is Equilibrium concentration or final concentration of adsorbate in solution (mg/L or ppm). The equation is as following:

$$q_e = (C_i - C_e) / S$$

Furthermore, Dose of adsorbent is expressed by:

$$S=m/v$$

Adsorption % is calculated using the following equation:

$$\% \text{ adsorption} = \frac{C_i - C_e}{C_i} \times 100$$

Non-activated tea residue also subjected to batch conditions at optimum parameters as control adsorbent.

3. Results and Discussion

This contemporary study focused on removing environmental pollutants (pesticide) from aqueous solution with the help of a low-cost adsorbent (used-tea residue). The characterization of activated and non-activated tea residue as adsorbents in the form of FTIR was conducted. Its performance was further assessed for 2,4-D, carbaryl and imidacloprid removal from synthetic water solutions under various experimental conditions, such as initial adsorbate concentration, pH and adsorbent dose.

3.1. Fourier-Transform Infrared (FTIR)

The FTIR results indicated a shift in the adsorption peaks which means that the adsorption sites were modified after activation and the inter-porosity along with the surface increased as well. The FTIR spectrum of non-activated and activated tea residue is shown in Figure 3.1 and 3.2, respectively. The complex nature of the adsorbent is displayed by the number of adsorption peaks in the spectra.

In study the FT-IR spectrum of tea powder biomass exhibited a broad peak at 3390cm^{-1} which indicates the existence of macromolecular association (cellulose, pectin, etc.) and may denote the presence of both H-bonded amine and OH groups. The doublet peak appeared in the spectra at wave numbers $2854\text{--}2923\text{cm}^{-1}$ which maybe due to the asymmetric and symmetric stretch of aliphatic chains (--CH) respectively. The peak at 1621cm^{-1} is assigned to the characteristic symmetrical stretching vibrations of carbonyl groups. The band at 1027cm^{-1} regions is attributed to the asymmetric C-O-C stretching vibrations (Gangadhar *et al.*, 2016). Figure 4.1 shown the recorded spectra for non-activated tea residue showed a sharp bend at 3385.18cm^{-1} is due to OH group, while 2924.18cm^{-1} is likely due to the C-H, while the peak generated at 1647.26cm^{-1} is due to the aromatic ring vibration. The peak at 1321.28cm^{-1} is due to N-O stretching of nitro compound, while 1261.49cm^{-1} is due to C-O stretching of alkyl aryl ether. The peak of 1095.60cm^{-1} is due to C-O and 802.41cm^{-1} is due to C=C bending alkene, while 669.32cm^{-1} is due to stretching of C-Br halo compound. In the contemporary study, both types of adsorbent (Activated and Non-activated) were prepared by KBr pellet for IR study. The infrared spectrum of the activated tea residue depicted the following functional groups on the basis of the adsorption peaks obtained. Table 3.1 further shows the details of the adsorption peaks and the corresponding functional groups. The activated tea residue might include the following functional groups in accordance with the presence of specific adsorption peaks.

1. (C-Br) from the Alkyl Halide functional group
2. (=C-H) from Alkyne
3. (CN) from Amine group
4. (C-F) from Alkyl Halide
5. (C-H) from Alkyne functional group

Shift in peaks from 3385.18cm^{-1} to 2962.76cm^{-1} indicates modification of sorption sites with activation (Reddy *et al.*, 2013).

The activation process increases the inter-porosity and surface area of the tea residue that consequently give rise to the amount of the pesticide adsorbed within the pores of the natural sorbent due to an increase in the active sites.

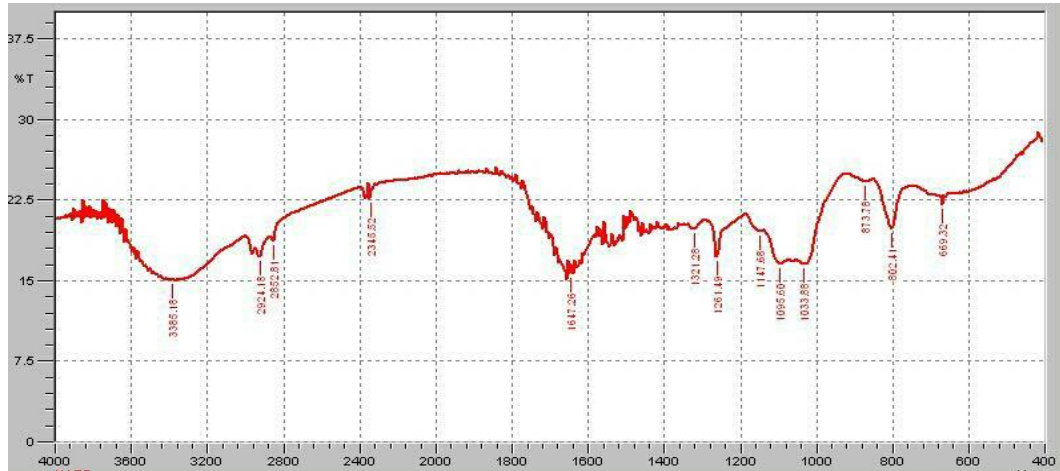


Figure 1: FTIR spectra of Non-activated Tea residue

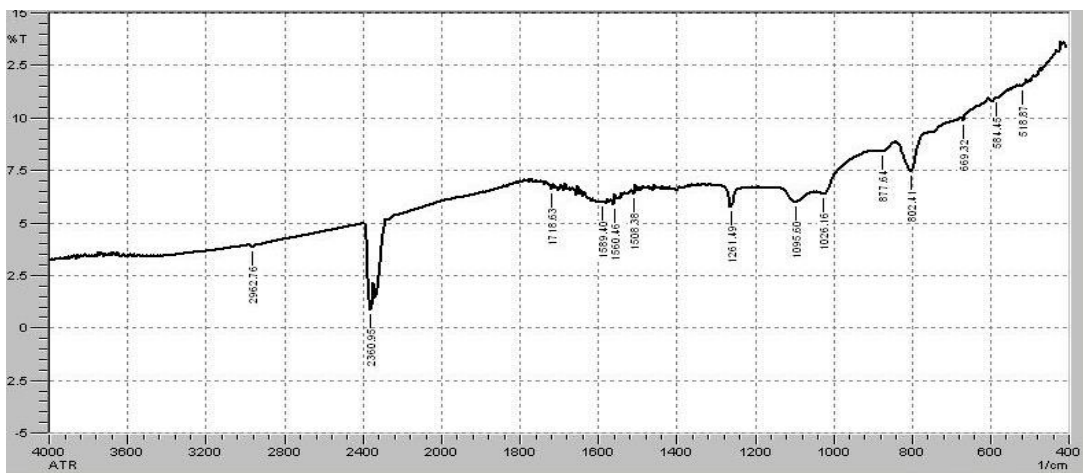


Figure 2: FTIR spectra of Activated Tea residue

Table 1: FTIR spectral Peaks, Intensity and representative Functional Groups in Non-activated and Activated Tea residue

Peaks	Functional Groups	Intensity
518.87	C-Br (Alkyl Halide)	Strong
802.41	(=C-H) Alkyne	Strong
1026.16	(CN) Amine	Medium-weak
1095.6	C-F (Alkyl halide)	Strong
1261.49	C-F (Alkyl halide)	Strong
2962.76	(C-H) Alkyne	Strong-Sharp

3.2. Batch Adsorption Experiment

Twenty seven sets of batch experiment were conducted for each pollutant pesticide in order to investigate the effects of varying pH, adsorbent dose and initial concentration of induced adsorbate on adsorption. Non-activated tea residue (NATR) as control adsorbent was also added to record adsorption capacity with respect to time.

3.3. Adsorption as a function 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 (Nuhoglu et al., 2003).

- **2,4-D:** The adsorption process was quite rapid in all pH conditions but more in acidic and basic condition in the case of 2,4-D removal.
- **Carbaryl:** In the case of Carbaryl, the increase in pH resulted into an increase in the adsorption process. Best % removal values were obtained at acidic pH.
- **Imidacloprid:** Moreover, for Imidacloprid removal pH 7 was the best.

3.4. Adsorption as a function of Adsorbent Dose

In order to investigate the effect of adsorbent dose on the removal, three varying doses of ATR were used (10mg, 30mg and 50mg).

10mg was the optimum dose for the removal of all pesticide.

Maximum adsorption of 2,4-D, Carbaryl and Imidacloprid was 99.99%, 96% and 99.7%, respectively at 10mg dose. The reason of this might be related to the number of active sites. As the number of adsorbent sites increase they might have neutralized each other consequently decreasing the % removal.

3.5. Adsorption as a function of Initial Concentration

The experiments were conducted at three different concentrations for all three pesticides.

- **2,4-D:** 10ppb, 30ppb and 50ppb were chosen for 2,4-D according to the maximum wavelength absorbed. At 10mg the adsorption process increased with a decrease in pesticide's initial concentration. Whereas, at 30mg and 50mg the adsorption process increased with an increase in the initial concentration.
- **Carbaryl and Imidacloprid:** 1ppb, 3ppb, 3ppb concentrations were chosen for both pesticides. In both the pesticides maximum removal % were obtained at lowest initial pesticide concentration.

3.6. Effect of Activation

The activation process increased the inter-porosity of the adsorbent which makes the adsorbent more efficient for the removal of all three pesticides. Activation lead to the development of more adsorption sites. Hence, in this study, H₃PO₄ activated tea waste (ATW) was used as the adsorbent for the removal p-NP from aqueous solution, which increased the tea waste's efficiency (Ahmarruzaman and Gayatri, 2010). Fig.3.3, 3.4 and 3.5 shows the comparison between NATR and ATR with all three pesticides.

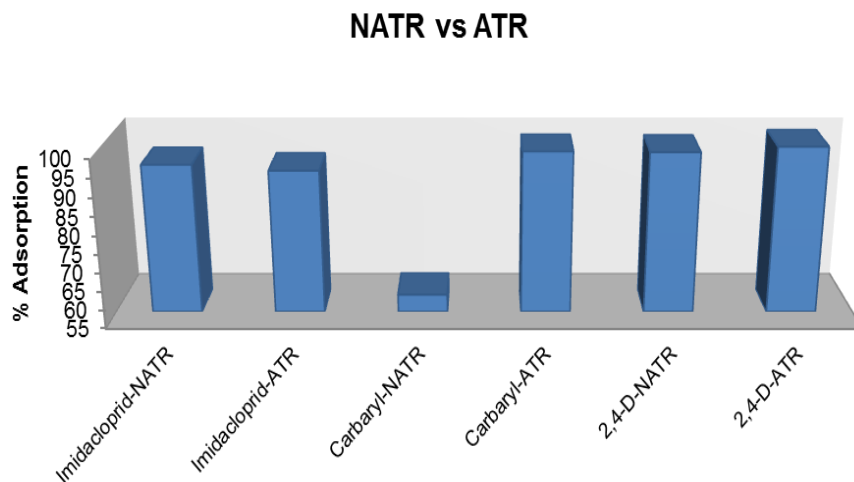


Figure 3: Removal (%) of 2,4-D, Carbaryl and Imidacloprid at NATR and ATR under Optimum conditions at equilibrium time

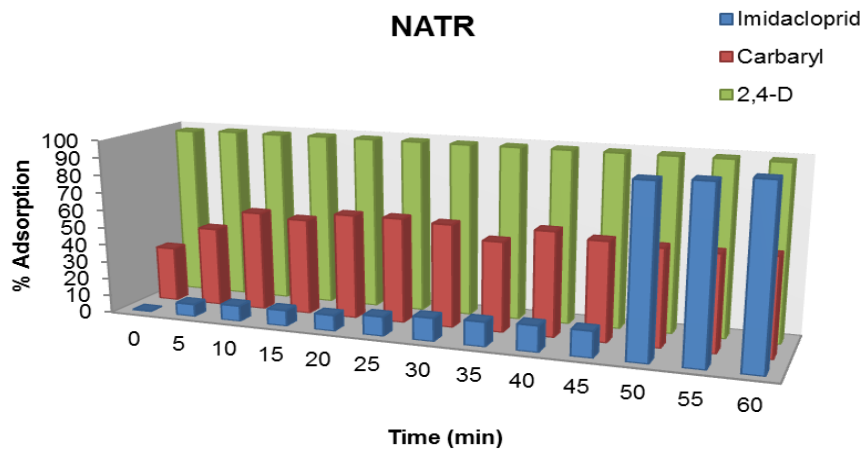


Figure 4: Removal (%) of 2,4-D, Carbaryl and Imidacloprid at NATR under Optimum conditions at variable contact time

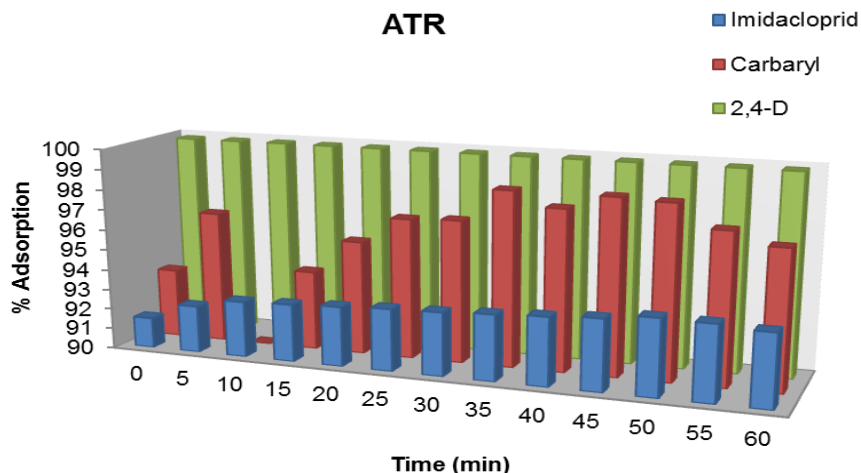


Figure 5: Removal (%) of 2,4-D, Carbaryl and Imidacloprid at ATR under Optimum conditions at variable contact time

4. Conclusion

This study led to the following conclusions:

- The physical and chemical properties of the adsorbent such as surface area and surface functional groups can be improved by activation.
- The non-activated tea residue adsorbed 91.8%, whereas the activated used tea residue adsorbed 99.99% of 2,4-D. These results show that this natural sorbent is commendable in removing 2,4-D from waste-water.
- In case of carbaryl, activation increases its capability to remove large amount of pollution from aqueous solutions. However, results show that % removal of activated tea residue is 96.8% and the % removal of non-activated tea residue is 59.7% for Carbaryl. Moreover, activation increased the sorption of Imidacloprid up to 99.7%.
- Consequently, it can be concluded that the activated tea residue can be a beneficial and efficient low-cost bio-adsorbent for the removal of these pesticides from aqueous solutions due to its efficiency, availability and abundance.

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