Civil and Environmental Research
ISSN 2224-5790 (Paper) ISSN 2225-0514 (Online)
Vol.8, No.2, 2016

Removal of Pesticides from Iraqi Soils and Water

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Abstract

Contamination of soil and water with various types of pesticides, resulting from accidental spills at agrochemical manufacturing, formulation, and distribution facilities, farm loading/washdown sites, or abandoned waste sites, is a serious environmental problem in many places in the world. The remediation of two types of pesticides which were (carbofuran and chlorpyrifos) from three types of Iraqi soils (sandy, silty and clayey) was investigated in the present study. The treatment process was performed through washing method using distilled water in batch mode then; a continuous fixed bed unit was used to perform the removal of the same two types of pesticides from wasted washing polluted water using adsorption technique at different operating conditions with low-cost adsorbents which were watermelon peel (WP) and used tea leaves (UTL). The results show that the maximum removal efficiencies of pesticide from polluted soils were 81.268, 99.531 and 89.151 for clayey, sandy and silty soils respectively for carbofuran and 77.420, 94.790 and 85.481 for clayey, sandy and silty soils respectively for chlorpyrifos. Adsorption isotherm and kinetic models have been used to fit the experimental data. Finally, in this study a novel way was suggested and experimented as a safe, economic, beneficial and eco-friendly non-conventional method to get rid of the WP and UTL loaded with carbofuran and chlorpyrifos pesticides wasted. This method was trying to convert these toxic residues to applicable useful material like rodenticide. The results show that good ability for these residue to be an active rodenticide through the LD_{50} calculated.

1. INTRODUCTION

Soil can be defined as the top layer of the earth's surface in which plants can grow, consisting of rock and mineral particles mixed with decayed organic matter and having the capability of retaining water. It is associated with everything around us and represents many paramount functions in perpetuating life on our planet **(MacBean, 2012)**. Soil plays seven important roles which were providing the basis for food and biomass production, controlling and regulating environmental interactions- regulating water flow and quality, storing carbon and maintaining the balance of gases in the air, providing valued habitats and sustaining biodiversity, providing a platform for buildings and roads, providing raw material and preserving cultural and archaeological heritage **(Singh, 2008; Kumar et al., 2013)**. On the other hand, water is one of the most essential elements to health and is so important that our bodies actually have specific drought management system in place to prevent dehydration and ensure our survival **(Abbas, 2014a)**. Water benefits cannot be counted; it makes up more than two thirds of human body weight, 95% of brain, 82% of blood and 90% of lungs **(Chu et al., 2011)**. Water serves as a lubricant in digestion and almost all other body processes, regulates our bodies temperature, removes harmful toxins from the body in many different ways, transports valuable nutrients and oxygen throughout the body, etc. Without water, we would die in a few days **(Abbas, 2014b)**. Water is the lifeblood and the most important resource of natural resources on the earth. The lives of all living organisms, agriculture and industry depend on the water; so it's not surprising to find that most ancient human civilizations focused around the rivers and water sources such as the civilizations of Mesopotamia and the Nile Valley **(Abbas, 2014c)**. A synopsis of the foregoing there are permanent and large correlative between soil and water in almost every place on the blue planet's surface. The soil contains water in its various forms, surface and groundwater, cleavage its streams and transports from one place to another through the soil carrying all life forms with it **(Abbas, 2014d)**. Alternatively, soil without water become a dead, barren, desolate and wasteland no life in it for any creature. Together these two important elements constitute two-thirds of the environment **(Abbas, 2014e)**. Therefore, it is incumbent upon the human preserved soil and water from all problems lead to ravage or damages them. Whether these problems were naturally (such as earthquakes, volcanoes, floods, mudslides, and erosion) or human made due to continuous development sought by accessing for luxury and comfort **(Đurović et al., 2009; Karim and Adnan, 2012)**. The most important and serious problem for both soil and water is pollution. Pollution may be defined as "any change occurs on the elements involved in the composition of it either directly or indirectly manner due to human activity", which makes the soil or water has less validity of uses for natural uses allocated to them or some of them. In other words, pollution is "the changes occur in the natural biological and chemical properties of soil or water, making it unfit for drinking or household use, industrial and agricultural" **(Khuntong et al., 2010)**. Soil and water are contaminated through the waste of humanity, plant, heavy metals, agricultural, industrial, and toxic chemicals draining into the water sources (water bodies, rivers, lakes, bays, and oceans) **(Wang, 2000)**. Also, groundwater is polluted as a result of a chemical as well as sewage spill to it, and later to soil including the harmful substances, bacteria, microorganisms, and pathogens **(Abbas, 2014f)**. Many of human activities on the environment cause pollution for both soil and water, therefore, there are many sources of pollution, among them pollution by sewage, heavy metals, radioactive contaminants, dyes wasted from textile factories, petroleum extraction and refining of oil, as well as pesticide contamination **(Changa et al., 2012; Abbas, 2014g)**. Because of the agricultural expansion taking place in all regions and countries of the world due to rise the demand for food as a result of increasing the population growth and the threat formed by this agricultural expansion on the depletion of soil and water resources. Another problem associated with agricultural expansion and depletion of soil and water have emerged, namely, the extensive use of agricultural fertilizers and pesticides. Pesticides are chemical substances which kill or inhibit or limit the proliferation and spread of organisms that compete human in nutrition, health and property (Pets) **(Alalm and Tawfik, 2013)**. It is well known that in the recent years become about 56% of the world's population suffer from shortage of food, and this ratio increases to about 79% in the third world countries. With the expectations of arrival the world population in 2050 to about 10 billion people, it is very necessary and imperative to increase agricultural production to satisfy pressing and urgent need for such a number of people for food **(Abdulhamid, 2012; Copplestone, 1998)**. Chemical pesticide became in general, one of the modern technological means adopted to increase agricultural production and to combat deadly diseases to humans and animals. However, these chemical pesticides have many adverse impacts, if not used according to precise criteria **(Xiong et al., 2011; WHO, 2009)**. Recently, emerged the problem of increasing the amounts of chemical pesticides in the soil, surface, and ground water globally, where many studies have been shown that the presence of chemical pesticides in these two elements, and as a result the attention of environmental scientists and researchers were growing with contamination of soil and water with chemical pesticides has significantly increased **(Valičkováa et al., 2013; Kah, 2007)**. Chemical pesticide is considered from the most important environmental contaminants to their comprehensive impact on all living components of the environment, including its impact on the ecological balance, especially in third world countries, they led to serious pollution of the food eating, the water drinking, the breathing air, and the soil that eating its benevolence **(Jokanovic, 2012; Jilani, 2013)**. Existing technologies to remove pesticides pollutants from soil or water included many problems during and after treatment process and have several downsides such as their high costs for operation, need particular equipment, consume high energy, decreases the efficiency of remediation during the process, long time for treatment, continuous perpetuate, and often generate huge amounts of remaining toxic by-products which required safe way to poses it. Therefore, the conventional treatments are no longer able to achieve required treated water quality **(Marincas et al., 2009; Campo et. al., 2013)**. Adsorption method has been demonstrated to be an excellent technique to remediate pesticides in comparison with other traditional methods through various importance, usefulness, and advantages properties such as high efficiency, low initial operating cost, simplicity of design, comfort of operation, economic, insensitivity to toxic substances, suitable for most types of contaminated water, and complete removal of contaminants even from dilute solutions **(Abbas and Abbas, 2014a)**. Many non-conventional low-cost adsorbents, including agricultural wastes or industrial by-products are different degrees of success in applying for the treatment of the pesticides effluents. Compared to conventional adsorbent (activated carbon), this kind of adsorbent show a lot of advantages like readily and local available, technical feasibility, inexpensive, engineering applicability, and disposable without regeneration **(Abbas and Abbas, 2014b)**. The target of this thesis is studying the removal of two types of pesticides from soil by water in batch mode and from washing water using a renowned, low cost and available agricultural wastes which were watermelon peel (WP) and used tea leaves (UTL) as a natural adsorbent media to commercial adsorbent material existing in continuous mods. Finally try to benefit from the wastes residue by preparing a simple rodenticide accessing to Zero Residue Level (ZRL).

2. EXPERIMENTAL WORK

2.1 Soil Properties

Three types of soils: sand, clay and silty loam were used in present study, as shown in **Figure 1**. Sand and clay soil samples were obtained from the Soil Laboratory – Civil engineering department – College of Engineering – Al-Mustansiriyah University while the third type of soil (Silty loam) was taken from the College of Agriculture – Baghdad University. All above soil samples were sieved to 2mm before treated with pesticides (before polluted), and analyzed in (Soil Laboratory – civil engineering department and Sanitary Laboratory – environmental engineering department) – College of Engineering – Al-Mustansiriyah University. The physical and chemical properties of the three soil types are shown in **Table 1**.

Clayey soil Silty loam soil Sandy soil

Figure 1 Three types of Iraqi soils used in this study

Table 1 Characteristics properties of the three types of Iraqi soils used in this study

Soil Type	Soil Texture (%)		Soil pH	OMC %	EC (ms/cm)	CEC (meq/100g)
Sandy	Sand	96.3	6.54	0.939	0.556	14.732
	Silt	3.7				
	Clay	--------				
Silty loam	Sand	22	7.8	0.14	4	21.4
	Silt	52				
	Clay	26				
Clayey	Sand	--------	6.34	2.322	6.08	24.746
	Silt	35				
	Clay	65				

2.2 Stock Solutions

In order to avoid interference with other elements that may be present in the real wastewater, the removal experiments of two types of pesticides were carried out using simulated aqueous solutions of pesticides. A quantity of 1000 mg/l stock from each type of pesticide solution was prepared by dissolving a known weight of each pesticide (5 gm of carbofuran pesticide and 2.08 ml of chlorpyrifos pesticide) in 1 liter of distilled water. All solutions used in the experiments were prepared by diluting the stock solution with distilled water to the desired concentration. The pesticide concentrations were measured using a spectrophotometer thermo-Genesys 10 UV.

2.3 Calibration Curves

The calibration curves of two types of pesticides used was carried out using a spectrophotometer thermo-Genesys 10 UV, USA. The spectrophotometer was installed due to manufacture's instruction with the wave length corresponding to carbofuran and chlorpyrifos pesticides. The spectrophotometer device was firstly set to zero absorbance using the blank solution. Absorbance at λ = 263 nm and λ= 348 nm for carbofuran and chlorpyrifos respectively was determined using several experiments with dilute solution samples. From the determined absorbance above, it can prepare the calibration curves for two types of pesticides. **Figure 2** and **Figure 3** showed the calibration curves of carbofuran and chlorpyrifos pesticides respectively.

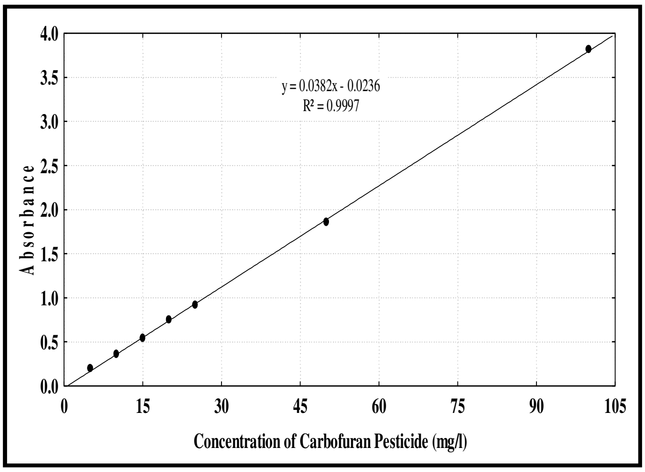


Figure 2 Carbofuran pesticide calibration curve

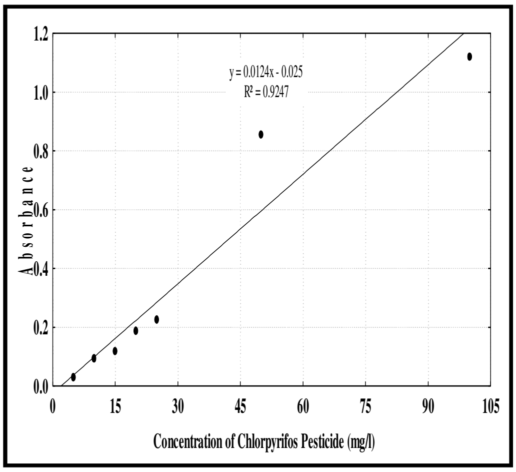


Figure 3 Chlorpyrifos pesticide calibration curve

2.4 Preparation of Simulated Soil (Polluted Soil)

Five grams of each soil samples were added to 250 ml conical flasks containing 100 ml of solution having 100 mg/l of carbofuran and chlorpyrifos pesticides each one alone. All experiments were conducted at nearly constant room temperature (28°C ± 2) and duplicated. The mixture was kept in an orbital shaker at agitation speed of 150 rpm over night while pH of pesticide solution was kept neutral. From the flasks, 5 ml of samples were collected at regular intervals (every 15 minutes) using a clean syringe from the aqueous phase, centrifuged at 4000 rpm for 10 min and the supernatant passed through 0.45 µm PTFE syringe filter and then put it in the spectrometric device to determine the rest of pesticide in the solution until reach equilibrium. Finally the equilibrium concentration of carbofuran pesticide in the Iraqi soils was 8.1774, 5.9484 and 3.5468 g/kg for sandy, silty loam and clayey respectively while the equilibrium concentration of chlorpyrifos pesticide in the Iraqi soils was 17.0774, 15.0822 and 2.4738 g/kg for sandy, silty loam and clayey respectively.

2.5 Remediation of Pesticide from Polluted Soil

The remediation process of pesticides from polluted soils was achieved by washing process using distilled water for each soil samples prepared in orbital shaker at agitation speed varied from 100-400 rpm for a treatment time 600 minutes while pH of pesticide solution was varied from 1-8. All experiments performed at nearly constant room temperature (28°C ± 2). To determine the concentration of pesticide removal from the different kinds of soils and transferred to washing water, samples were taken periodically, centrifuged at 4000 rpm as in section 2.4 aforementioned and tested spectrophotometrically until reach equilibrium.

2.6 Removing of Pesticide from Polluted Washing Water

2.6.1 Preparation of Adsorbent Materials

Mature watermelon peel (WP) and Used tea leaves (UTL) were obtained freely from the domestic usage. The collected WP and UTL were excess washing with distilled water for removing any impurities, dust and other filth particles or other fine dirt particles that may be stucked in the surface of WP and UTL. The washed WP was cut into 0.5-1 cm small pieces then WP and UTL dried for 24 hours at 50°C. The dried WP and UTL were milled and sieved to sizes 0.6 mm. WP and UTL used in this study are shown in **Figure 4** and **Figure 5** respectively.

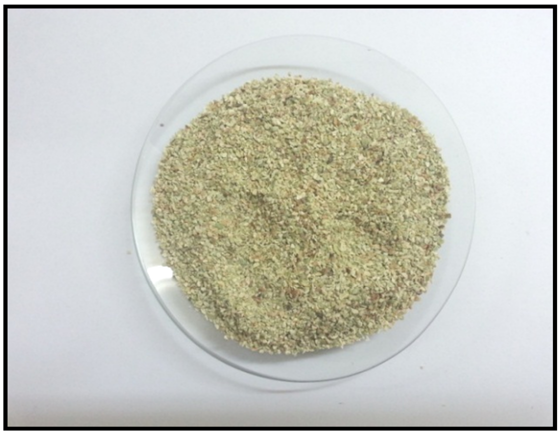


Figure 4 Watermelon Peel (WP)

Figure 5 Used Tea Leaves (UTL)

2.6.2 Characterization of Adsorbent Materials

The surface area, Fourier transform Infra-red (FTIR) spectrum and Scanning Electron Microscopy (SEM) for both WP and UTL were conducted for adsorbent materials WP and UTL as elucidated below.

2.6.2.1 Specific surface area and porosity

Specific surface area of WP and UTL were determined using nitrogen (N2) physical adsorption isotherm data on the surface of the WP and UTL by Brunauer, Emmett, and Teller (BET) method. The samples measured at Catalysts Department in the Center of Petroleum Research and Development – Ministry of Oil by using (ASAP 2020, Micromerities Co., USA) and (surface area analyzer, Qsurf M1, Thermo CO., USA) devices.

2.6.2.2 Fourier transform Infra-red (FTIR) spectrum

The Fourier transform Infra-red (FTIR) spectrum analysis of WP and UTL was performed at the laboratories of Ibn Sina State Company – Ministry of Industry and Minerals. The samples of WP and UTL were analyzed using a spectroscope FTIR equipment of (FTIR spectrophotometer, Irprestige-21, Shimadzu, Japan) incorporated with software (Perkin Elmer Instruments version 3.02.01) for the examination of the spectra. For sample analysis, 0.5 g of WP or UTL was mixed with about the same amount of potassium bromide KBr. The mixture thus obtained was crushed in a mortar to obtain a homogeneous powder which was then introduced into a mould to obtain very fine plates. The plates were then introduced into the spectrophotometer for analysis. The wave number was found to vary between 4000 and 500 cm^{-1}.

2.6.2.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is one of the most versatile and well-known analytical techniques. Compared to conventional optical microscopes, an electron microscope offers advantages including high magnification, large depth of focus, great resolution and ease of sample preparation and observation. WP and UTL samples were subjected to SEM measurement by the following procedure. The samples were sputter coated with gold using (Fine coat JFC-1100E, JEOL Co., Japan) ion sputter in order to reduce charging effect. This device, consisting of the basic device and a rotary pump, is used mainly for preparing specimens for scanning electron microscopes. It applies various metal coatings to nonconductive specimens. The thickness of the coated gold was 200 Å. The time required to reach an optimum thickness was 2 minutes. The samples scanned at the Central Service laboratory of College of Education for Pure Science (Ibn Al-Haitham) – Baghdad University. The SEM characterization was conducted using SEM device (multi-function scanning electron microscope model AIS 2300C Angstrom, USA).

2.6.3 Adsorption Unit Experiments

The removal process of two types of pesticides i.e. carbofuran and chlorpyrifos were performed by adsorption technique using low cost adsorption materials which were watermelon peel (WP) and used tea leaves (UTL) as adsorbents at different operating conditions continuously using fixed bed adsorption column. Adsorption column of continuous mode experiments were conducted in order to test carbofuran and chlorpyrifos removal by treated polluted washing water with pesticides each one alone at desired concentration with the various bed heights of the adsorbent media (WP and UTL) using different flow rates of polluted washing water of pesticide at various pH. The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl solutions. An arrangement representation of the sorption unit is shown in **Figure 6** where the flow direction is downward by gravity. The adsorption unit consists of plastic container of polluted washing water of pesticide of (5 liter) capacity. Glass column has 5 cm ID and 50 cm height. The sorption column packed with adsorbent media to a height of (10, 20, 30 and 40 cm). Before starting the runs, the packed bed sorption column was rinsed by distilled water down flow through the column. The adsorbent media (WP and UTL) is packed in the column to the desired depth, and fed to it as slurry by mixing the media (WP and UTL) with distilled water in order to avoid the formation of air bubbles inside the adsorption media. After the packed bed column was accommodation and putting the required amount of adsorbent media, the adsorption process started by allowing the pesticide polluted solution of required concentration and pH down flow through the sorption column from inlet container by gravity at a precise flow rate in experiment which is adjusted by the valve as shown in **Figure 6**. To determine the best operational conditions, the experiments were carried out at nearly constant room temperature between (28°C±2), various pH values which are (1–8) and initial feed concentrations of polluted washing water of different pesticide (carbofuran and chlorpyrifos) which are between (1–100) mg/l and at different flow rates which are between (5–100) ml/min for pesticide initial feed concentration. Outlet samples after treatment in each experiment were collected every 5 minutes from the bottom of packed column and the unadsorbed concentration of pesticide in treated solution was analyzed by spectrophotometer.

Figure 6 Fixed Bed Adsorption Unit

3. RESULTS AND DISCUSSIONS

3.1 Removal of Pesticides from Simulated Soils:

3.1.1 Effect of treatment time

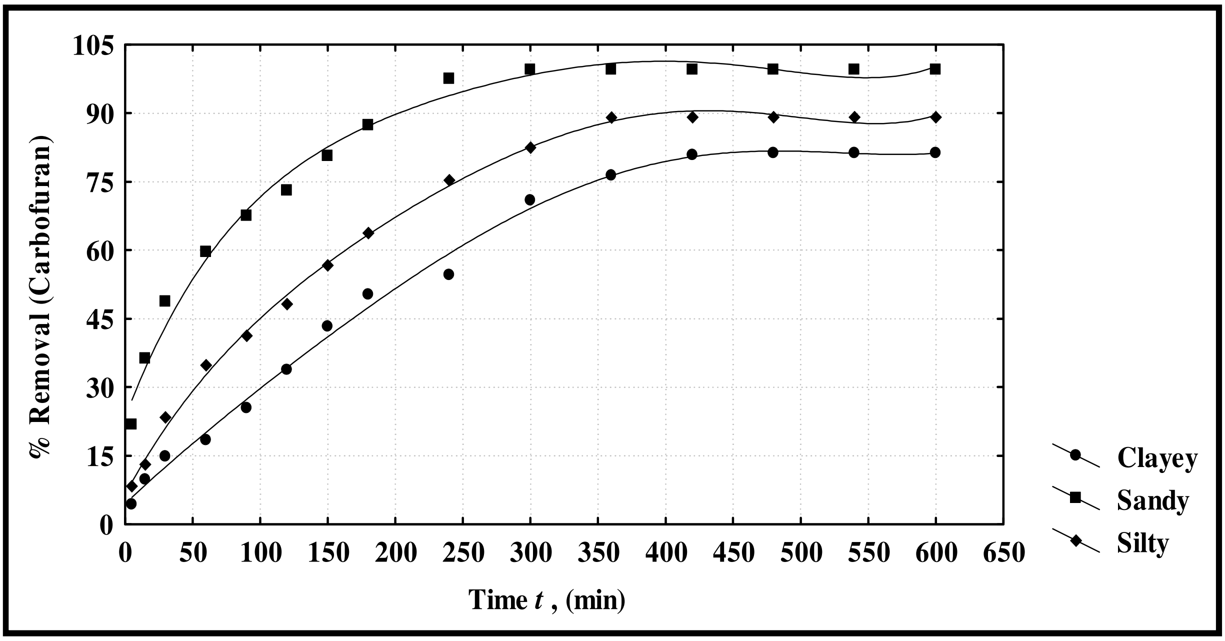
The effects of treatment time on desorption removal efficiency of two types of pesticides from contaminated simulated soils are shown in **Figure 7** and **Figure 8**. These Figures indicate that the two types of pesticides (Carbofuran and Chlorpyrifos) were rapidly desorbed from all kinds of soils (clayey, sandy and silty) initially due to the large difference in concentration gradient between soils and washing water. When the concentration of pesticides in soil and water nearly reached to equilibrium, pesticides still continuously desorbed albeit at a slower rate than the rate at the beginning. At the final state, equilibrium in desorption of pesticides may be conducted.

3.1.2 Effect of pH

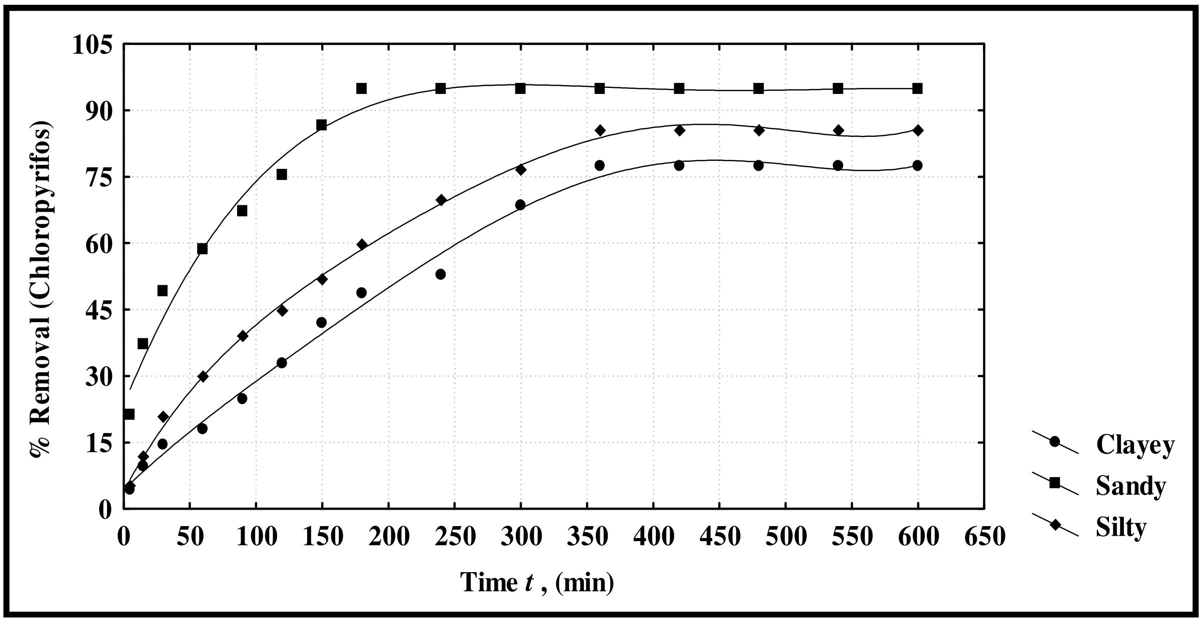
The effects of pH on desorption removal efficiency of pesticides from simulated contaminated soils are shown in **Figure 9** and **Figure 10**. Generally, it is well known fact that desorption process is governed by pH of the soil and the pH value had a considerable action on the adsorption removal efficiency. The investigation of the significant role played by pH in desorption process of two types of pesticides (Carbofuran and Chlorpyrifos) from three kinds of soils (clayey, sandy and silty) was performed in this study via changing the pH value from (1-8) including all the range of pH (i.e. acidic, neutral and basic) while keeping all other parameters are constants at optimum values obtained at equilibrium time. It's obvious from **Figure 9** that desorption removal efficiency of carbofuran pesticide was decreased when increasing the pH, indicated that carbofuran desorption is pH dependent, and in strongly acidic desorption is favoured. This result may be due to the masking of functional groups at elevated pH of carbofuran adsorption and under strongly acidic conditions, carbofuran yields to carbofuran phenol, which is strongly bound to soil by forming a complex with organic matter. In addition, the acidity may convert carbofuran from negatively charged anions to uncharged molecules or even to positively charged cations, and thus dramatically increase their adsorption. The results of this study also revealed that strongly acidic pH had a higher capacity to desorb carbofuran from soil by washing water. This result is agreement with **(Abbas and Abbas, 2014a,b)**. On the other hand **Figure 10** shows that desorption removal efficiency of chlorpyrifos pesticides was increased with increasing pH. Desorption of chlorpyrifos is pH dependent and at pH > 7.5-8.0 desorption increases dramatically. There are two hypotheses regarding the relationship between increased pH value and desorption of chlorpyrifos. First hypothesis suggests that desorption increases fairly consistently with increased pH. The second hypothesis suggests that desorption of chlorpyrifos is fixed from acidic to neutral conditions, while it proceeds at an increased rate under alkaline conditions. This result is agreement with **(Abbas and Abbas, 2014a,b)**.

3.1.3 Effect of agitation speed

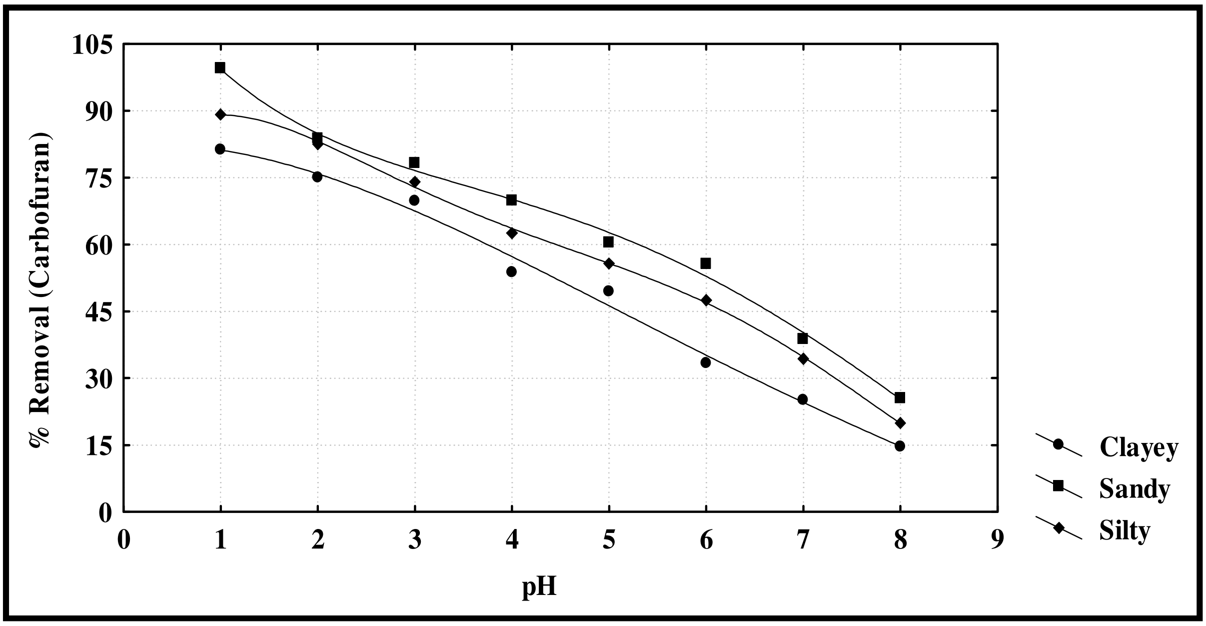
The effects of agitation speed on desorption removal efficiency of carbofuran and chlorpyrifos are presented in **Figure 11** and **Figure 12** respectively. Agitation speed effect was studied by varying the speed of agitation from 100 to 400 rpm, while keeping the other variables constant at optimum values obtained at equilibrium time. As can be seen from **Figures 11** and **12** the removal efficiency of two types of pesticides from all kinds of soils are generally increased with increasing agitation speed (i.e. proportional relation) until equilibrium approach. This is due to the fact that, the increase of agitation speed, improves the diffusion of carbofuran and chlorpyrifos towards the water.



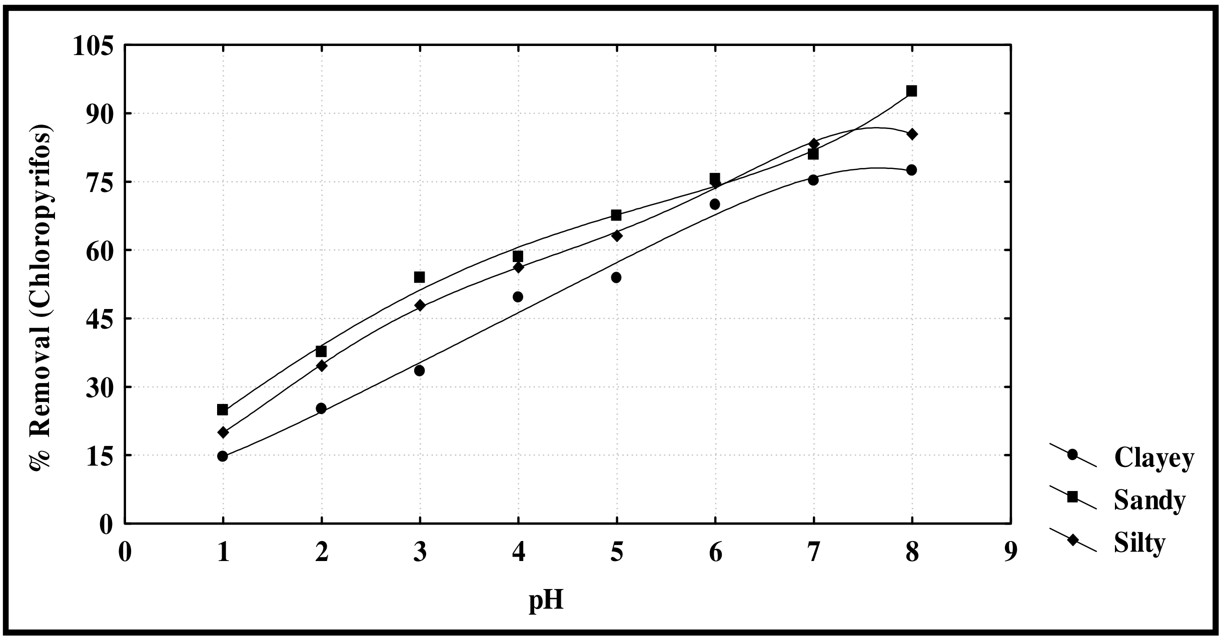
Figures 7 Effect of Contact Time on the % Removal of Carbofuran Pesticide from Different Kinds of Soil Using Washing Water



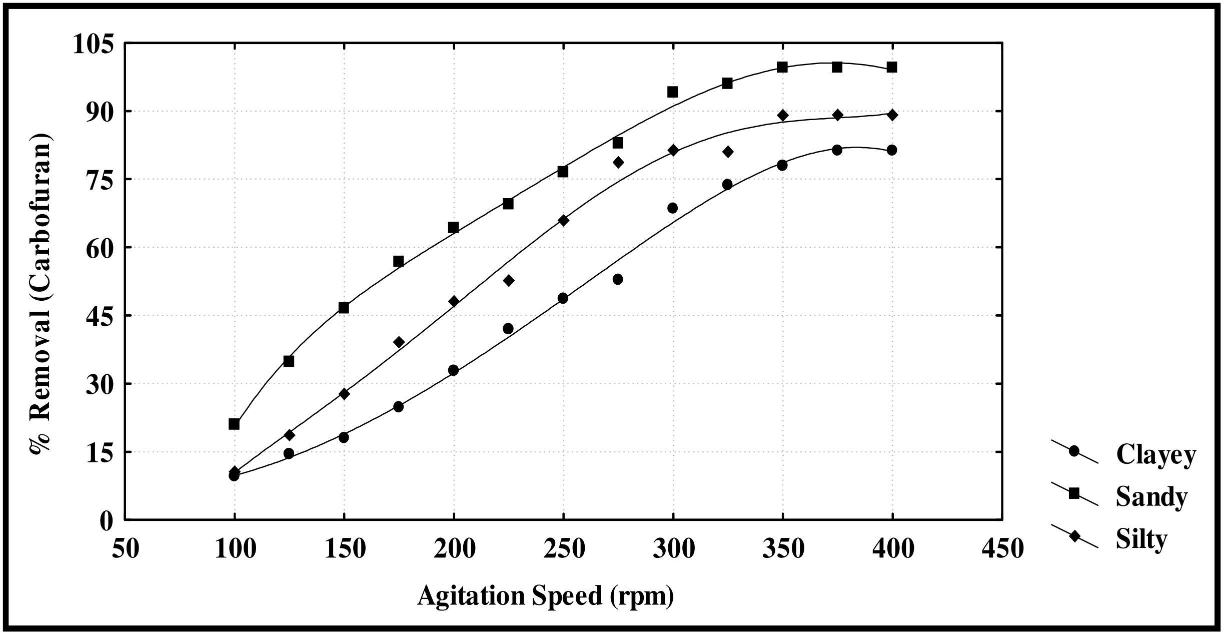
Figures 8 Effect of Contact Time on the % Removal of Chlorpyrifos Pesticide from Different Kinds of Soil Using Washing Water



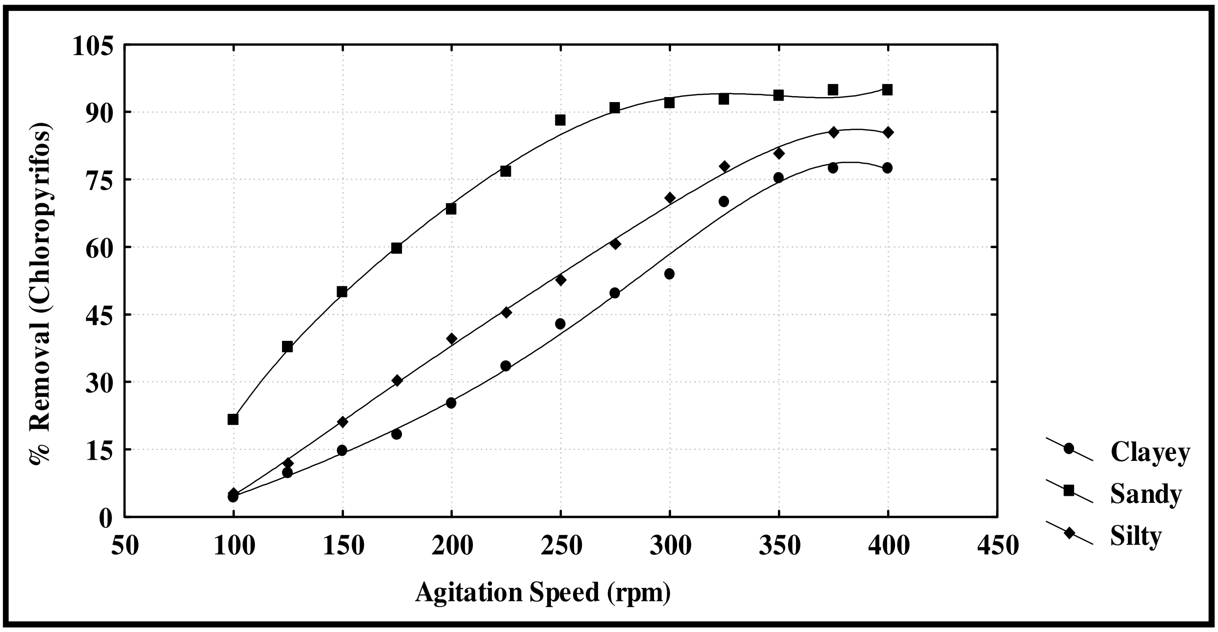
Figures 9 Effect of pH on the % Removal of Carbofuran Pesticide from Different Kinds of Soil Using Washing Water



Figures 10 Effect of pH on the % Removal of Chlorpyrifos Pesticide from Different Kinds of Soil Using Washing Water



Figures 11 Effect of Agitation Speed on the % Removal of Carbofuran Pesticide from Different Kinds of Soil Using Washing Water



Figures 12 Effect of Agitation Speed on the % Removal of Chlorpyrifos Pesticide from Different Kinds of Soil Using Washing Water

3.2 Removal of Pesticides from Polluted Washing Water:

3.2.1 Influence of initial concentration:

The results showed that using WP and UTL as an adsorbent material, the percent removal of pesticides (for both carbofuran and chlorpyrifos) from polluted washing water was decreased when the initial concentration (C_o) of pesticides was increased at constant other variables as **Figure 13**. This can be explained by the fact that the initial concentration of both carbofuran and chlorpyrifos had a restricted effect on the pesticides removal capacity; simultaneously the adsorbent media (WP and UTL) have a limited number of active sites, which would have become saturated at a certain concentration. This was lead to the increase in the number of pesticide molecules competing for the available functions sites on the surface of adsorbent media. Since the solution of lower concentration has a small amount of pesticides than the solution of higher concentration of it, therefore the percent removal was decreased with increasing initial concentration of pesticides. For adsorbent media, higher percent removal of carbofuran Pesticide was (99.25, and 99.19) % using WP and UTL respectively while for chlorpyrifos Pesticide was (95.41, and 92.75) % using WP and UTL respectively, at initial pesticide concentration of 1 mg/l, so these adsorbent medias was found to be efficient to remove pesticides from polluted washing water.

3.2.2 Influence of pH:

The results showed that using WP and UTL as an adsorbent material, the percent removal of carbofuran pesticide was decreased when the pH of washing water of above pesticide was increased at constant other variables, while the percent removal of chlorpyrifos pesticide was increased when the pH of washing water of above pesticide was increased at constant other variables as shown in **Figure 14**. It is well recognized that the pH of the solution is an important parameter in affecting adsorption of pesticides **(Abbas and Abbas, 2014)**. High adsorption of carbofuran pesticide at low pH can be explained in both terms; the species of the pesticide and the adsorbent surface. For this case, at low pH, i.e. acidic conditions, the surface of the adsorbent (WP and UTL) becomes highly protonated and favours adsorb of above group of pesticides in the anionic form. With increasing the pH of polluted water, the degree of protonation of the surface reduces gradually and hence adsorption is decreased **(Abbas and Abbas, 2013)**. Furthermore, as pH increases there is competition between hydroxide ion (OH^-) and pesticide, the former being the dominant species at higher pH values. The net positive surface potential of adsorbent media decreases, resulting in a reduction the electrostatic attraction between the (sorbent) pesticide species and the (sorbate) adsorbent material surface (WP and UTL), with a consequent reduced sorption capacity which ultimately leads to decrease in percentage adsorption of pesticides **(Abbas and Abbas, 2013)**. In the other hand, the adsorption of chlorpyrifos pesticide can be explained by ion-exchange mechanism of adsorption in which the important role is played by functional groups that have cation exchange properties. For this case at lower pH values, pesticides removal was inhibited, possibly as a result of the competition between hydrogen and pesticides on the adsorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of pesticide as in consequence of the repulsive force. As the pH increased, the ligand functional groups in adsorbent media (WP and UTL) would be exposed, increasing the negative charge density on the adsorbent material surface, increasing the attraction of pesticides with positive charge and allowing the adsorption onto adsorbent material surface.

3.2.3 Influence of fixed bed height:

The results elucidated that when the adsorbent media (WP and UTL) height in fixed bed column was increased, the percent removal of two types pesticides (carbofuran and chlorpyrifos) was increased too at constant other variables as shown in **Figure 15**. The increased of bed height (*l*) meaning increased in the amount of adsorbent media i.e. (WP and UTL), thus increasing the surface area of adsorbent material, hence increased the number of active sites in the adsorbent material surface i.e. increased the availability of binding sites for adsorption and consequently increase the pesticides removal capacity on WP and UTL. This lead to increase the ability of adsorbent media to adsorb greater amount of carbofuran and chlorpyrifos pesticides at different initial concentrations of polluted water and ultimately the percent removal of all pesticides (carbofuran and chlorpyrifos) was increased.

3.2.4 Influence of flow rate:

The results illustrated that when the flow rate of polluted washing water of pesticides was increased, the percent removal of pesticides was decreased (for both carbofuran and chlorpyrifos) at constant other variables as shown in **Figure 16**. This may be due to the fact that when the flow rate of pesticides in polluted solution was increasing, the velocity of solution in the fixed bed column packed with the adsorbent media (WP and UTL) was increasing too, so the solution spend shorter time in contact with adsorption media than that spend in the column, while at low flow rate, the solution of pesticides resides in the column for a longer time, and therefore undergoes more treatment with the adsorbent media (WP and UTL), thus the adsorbent media uptake low amount of pesticides from polluted solution for high flow rate, therefore the percent removal of both carbofuran and chlorpyrifos pesticides was decreased when the flow rate was increased.

3.2.5 Influence of treatment time:

The results demonstrated that when the treatment time of carbofuran and chlorpyrifos pesticides in polluted washing water was increased the percent removal of pesticides was increased too (for both carbofuran and chlorpyrifos) at constant other variables as shown in **Figure 17**. This may be due to the fact that when the treatment time of pesticides in polluted solution was increasing and the velocity of solution in the fixed bed column packed with the adsorbent material (WP and UTL) was remaining constant, the pesticide solution spend longer time in contact with adsorbent material (WP and UTL) than that spend it when the time of treatment decreased, so the adsorbent material uptake more amount of pesticides from polluted solution feed, therefore the percent removal of pesticides from pesticide solution feed was increased.

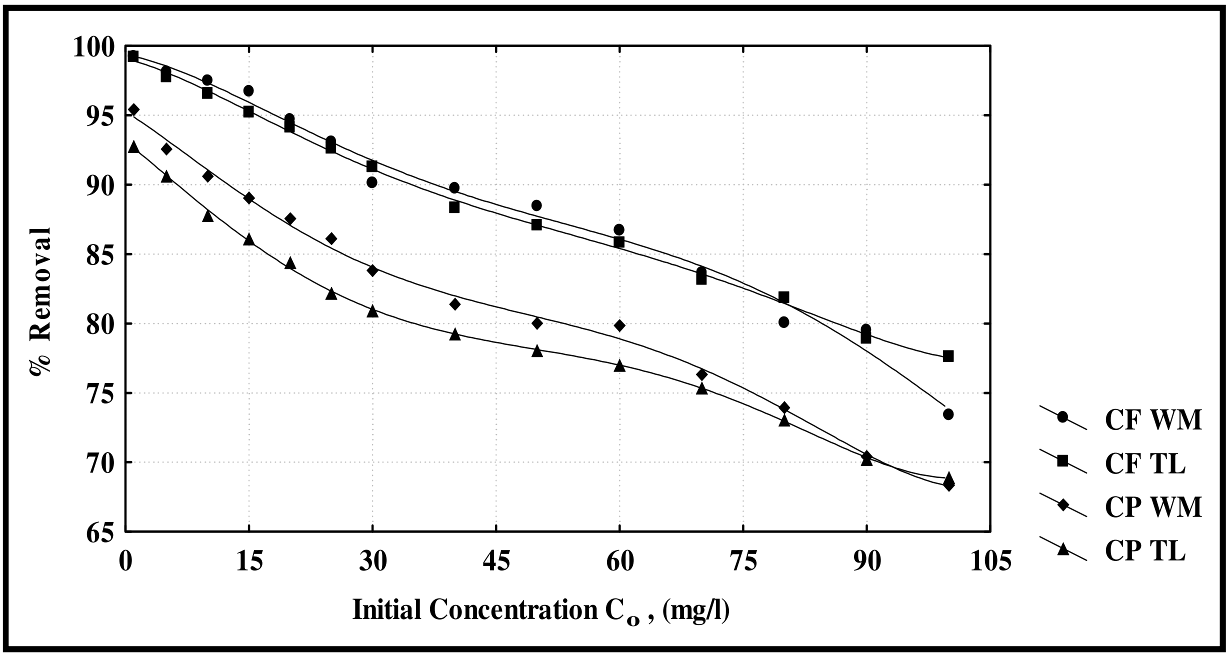


Figure 13 Influence of Initial Concentration on % Removal of Pesticides Using Residues
(CF WP: Carbofuran *removed by* Watermelon Peels)
(CF TL: Carbofuran *removed by* Used Tea Leave)
(Ch WP: Chlorpyrifos *removed by* Watermelon Peels)
(Ch TL: Chlorpyrifos *removed by* Used Tea Leave)

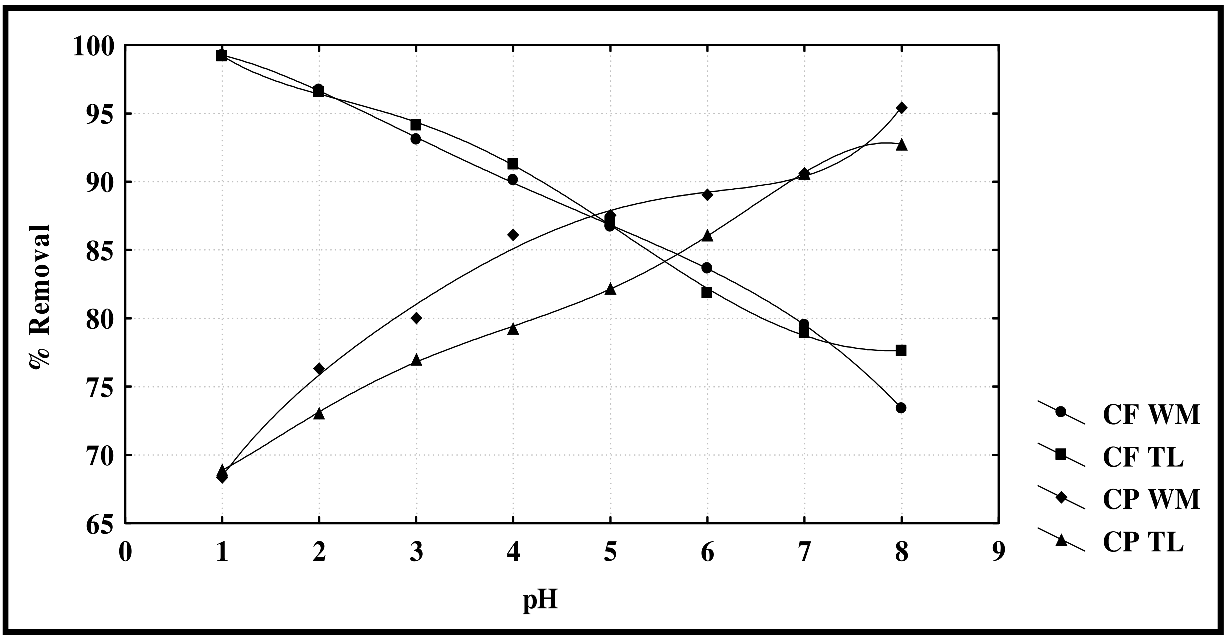


Figure 14 Influence of pH on % Removal of Pesticides Using Residues
(CF WP: Carbofuran *removed by* Watermelon Peels)
(CF TL: Carbofuran *removed by* Used Tea Leave)
(Ch WP: Chlorpyrifos *removed by* Watermelon Peels)
(Ch TL: Chlorpyrifos *removed by* Used Tea Leave)

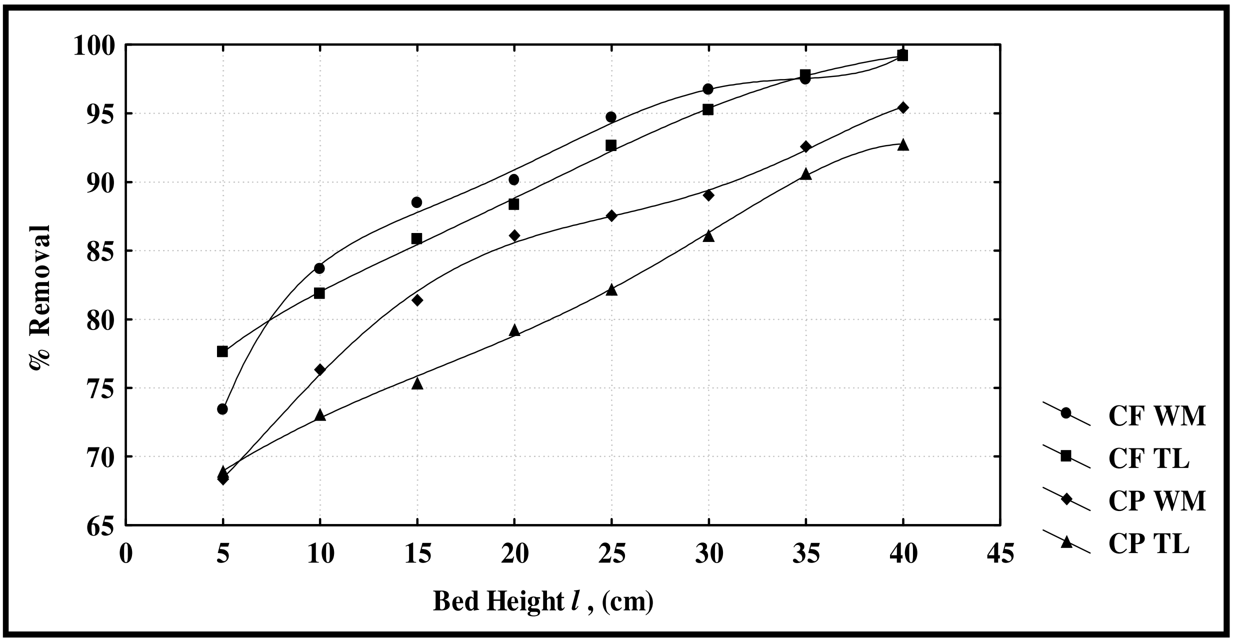


Figure 15 Influence of Fixed Bed Height on % Removal of Pesticides Using Residues
(CF WP: Carbofuran *removed by* Watermelon Peels)
(CF TL: Carbofuran *removed by* Used Tea Leave)
(Ch WP: Chlorpyrifos *removed by* Watermelon Peels)
(Ch TL: Chlorpyrifos *removed by* Used Tea Leave)

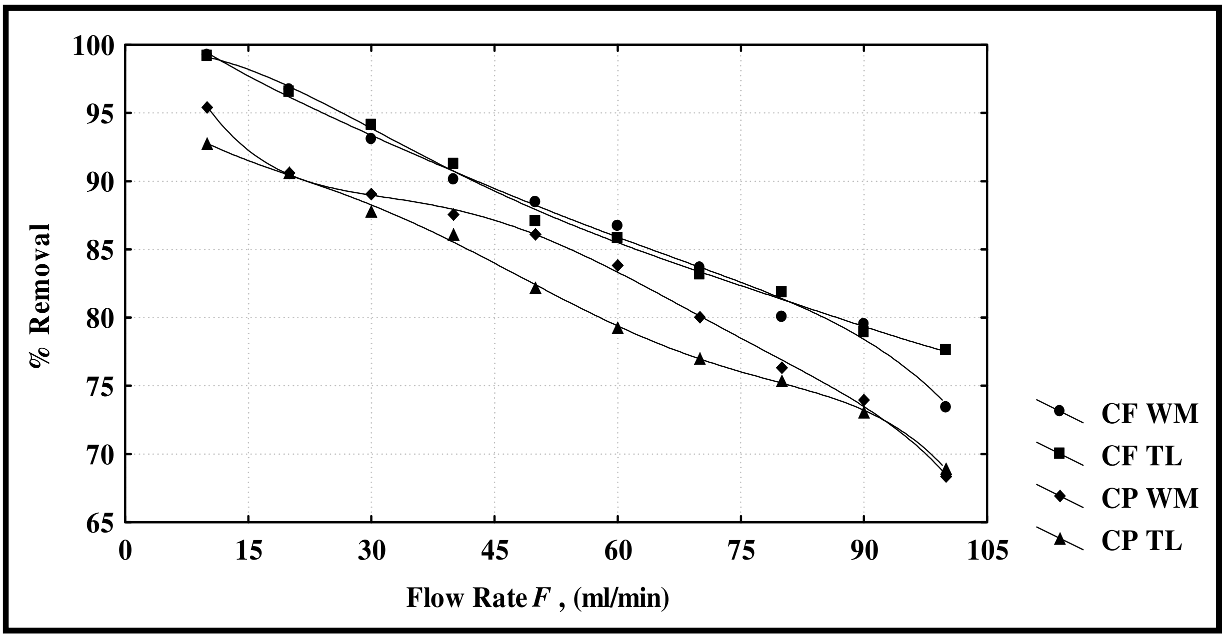


Figure 16 Influence of Flow Rate on % Removal of Pesticides Using Residues
(CF WP: Carbofuran *removed by* Watermelon Peels)
(CF TL: Carbofuran *removed by* Used Tea Leave)
(Ch WP: Chlorpyrifos *removed by* Watermelon Peels)
(Ch TL: Chlorpyrifos *removed by* Used Tea Leave)

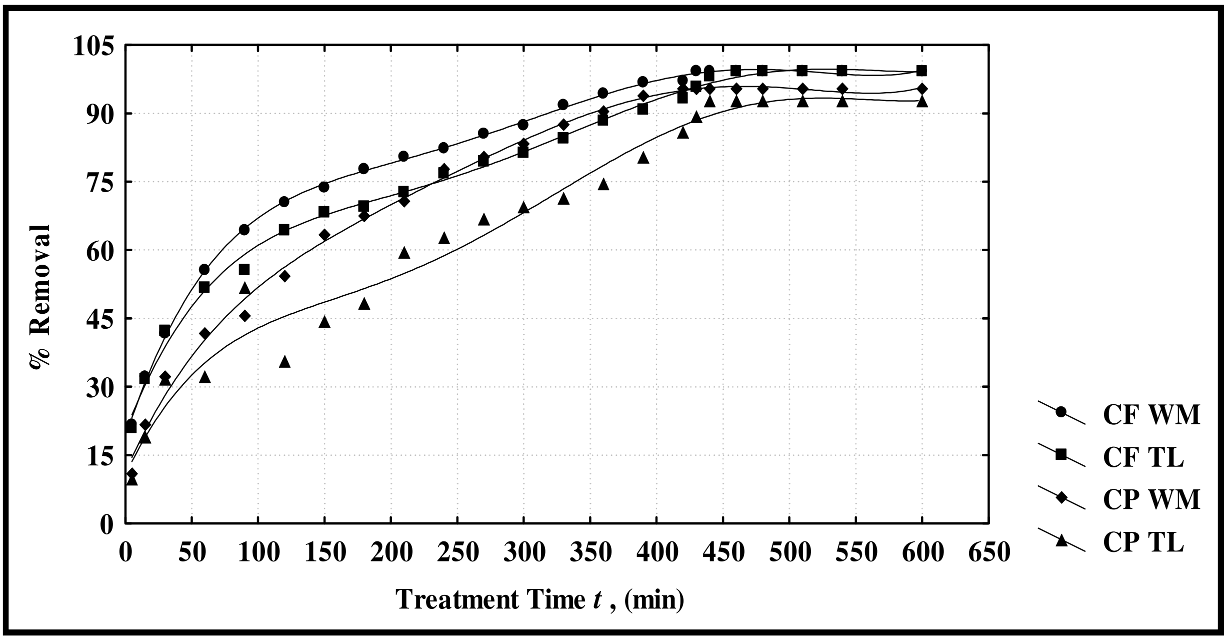


Figure 17 Influence of Treatment Time on % Removal of Pesticides Using Residues
(CF WP: Carbofuran *removed by* Watermelon Peels)
(CF TL: Carbofuran *removed by* Used Tea Leave)
(Ch WP: Chlorpyrifos *removed by* Watermelon Peels)
(Ch TL: Chlorpyrifos *removed by* Used Tea Leave)

3.3 Characterization of Adsorbent Materials:

3.3.1 Fourier transform infrared spectroscopy (FTIR):

Both fresh and loaded watermelon peels (WP) and used tea leaves (UTL) with carbofuran and Chlorpyrifos pesticides after adsorption process, in the powdered form, were analyses by Fourier transform infrared spectroscopy (FTIR). FTIR were used to investigate the changes in vibration frequency in the functional groups of the WP and UTL adsorbents due to carbofuran and Chlorpyrifos pesticides adsorbed from polluted water.

Each fresh and pesticides loaded adsorbents were mixed separately with KBr of spectroscopic grade and made in the form of pellets at a pressure of about 1 MPa. The pellets were about 10 mm in diameter and 1 mm thickness. Then the adsorbents were scanned and recorded in the spectral range between 4000 and 400cm^{-1}. The FTIR analysis of WP and UTL were shown in **Figure 18** and **Figure 19**. According to **Figure 18** and **Figure 19**, numerous chemical functional groups have been identified onto WP. From these Figures the IR spectrums (green line) represent WP alone without any treatment, while the IR spectrums (red line) represents WP adsorbed chlorpyrifos pesticide and the IR spectrum (black line) represents WP treated with carbofuran pesticide. **Table 2** and **Table 3** explain the shift in the %Tr of dominant peaks associated with the fresh adsorbents (WP and UTL) and loaded with pesticides (chlorpyrifos and carbofuran) in the FTIR graphs. These shifts in the %Tr showed that there was pesticides binding process occurring at the surface of the adsorbent. There was a clear shift from %Tr of hydroxyl groups which indicate surface O-H group is one of the functional group is one of the functional group responsible for adsorption of two types of pesticides. C-H group may also responsible for pesticides adsorption. C-X, P-O, P-H and P=O bonds were found to have major shift of %Tr, therefore these groups are also responsible for pesticides adsorption on the surface of adsorbents. The summation of difference in %Tr before and after adsorption is 445.5 and 227.1 cm^{-1} for adsorption of carbofuran and Chlorpyrifos by WP respectively. While the summation of difference in %Tr before and after adsorption is 231.5 and 119 cm^{-1} for adsorption of carbofuran and chlorpyrifos by UTL respectively. This confirm the results that WP had more adsorption capacity than UTL

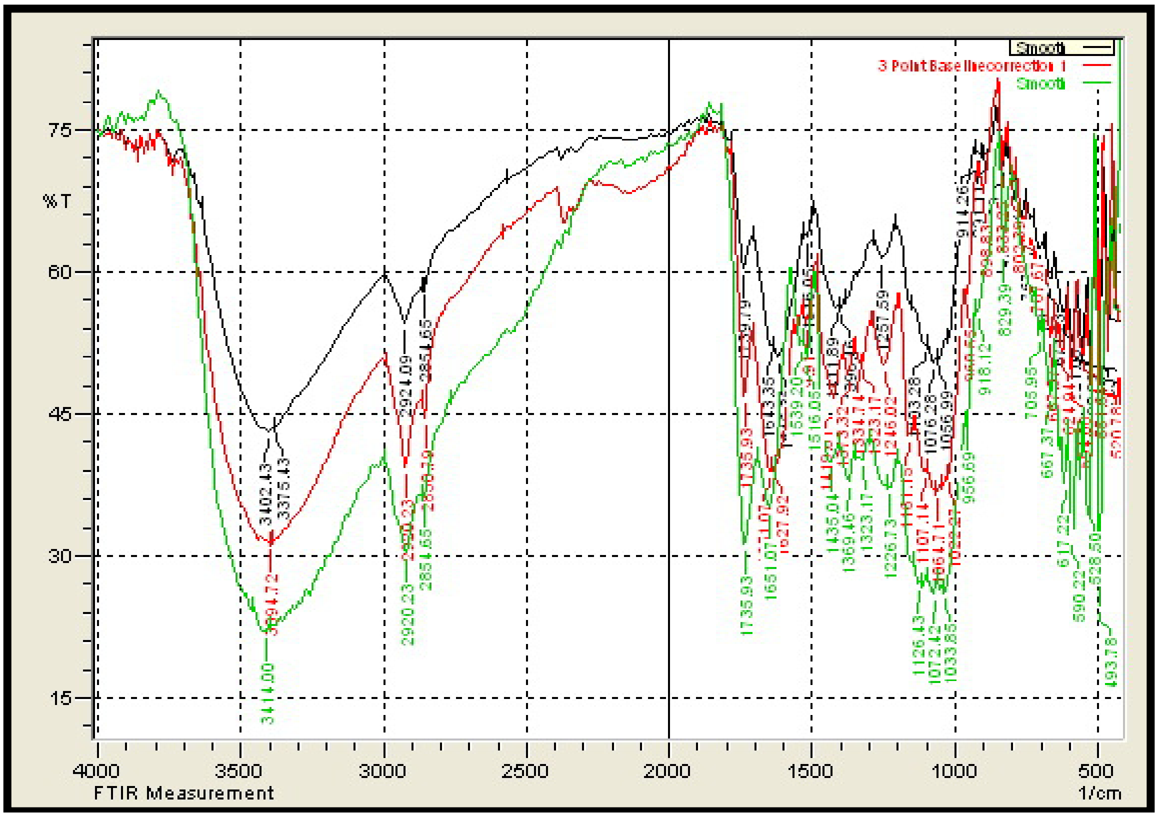


Figure 18 FTIR of Watermelon Peels

Table 2 Functional groups of WP responsible for pesticides adsorption

Wave number (cm^{-1})	Type of Bond	Functional Groups	Carbofuran			Chlorpyrifos		
			% Tr before adsorption	% Tr after adsorption	Δ	% Tr before adsorption	% Tr after adsorption	Δ
3414.00	Carboxylic acid, Amide, Amine	O-H, N-H, N-H$_2$	22	43	21	22	32	10
2920.23	Alkane	C-H	33	54	21	33	43.5	10.5
2854.65	Alkane	C-H	36	57.5	21.5	36	46.5	10.5
1735.93	Carboxylic acid	C=O	31.5	57	25.5	31.5	44.5	13
1651.07	Carboxylic acid	C=O	35.5	51	15.5	35.5	43.5	8
1539.20	Carboxylic acid	O-H	48	54	6	48	51	3
1516.05	Alkene	C=C	47.5	59	11.5	47.5	53	5.5
1435.04	Carboxylic acid	O-H	40.5	56.5	16	40.5	48	7.5
1369.46	Alkene	C-H	38.5	57	18.5	38.5	47.5	9
1323.17	Amine	C-N	40	62	22	40	51	11
1226.73	Carboxylic acid	C-O	37	64.5	27.5	37	50.5	13.5
1126.43	Carboxylic acid	C-O	27	54.5	27.5	27	40	13
1072.42	Phosphines alcohols	P-H C-O	26.5	53.5	27	26.5	42.5	16
1033.85	Phosphines alcohols	P-H C-O	26	55	29	26	41.5	15.5
956.69	Phosphines	P-H	45	69	24	45	57.5	12.5
918.12	Phosphines	P-H	54	77	23	54	65.5	11.5
829.39	Phosphines	P-H	63	81	18	63	72.1	9.1
705.95	alkyl halides	C-X	55.5	63	7.5	55.5	59	3.5
667.37	alkyl halides	C-X	45.5	60.5	15	45.5	55.5	10
617.22	alkyl halides	C-X	38	57	19	38	46.5	8.5
590.22	alkyl halides	C-X	36	60	24	36	48.5	12.5
528.50	alkyl halides	C-X	28.5	54	25.5	28.5	42	13.5
					445.5			227.1

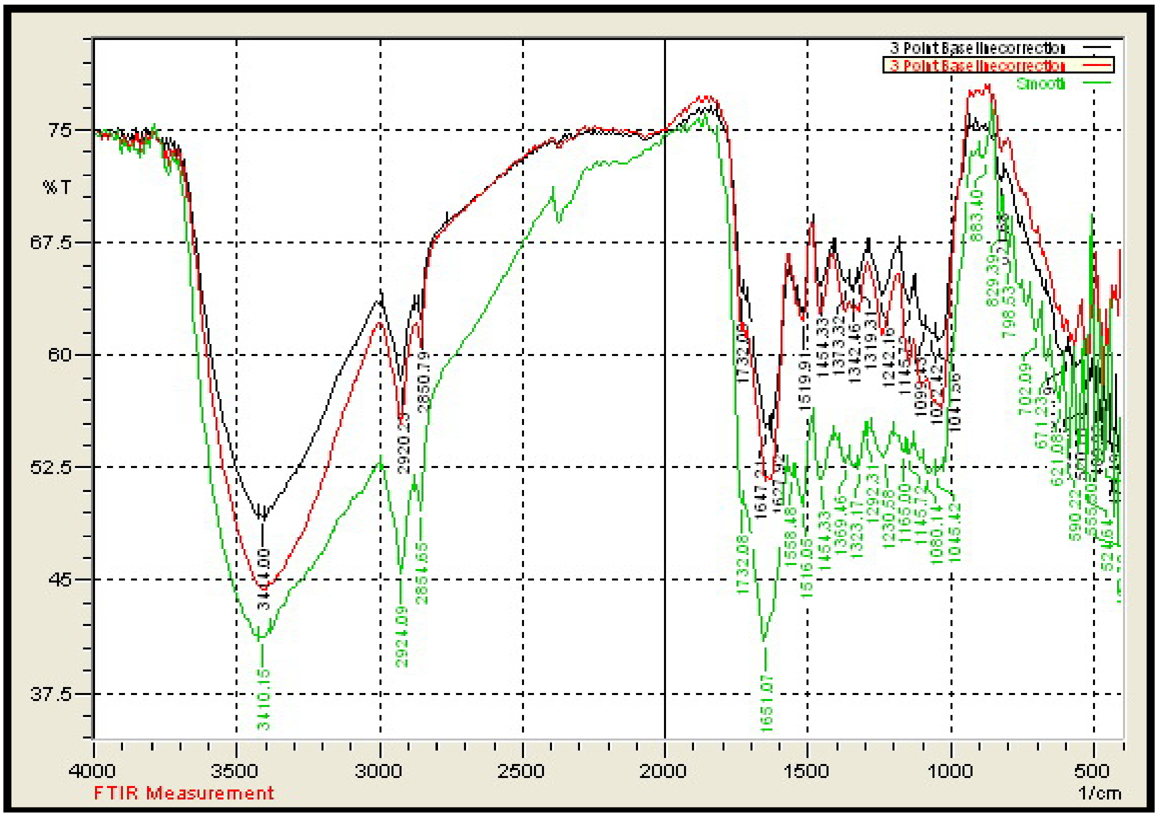


Figure 19 FTIR of Used Tea Leaves

Table 3 Functional groups of UTL responsible for pesticides adsorption

Wave number (cm^{-1})	Type of Bond	Functional Groups	Carbofuran			Chlorpyrifos		
			% Tr before adsorption	% Tr after adsorption	Δ	% Tr before adsorption	% Tr after adsorption	Δ
3410.15	Carboxylic acid, Amide, Amine	O-H, N-H, $N-H_2$	41	49.5	8.5	41	48	7
2924.09	Alkane	C-H	46	58.5	12.5	46	57.5	11.5
2854.65	Alkane	C-H	49.5	63	13.5	49.5	61.5	12
1732.08	Carboxylic acid	C=O	50	55	5	50	53.5	3.5
1665.07	Carboxylic acid	C=O	41.5	55.5	14	41.5	55	13.5
1558.48	Amide, Amine	N-H	52	67.5	15.5	52	67	15
1516.05	Alkene	C=C	50	67	17	50	65	15
1454.33	Carboxylic acid	O-H	51.5	66	14.5	51.5	63	11.5
1369.46	Alkene	C-H	52.5	67.5	15	52.5	65	12.5
1323.17	Amine	C-N	52	66.5	14.5	52	63.5	11.5
1292.31	Alcohol, Anhydride, Ketone	C-O C-C	55	65.5	10.5	55	63	8
1230.58	Carboxylic acid	C-O	53	67.5	14.5	53	66	13
1165.00	phosphine oxides	P=O	53.5	65	11.5	53.5	62	8.5
1145.72	phosphine oxides	P=O	54	66.5	12.5	54		-54
1080.14	Phosphines, alcohols	P-H C-O	52	61	9	52	56	4
1045.42	Phosphines, alcohols	P-H C-O	52.5	61.5	9	52.5	55	2.5
883.40	Phosphines	P-H	73	75	2	73	78	5
829.39	Phosphines	P-H	69	72	3	69	70	1
798.53	Phosphines	P-H	67	69	2	67	68.5	1.5
617.23	alkyl halides	C-X	60	65	5	60	63	3
621.08	alkyl halides	C-X	55	60	5	55	58.5	3.5
590.22	alkyl halides	C-X	52.5	57.5	5	52.5	55.5	3
555.50	alkyl halides	C-X	54	58.5	4.5	54	55	1
524.64	alkyl halides	C-X	55.5	63.5	8	55.5	61.5	6
					231.5			119

3.3.2 Scanning Electron Microscopy (SEM):

Scanning Electron Microscopy (SEM) micrographs of PW and UTL surface adsorbents are represented by **Figures (20 to 25)** before and after treated with (carbofuran and chlorpyrifos) pesticides. These Figures show that the two types of adsorbents present all of the cavities to the level of their surfaces. Indeed, the two kinds of pesticides (carbofuran and chlorpyrifos) permit the development of the porosity of both adsorbent materials which were (WP and UTL) more than there is in the precursor (WP and UTL), so producing adsorbents of more open pores. The both types of adsorbents (WP and UTL) have compact structure and homogeneous surface with a developed porosity, because in this material some micropores are observed. This may be explain the reason of three results which are firstly the graduated of increasing in the removal efficiency from low to high because these pesticides change the morphology of the adsorbents and opened another block pores which permit to another molecules of pesticides to enter i.e. more removal, secondly the best results obtained always for carbofuran than chlorpyrifos and third why is WP better than UTL constantly.

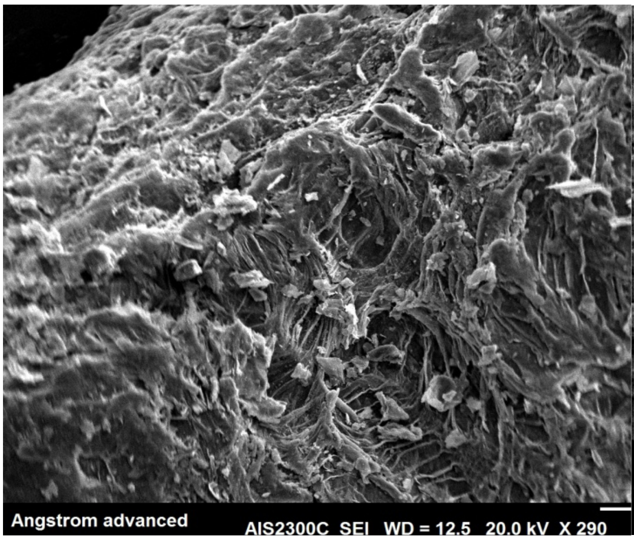


Figure 20 SEM of WP alone

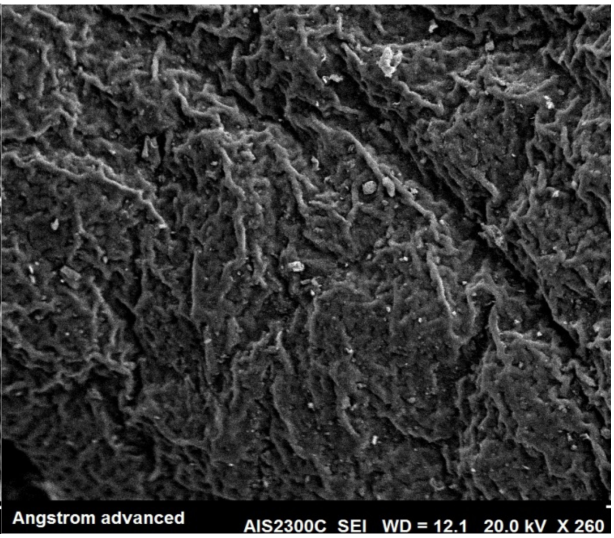


Figure 21 SEM of UTL alone

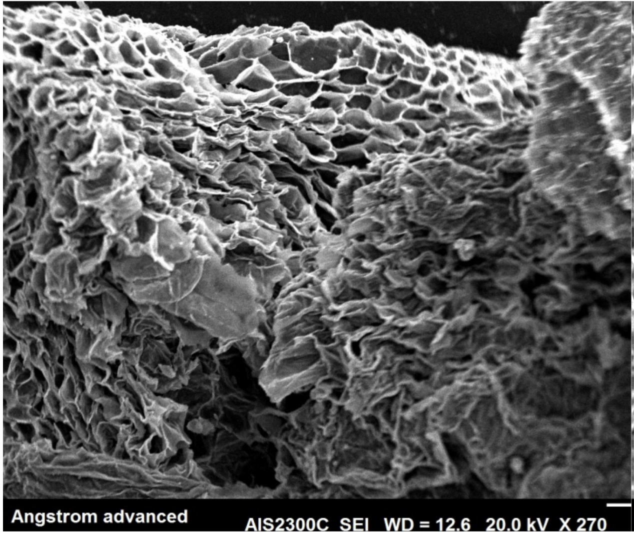


Figure 22 SEM of WP treated with Carbofuran

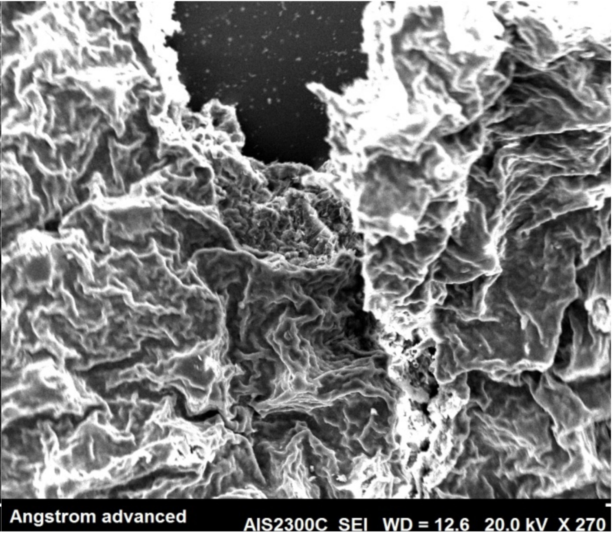


Figure 23 SEM of UTL treated with Carbofuran

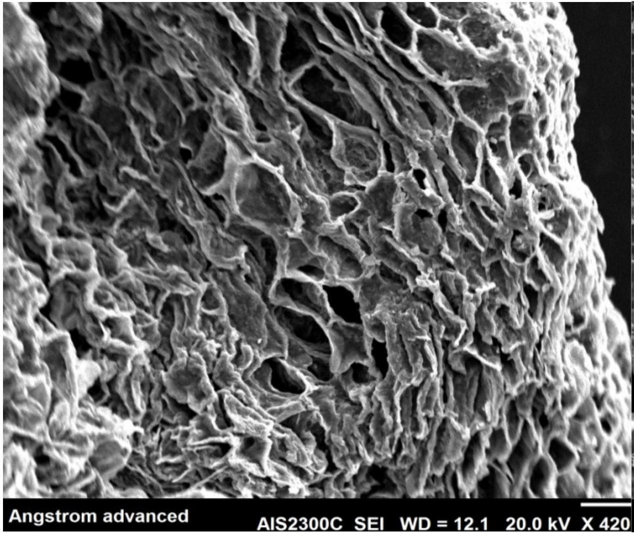


Figure 24 SEM of WP treated with Chlorpyrifos

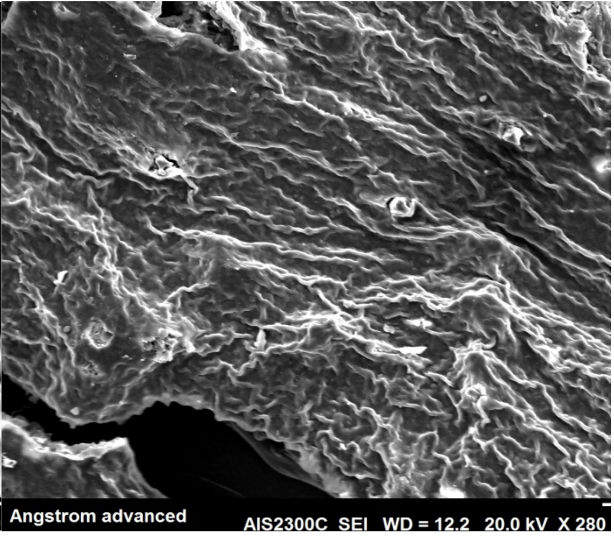


Figure 25 SEM of UTL treated with Chlorpyrifos

3.3.3 Specific Surface Area:

The specific surfaces area of two types of adsorbents which were (WP and UTL) was determined through N_2 adsorption isotherm and the results are shown in **Table 4**. The low value of specific surface area for both WP and UTL show that the entry of N_2 gas molecules to the existing pores in the WP and UTL are restricted and the pores are closed. In addition, these results make it possible to explain the influence of the residence time of the adsorption of the two types of pesticides (carbofuran and chlorpyrifos). Longer treatment time is required to adsorb the pesticides by these adsorbents. This tine of treatment is also needed to open the closed pores inside the surface of these materials (as explained in section 3.3.2 above), therefore the removal efficiency was increased with increasing the treatment time due to the increasing that occurs in specific surface area and more pores are opened. The adsorption of pesticides (i.e. impregnation) effect on porous volume also like affects the specific surface area and porosity. The higher impregnation with pesticides means slightly increases in specific surface area and porous volume for adsorbent materials after treatment with pesticides in compare with fresh adsorbent material.

Table 4 Specific Surface Area of Adsorbents Materials

Adsorbent material	Specific Surface Area (m^2/g)		
	Fresh	After treated with carbofuran	After treated with chlorpyrifos
Watermelon Peels (WP)	0.9771	11.3595	7.8863
Used Tea Leaves (UTL)	0.0919	5.4583	3.1564

3.4 Adsorption Isotherm Models:

The adsorption isotherms for two types of pesticides using two kinds of adsorbents are shown in **Figures (26** to **4.33)** using Langmuir and Fruendlich models. The parameters for each model were calculated from the experimental data and presented in **Table 5** The value of R^2 was higher for Langmuir isotherm than the other isotherm models; that mean Langmuir equation represented the adsorption process very well.

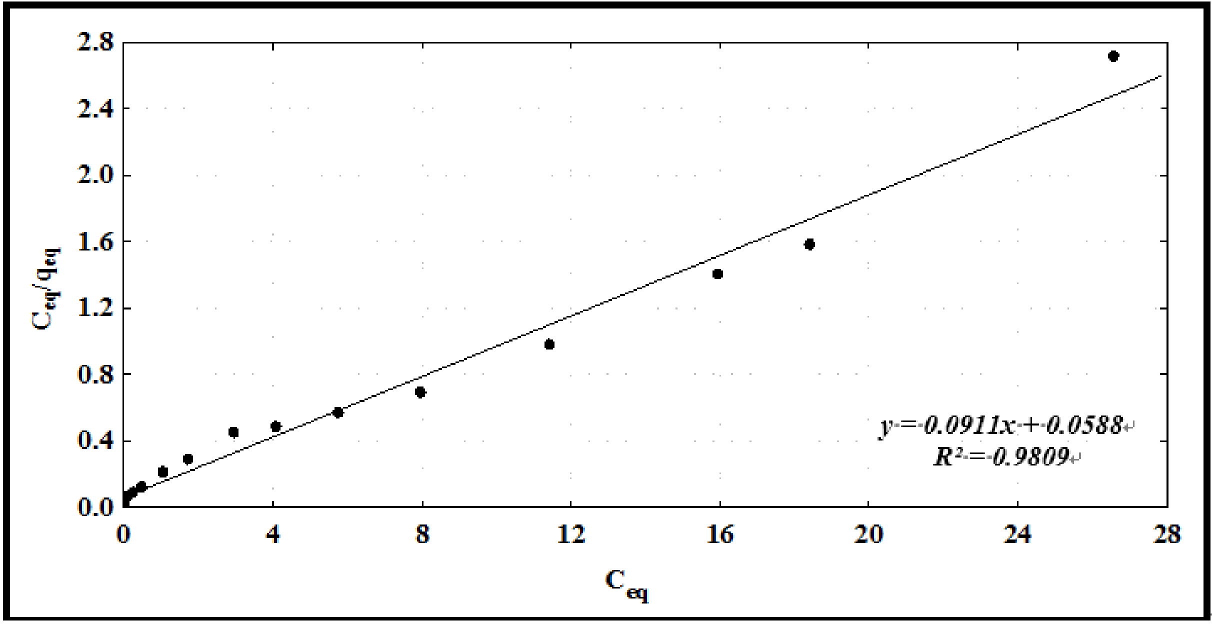


Figure 26 Langmuir isotherm plot for Carbofuran removal from Water using Watermelon peels. Conditions: pH: 1.0; Initial concentration (1mg/l); weight (13.5 g) and flow rate (10 ml/min)

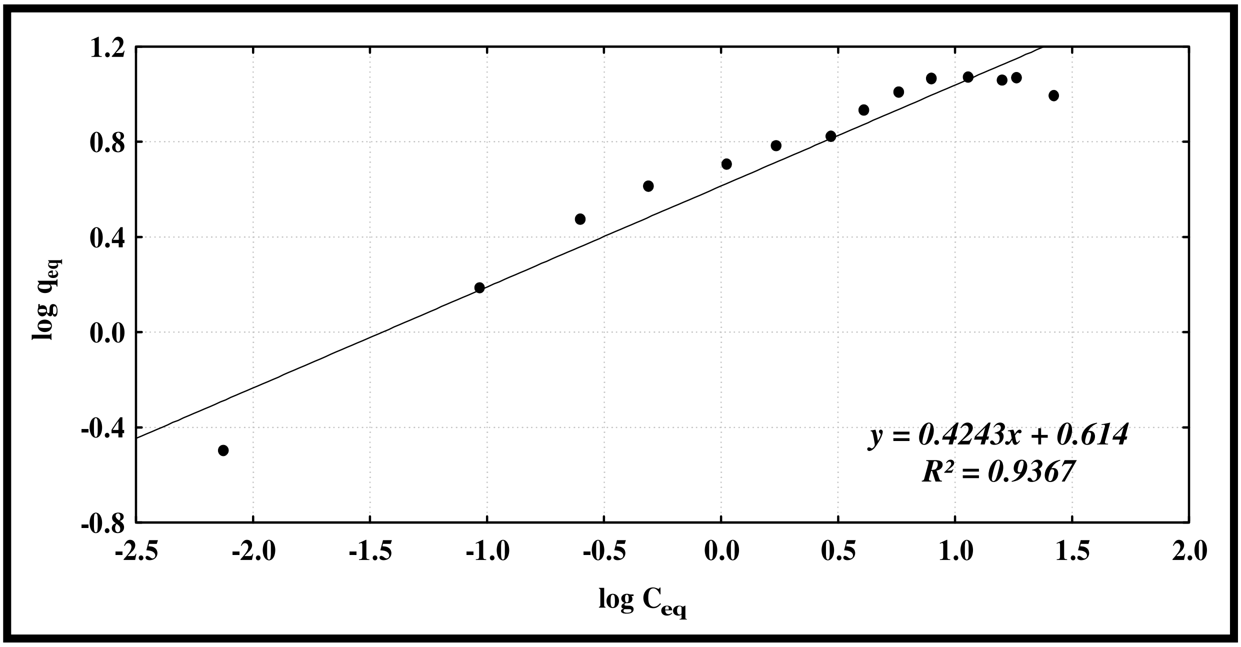


Figure 27 Freundlich isotherm plot for Carbofuran removal from Water using Watermelon peels. Conditions: pH: 1.0; Initial concentration (1 mg/l); weight (13.5 g); flow rate (10 ml/min).

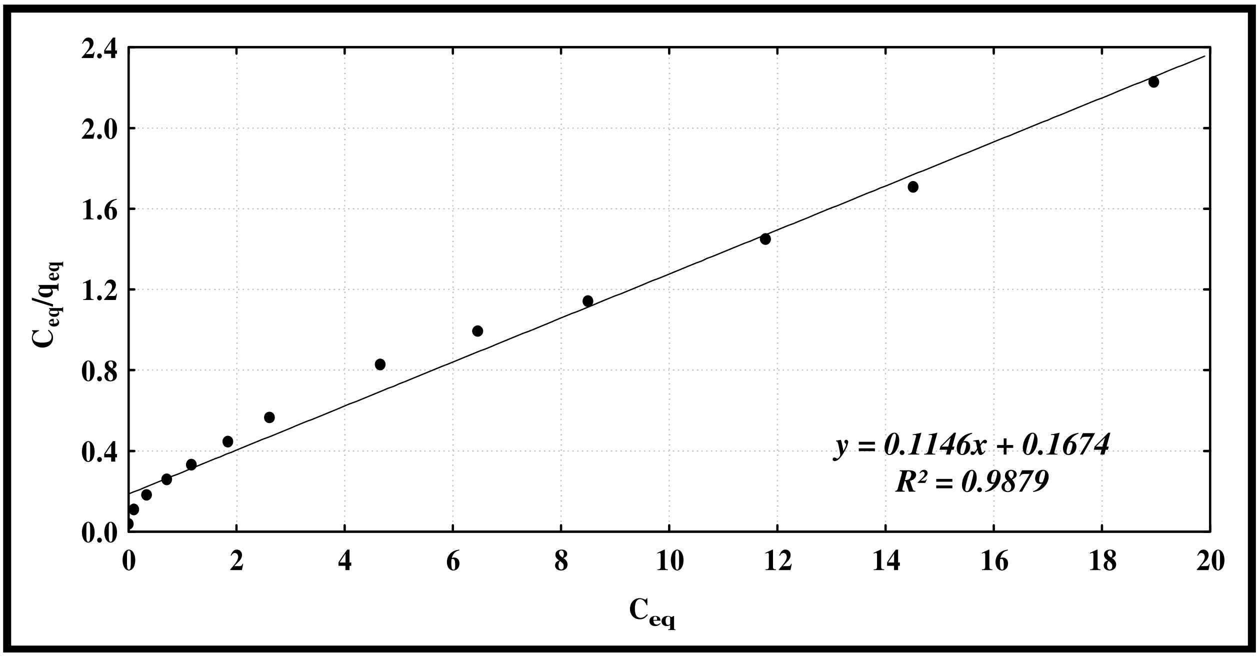


Figure 28 Langmuir isotherm plot for Carbofuran removal from Water using Tea Leaves. Conditions: pH: 1; Initial concentration (1 mg/l); weight (20 g) and flow rate (10 ml/min)

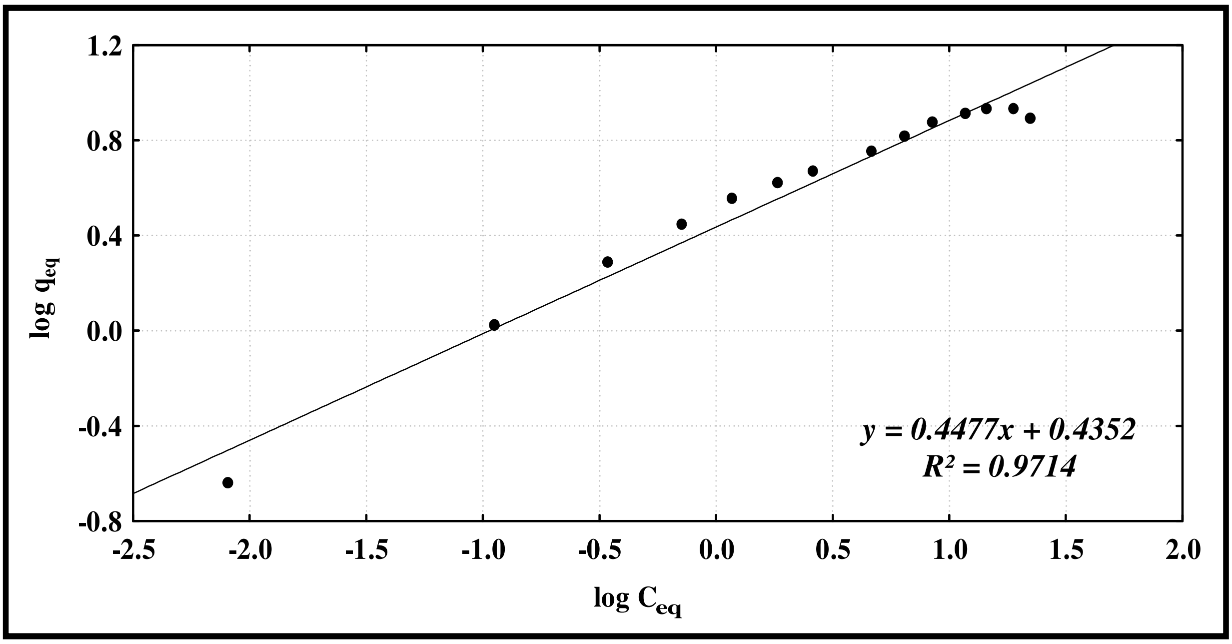


Figure 29 Freundlich isotherm plot for Carbofuran removal from Water using Tea Leaves. Conditions: pH: 1; Initial concentration (1 mg/l); weight (20 g); flow rate (10 ml/min).

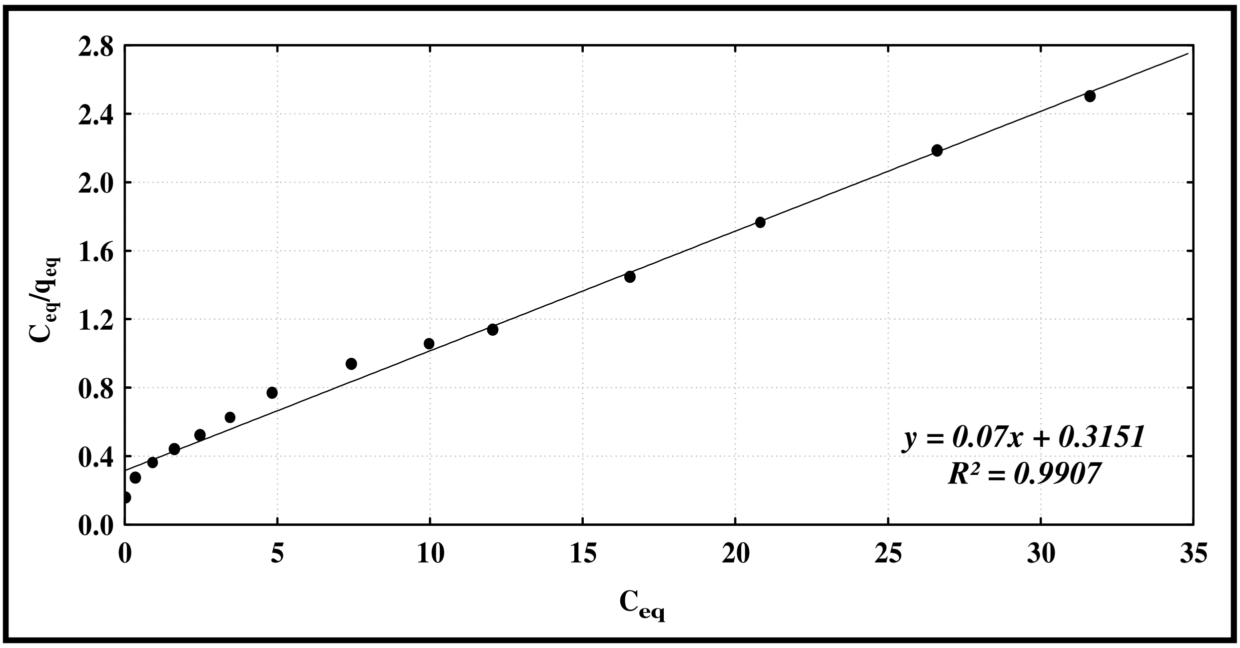


Figure 30 Langmuir isotherm plot for Chloropyrifos removal from Water using Watermelon peels. Conditions: pH: 8; Initial concentration (1 mg/l); weight (13.5 g) and flow rate (10 ml/min)

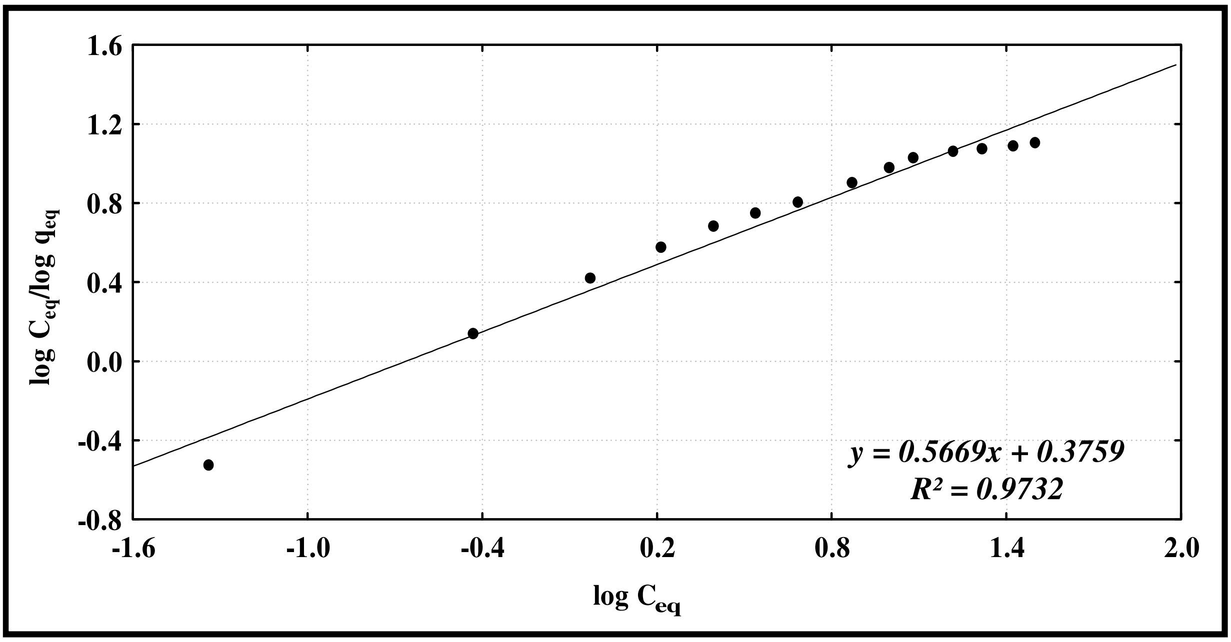


Figure 31 Freundlich isotherm plot for Chloropyrifos removal from Water using Watermelon peels. Conditions: pH: 8; Initial concentration (1 mg/l); weight (13.5 g); flow rate (10 ml/min).

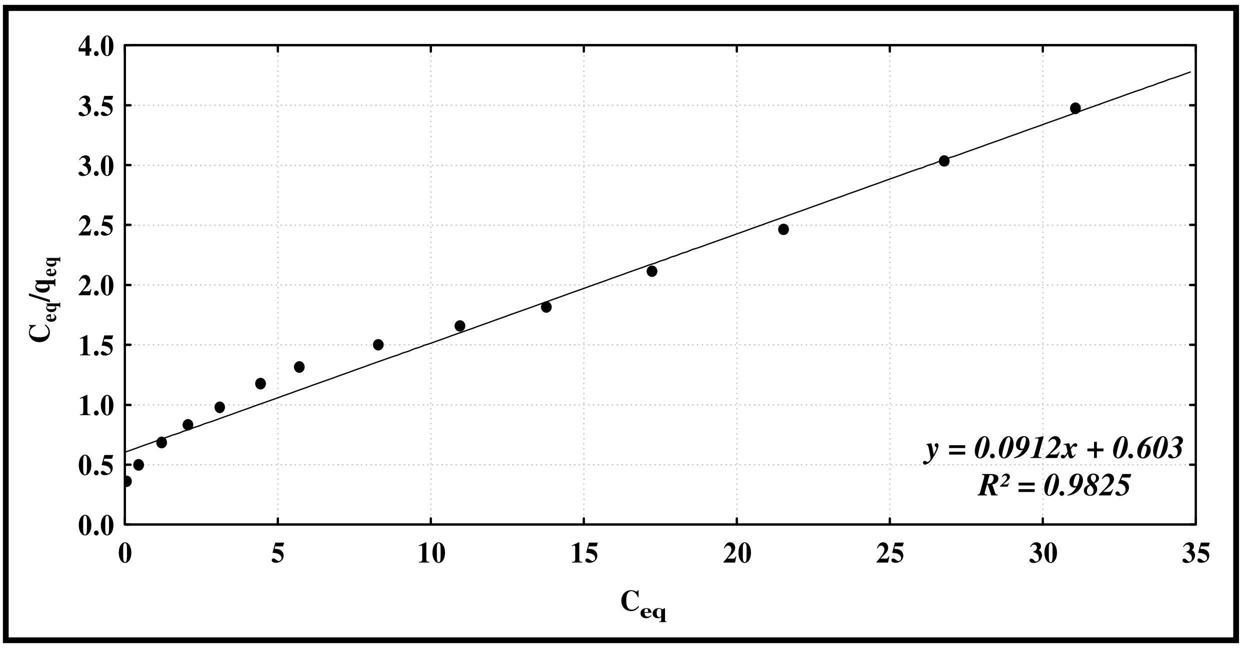


Figure 32 Langmuir isotherm plot for Chloropyrifos removal from Water using Tea Leaves. Conditions: pH: 8; Initial concentration (1 mg/l); weight (20 g) and flow rate (10 ml/min)

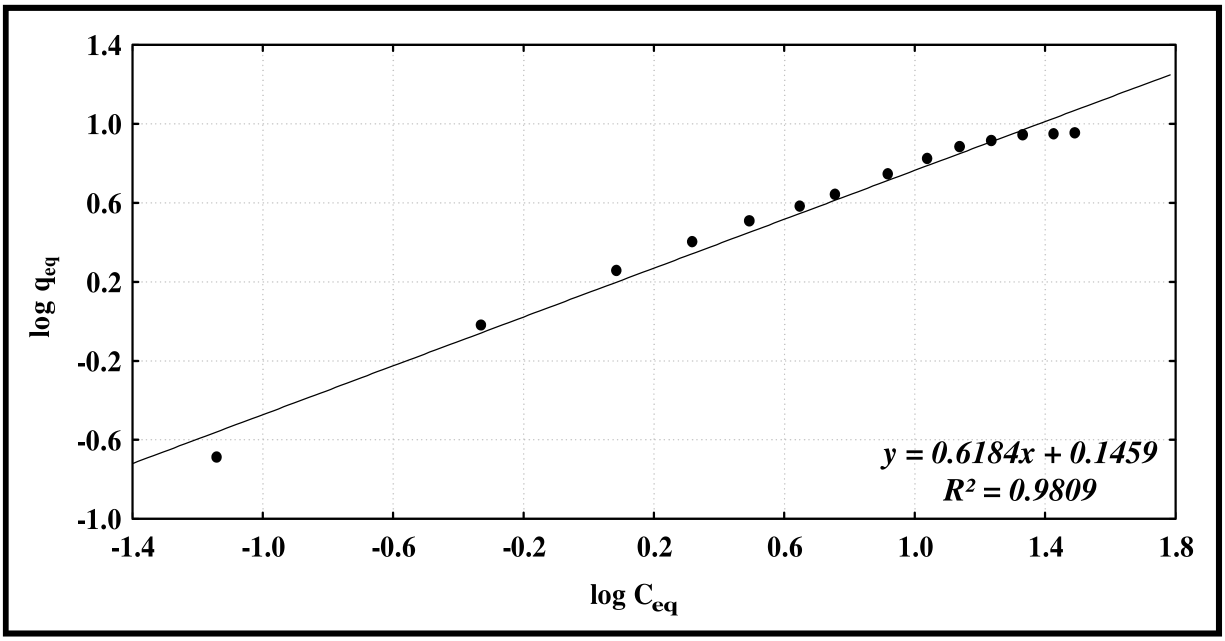


Figure 33 Freundlich isotherm plot for Chloropyrifos removal from Water using Tea Leaves. Conditions: pH: 8; Initial concentration (1 mg/l); weight (20 g); flow rate (10 ml/min).

Table 5 Adsorption Isotherm Models Constants

Pesticide	Adsorbent	Langmuir Isotherm $\frac{C_e}{q_e}=\frac{1}{K_L.Q^\circ}+\frac{1}{Q^\circ}C_e$				Freundlich Isotherm $\log q_e = \log K_F + \frac{1}{n}\log C_e$		
		K_L (mg/g)	Q° (l/mg)	R_L	R^2	K_F (l/g)	n	R^2
Carbofuran (CF)	Watermelon Peels (WP)	1.549	10.976	0.3932	0.9809	4.111	2.356	0.9367
	Used Tea Leaves (UTL)	6.658	8.726	0.1306	0.9879	2.724	2.234	0.9714
Chlorpyrifos (Ch)	Watermelon Peels (WP)	0.222	14.286	0.8183	0.9907	2.376	1.764	0.9732
	Used Tea Leaves (UTL)	0.151	10.965	0.8688	0.9825	1.399	1.617	0.9809

3.5 Adsorption Kinetic Models:

In order to determine the adsorption kinetic models of carbofuran and chlorpyrifos pesticides from polluted water, the pseudo first order, the pseudo second order, and the intraparticle diffusion kinetic models were applied to the obtained data from experimental work. The calculations were conducted at optimum operation condition to find the best kinetic model. The adsorption kinetic constant and correlation coefficients of these models were calculated and given in **Figures** (**34** to **36**) and **Table 6**. Good correlation coefficients R^2 were observed indicating that carbofuran and chlorpyrifos pesticides uptake processes can be approximated with the pseudo first order kinetic model and intraparticle diffusion model respectively which have the best correlation coefficient among other adsorption kinetic models. Thus, the pseudo first order kinetics and intraparticle diffusion model were the pathways to reach equilibrium.

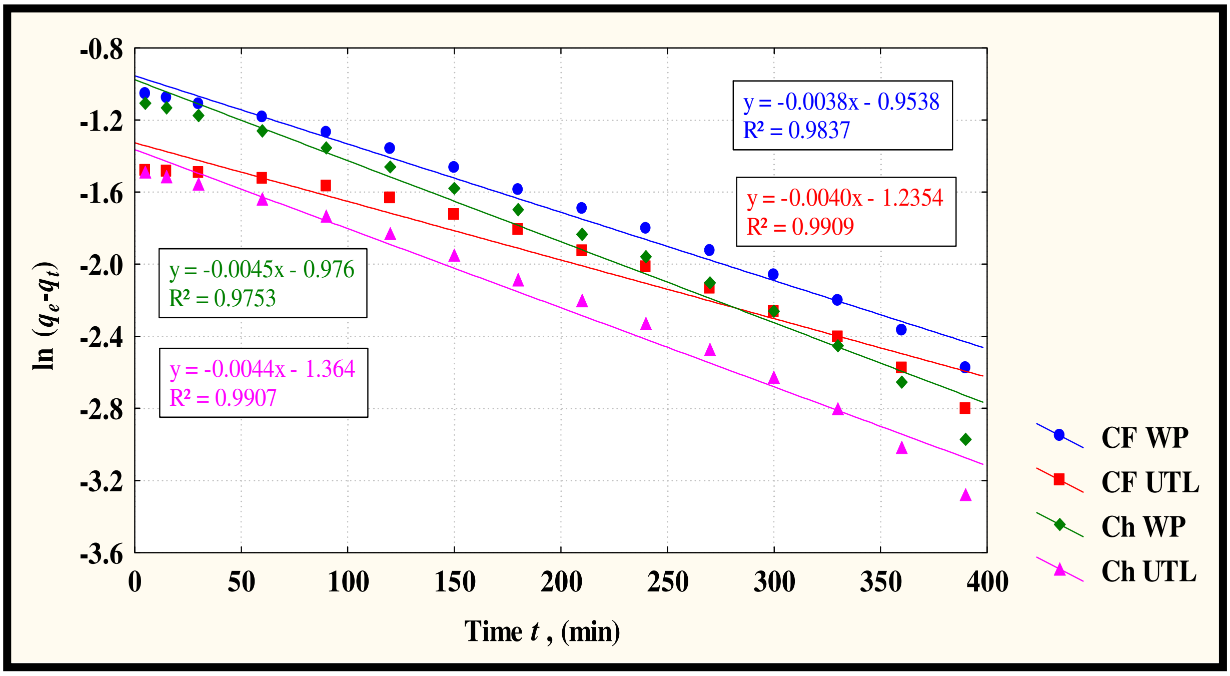


Figure 34 Pseudo First Order Kinetic Model for Adsorption of Pesticides Using Residues
(CF WP: Carbofuran *removed by* Watermelon Peels)
(CF UTL: Carbofuran *removed by* Used Tea Leave)
(Ch WP: Chlorpyrifos *removed by* Watermelon Peels)
(Ch UTL: Chlorpyrifos *removed by* Used Tea Leave)

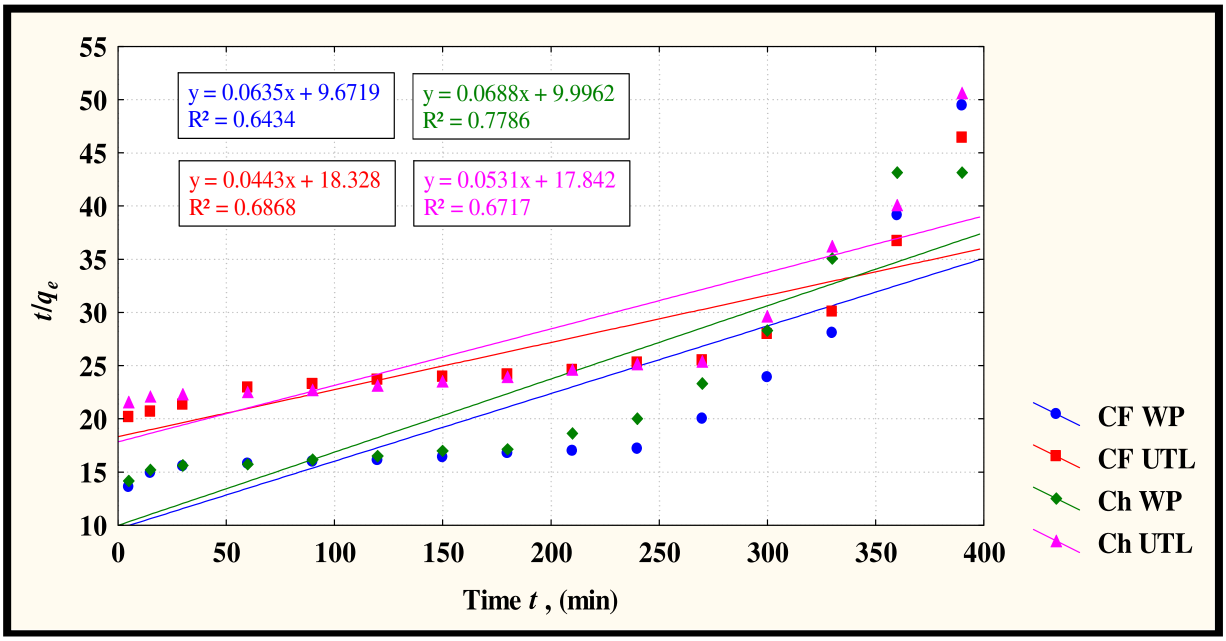


Figure 35 Pseudo Second Order Kinetic Model for Adsorption of Pesticides Using Residues
(CF WP: Carbofuran *removed by* Watermelon Peels)
(CF UTL: Carbofuran *removed by* Used Tea Leave)
(Ch WP: Chlorpyrifos *removed by* Watermelon Peels)
(Ch UTL: Chlorpyrifos *removed by* Used Tea Leave)

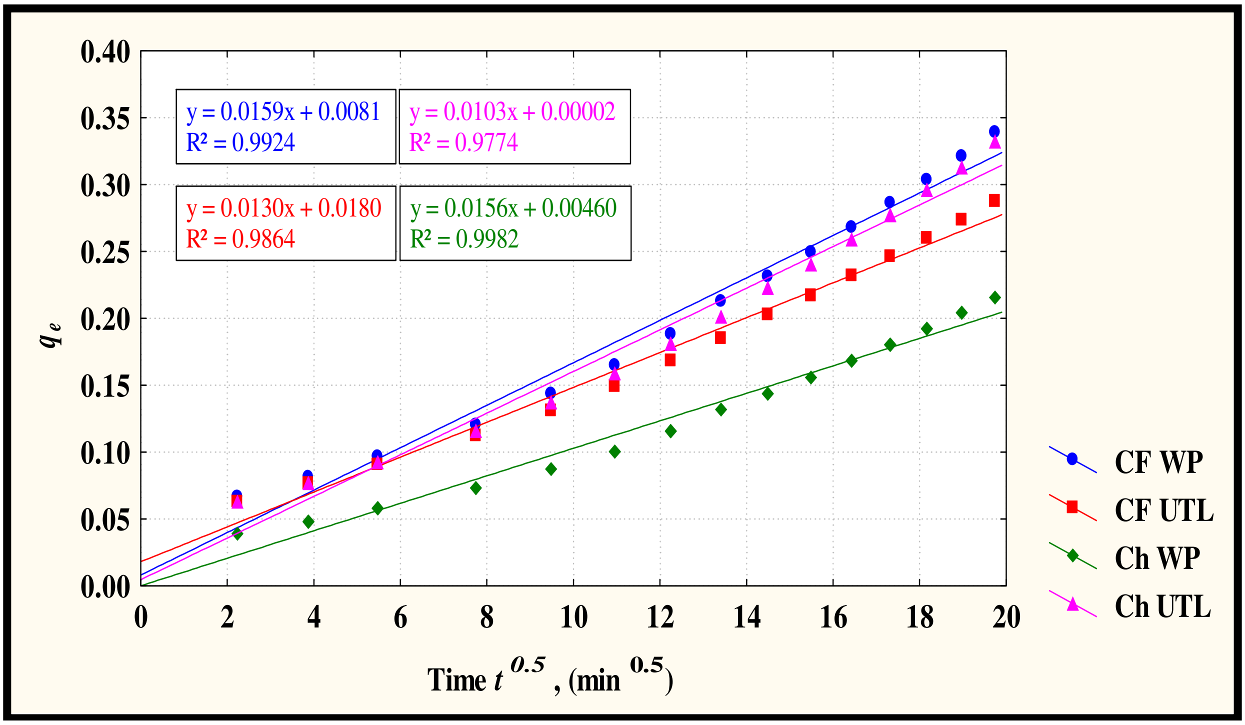


Figure 36 Intra-particle Diffusion Kinetic Model for Adsorption of Pesticides Using Residues
(CF WP: Carbofuran *removed by* Watermelon Peels)
(CF UTL: Carbofuran *removed by* Used Tea Leave)
(Ch WP: Chlorpyrifos *removed by* Watermelon Peels)
(Ch UTL: Chlorpyrifos *removed by* Used Tea Leave)

Table 6 Adsorption Kinetic Models Constants

Pesticide	**Adsorbent**	q_e (mg/l) Exp.	**Pseudo First Order Kinetic Model**			**Pseudo Second Order Kinetic Model**			**Intra-particle Diffusion Kinetic Model**		
			q_e (mg/g)	k_1 (l/min)	R^2	q_e (mg/g)	k_2 $(g/mg.min)$	R^2	k_i $(mg/g.min)^{0.5}$	I	R^2
CF	**WP**	0.3661	0.3853	0.0038	0.9837	15.748	4×10^{-4}	0.6434	0.0159	0.0081	0.9924
	UTL	0.2781	0.2907	0.0040	0.9909	22.573	1×10^{-4}	0.6868	0.0130	0.0180	0.9864
Ch	**WP**	0.3968	0.3768	0.0045	0.9753	14.535	4×10^{-4}	0.7786	0.0156	0.0046	0.9982
	UTL	0.2541	0.2556	0.0044	0.9907	18.832	1×10^{-4}	0.6717	0.0103	2×10^{-5}	0.9774

4. PROFITING FROM RESIDUES

After the adsorption removal process of carbofuran and chlorpyrifos was ended, considerable amount of polluted watermelon peels (WP) and used tea leaves (UTL) which were used as a low cost adsorbent material are wasted. Therefore, to eschew any harmful effect for these residues on organisms or soil or water it must to be disposing or decreased their amounts to minimum in a safe, economic, beneficial and eco-friendly method. The suggested method that may be used to dispose these toxic residues is to convert them to useful substance like rodenticide. The later method was investigated as a safe, economic, beneficial and eco-friendly non-conventional method to get rid of the WP and UTL loaded with carbofuran and chlorpyrifos pesticides.

5.5 Preparation of Rodenticide from Pesticides Adsorption Process Residue

The waste residue remaining after removal of carbofuran and chlorpyrifos pesticides from polluted washing water by adsorption process using WP and UTL were collected, a prelude to prepare a simple rodenticide. Twenty groups (ten for male and ten for female) of an outbred multipurpose breed of albino rat which was Sprague dawley rat (*Rattus rattus*) shown in **Figure 37** were used in this test; each group has ten rats besides another animal control group to compare the results. Before the test is beginning, the rats were left for one week in clean and convenient cages shown in **Figure 38** and nurtured with normal feed to make sure that it's were not suffer from anything leading to death. The residues which containing carbofuran and chlorpyrifos pesticides were sorted according to its containing of carbofuran and chlorpyrifos pesticides and mixed with little amount of waste fruit to give sweet test and feed to the rats directly as rodenticide without any further treatment. The results were fate the rats in different periods and the lethal dose for both types of pesticides was also calculated as shown in **Figures 39, 40, 41** and **42** and **Table 7.**

Figure 37 Sprague dawley rat (*Rattus rattus*)

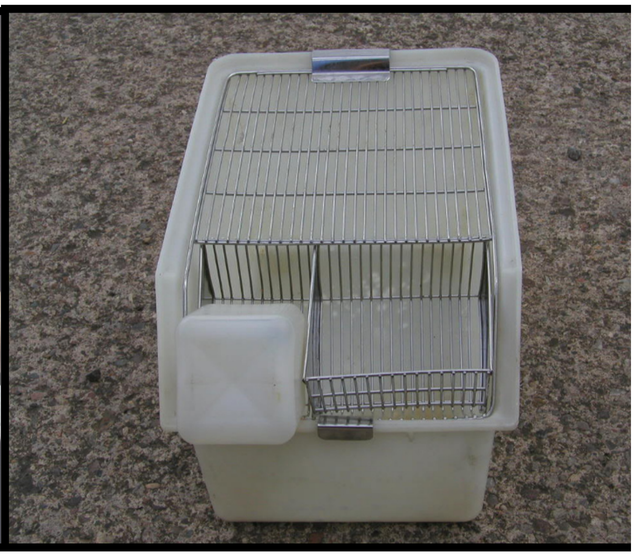


Figure 38 Rat Cage

Table 5.3 LD_{50} (mg of Pesticide/kg of body rat) of carbofuran and chlorpyrifos pesticides calculated in this Study

Pesticide Type	**LD_{50} Calculated for male (mg/kg)**	**LD_{50} Calculated for female (mg/kg)**	**Standard LD_{50} (mg/kg)**
Carbofuran	9	8	3 to 19
Chlorpyrifos	155	82	32 to 1000

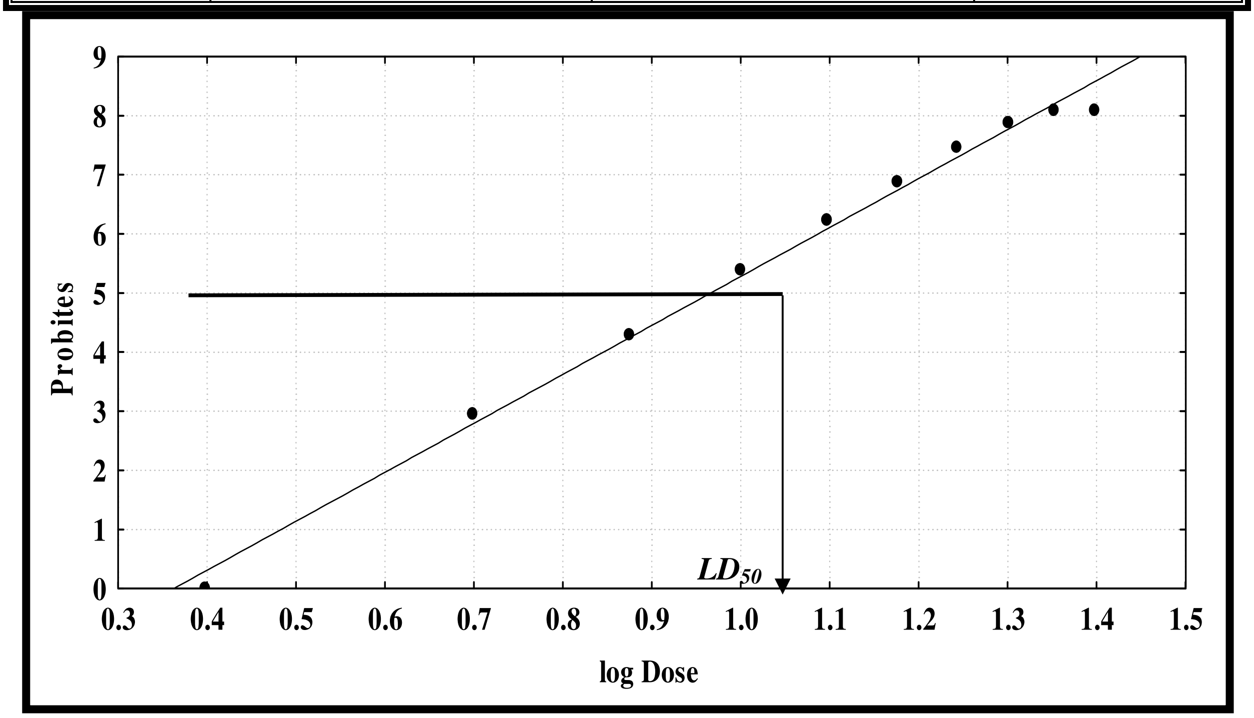


Figure 39 Lethal Dose LD_{50} for Carbofuran Test on **MAIL** Rat

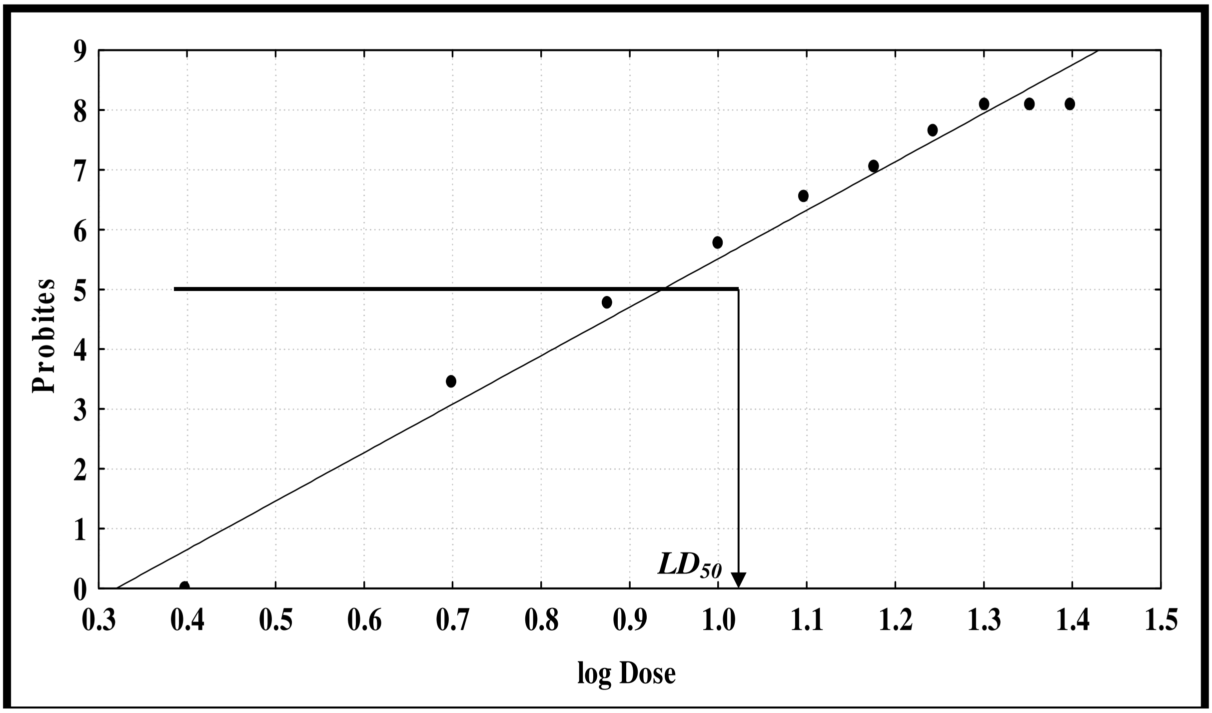


Figure 40 Lethal Dose LD_{50} for Carbofuran Test on **FEMAIL** Rat

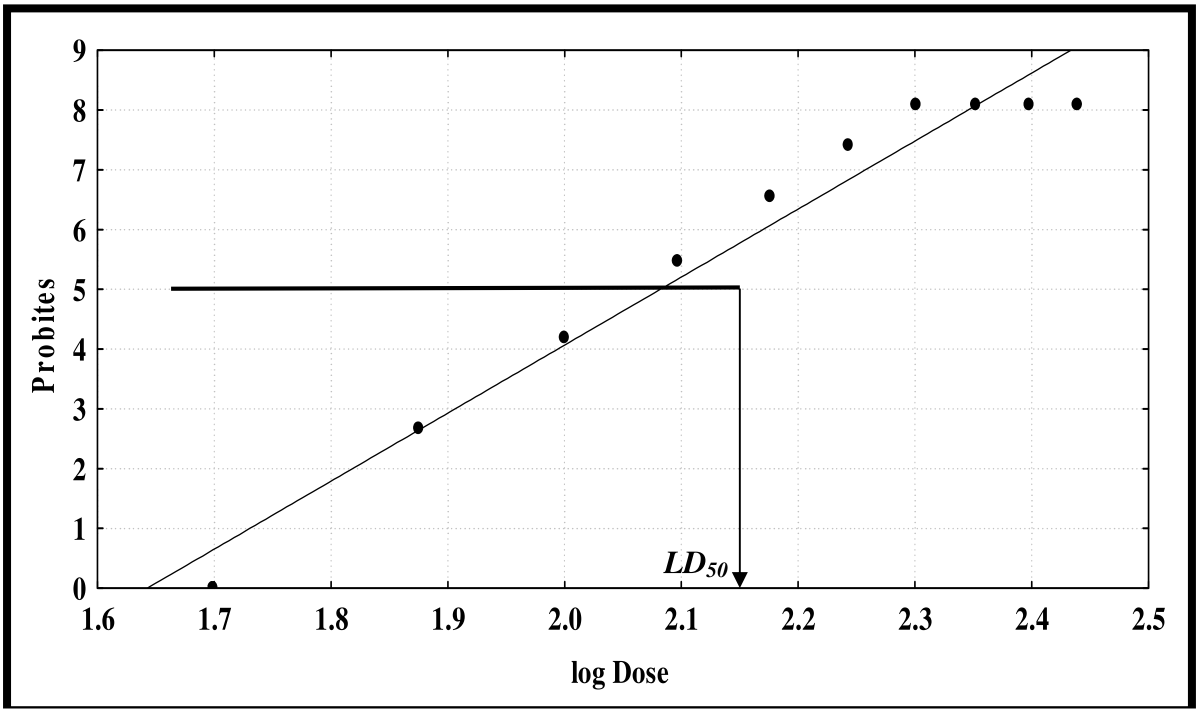


Figure 41 Lethal Dose LD_{50} for Chlorpyrifos Test on **MAIL** Rat

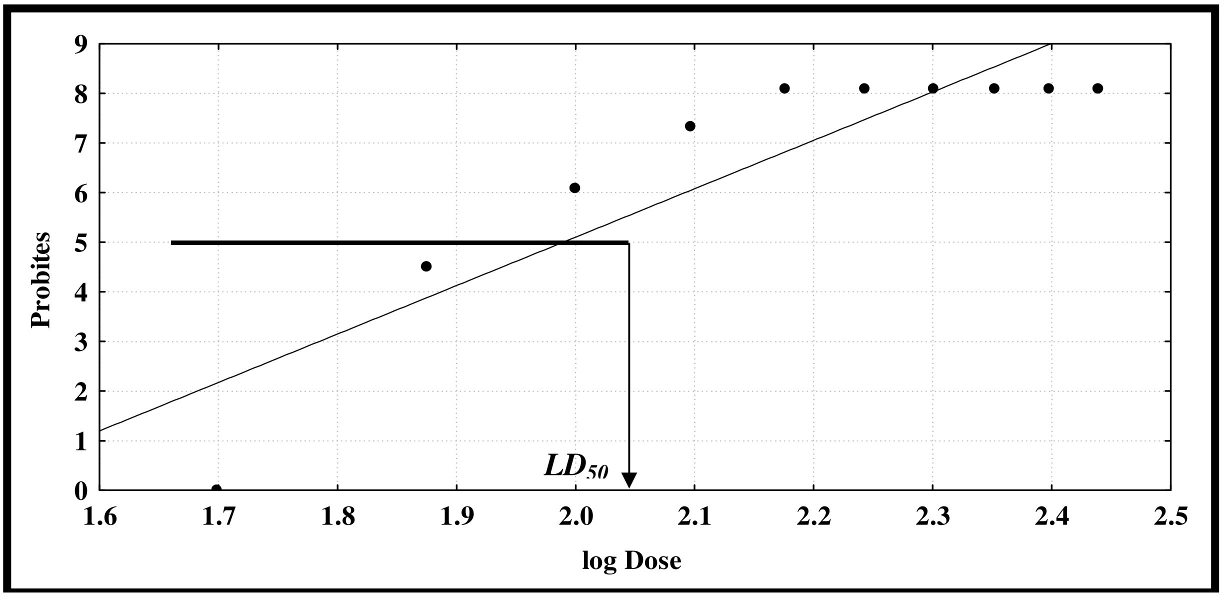


Figure 42 Lethal Dose LD_{50} for Chlorpyrifos Test on **FEMAIL** Rat

5. CNCLUSIONS

The following conclusions could be drawn out from the present work:

1. There is an ability to remove two types of pesticides which were carbofuran and chlorpyrifos from three kind polluted soils using washing method with distilled water in batch mode and form polluted washing water using adsorption technique by available low-cost adsorbent which were watermelon peel (WP) and used tea leaves (UTL) in continuous fixed bed adsorption unit.
2. The percent removal of carbofuran pesticide from polluted soils was reached to 81.268 at 480 min, 99.531 at 300 min and 89.151 at 420 min for clayey, sandy and silty soils respectively at pH=1 and agitation speed =400 rpm.
3. The percent removal of chlorpyrifos pesticide was reached to 77.420 at 360 min, 94.790 at 180 min and 85.481 at 360 min for clayey, sandy and silty soils respectively at pH=8 and agitation speed =400 rpm.
4. The percent removal of carbofuran pesticide from polluted washing water using WP as an adsorbent was reached to 99.25 at 430 min and 73.41 at 600 min for initial concentration 1 and 100 mg/l respectively at pH=1, fixed bed height=40 cm and flow rate of polluted solution=10 ml/min.
5. The percent removal of carbofuran pesticide from polluted washing water using UTL as an adsorbent was reached to 99.19 at 460 min and 77.61 at 600 min for initial concentration 1 and 100 mg/l respectively at pH=1, fixed bed height=40 cm and flow rate of polluted solution=10 ml/min.
6. The percent removal of chlorpyrifos pesticide from polluted washing water using WP as an adsorbent was reached to 95.41 at 420 min and 68.36 at 600 min for initial concentration 1 and 100 mg/l respectively at pH=8, fixed bed height=40 cm and flow rate of polluted solution=10 ml/min.
7. The percent removal of chlorpyrifos pesticide from polluted washing water using UTL as an adsorbent was reached to 92.75 at 440 min and 68.91 at 600 min for initial concentration 1 and 100 mg/l respectively at pH=8, fixed bed height=40 cm and flow rate of polluted solution=10 ml/min.
8. It can be utilize from the residual samples of WP and UTL that adsorb carbofuran and chlorpyrifos pesticides from polluted washing water as rodenticide for rodent control without any further treatment and get rid of these polluted materials in safe, economic, beneficial and eco-friendly method.

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