

REMOVAL OF PESTICIDE FROM WATER USING INDUSTRIAL WASTE AS ECONOMICAL ADSORBENT

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ABSTRACT:

In the last two decades, India has experienced a significant rise in pesticide use in agriculture, resulting in pollution of ground and surface water. Consequently, removing pesticides from water has become a crucial need in this new era. Therefore, this study aims to explore the potential of using manure waste as a low-cost adsorbent to remove carbofuran pesticides from water. We conducted batch experiments to investigate the adsorption properties of carbofuran

at varying initial concentrations, contact times, pH values, adsorbent volumes, temperatures, and particle sizes.

Our findings suggest that as the temperature increases from 298 K to 318 K, the

adsorption capacity decreases, indicating an exothermic adsorption system. Additionally, the Langmuir isothermal model reveals that while the fraction of adsorbed carbofuran decreases with increasing initial concentration, the adsorption capacity increases. Furthermore, our results indicate that increasing the adsorbent capacity enhances carbofuran removal, but it also decreases the adsorption capacity. Notably, our developed low-cost adsorbent exhibits a maximum carbofuran removal capacity of 204.7 mg/g, enabling the attainment of the required carbofuran concentration for drinking water as per Indian standards. Overall, this study provides valuable insights into the potential use of manure waste as an effective and affordable adsorbent for removing carbofuran from water.

Keywords: adsorption, pesticides, carbofuran, industrial waste

INTRODUCTION:

Water pollution is one of the most pressing problems facing society, due to chemical pollution caused by the use of organic and inorganic chemicals and pesticides. These chemicals have resulted in chronic toxicity to aquatic organisms. Accumulation of these chemicals in ecosystems leads to loss of habitat and biodiversity and poses a threat to human and animal health. In addition, these chemicals are not degradable and remain in the environment. Pesticide contamination of drinking water and groundwater has also become a serious threat to the environment and human and animal health. The contamination of drinking water and groundwater with highly hazardous pesticides is constantly increasing due to urbanization, industrialization and globalization. As a result, a large number of people are potentially at risk of various diseases. The most affected regions include India, Pakistan, Taiwan, etc. [1-10]. Pesticides are toxic organic compounds that enter the drinking water supply through natural deposits in the soil and through agricultural and industrial practices and affect the health of humans, animals and living organisms when they exceed the permissible limits according to WHO.

Humans and animals consume large amounts of water; therefore, pesticide contamination is very serious and can affect health.

Developed countries have become aware of water pollution and are taking serious measures for clean water, especially for pesticide compounds (0.1 mg/l limit) [11-14]. Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl-methylcarbamate) is a derivative of a carbamate pesticide commonly used to treat soybeans, rice, potatoes, fruits and vegetables. It is an insecticide and nematicide. It is highly soluble in water (700 mg/l), and concentrations as high as 6.8 µg/l have been detected in river water.

The half-life of the pesticide carbofuran is reported to be about 40 days, and the quality standard for drinking water set by the World Health Organization is 3.0 µg/l. Therefore, it is necessary to develop an effective adsorbent to reduce the concentration of pesticides in water to a safe level specified in BIS (10500:1991). Therefore, it is necessary to remove pesticides from water because of their harmful effects on human and animal health [15-20]. A variety of methods have been used in the past to remove pesticides from water, including: Photocatalytic degradation, electrochemical degradation, nanofiltration, membrane filtration, oxidation, and adsorption.

Several studies/reports have shown that adsorption method is one of the best methods to reduce the concentration of carbamate pesticides in water as recommended by WHO or BIS. Developing countries like India, which cannot afford expensive means, need to develop low-cost and environmentally friendly adsorbents to remove pesticides from water. In this study, we have developed a low-cost sorbent from fertilizer waste that is used to remove carbamate pesticides (carbofurans) from water. A major problem in the production of drinking water is the presence of pesticides in raw water, not only in sub-surface and surface water, but also in ground waters. The concentrations (in µg/l) of the various pesticides were determined. Pesticides are traditionally removed with granular or powdered activated carbon, which is an expensive process. Pesticides and natural organic matter competing for the adsorption sites of activated carbon increase the cost. Nanofiltration may be an interesting alternative for the removal of pesticides. B. Van der Bruggen *et al* [21] studied the results of four nanofiltration experiments. Li C Lu, *et al* [22] developed chitosan beads and powdered crab shell powder to remove pesticides from water. Ahmad T. Shawaqfeh [23] studied the removal of pesticides from water by anaerobic-aerobic biological treatment and the effect of pesticide concentration. Ormad, *et al* [24] studied the effect of H₂O₂ and TiO₂ on the degradation of organic pesticide in natural water an ozone-based treatment. Rodriguez, *et al* [25] investigated the adsorption of diuron and carbofuran from an aqueous solution on granular activated carbon and found that the adsorption capacity was affected by the initial pesticide concentration, pH, and temperature. An increase in pH resulted in a significant increase in adsorption capacity. Navarro, *et al* [26] reported photodegradation of pesticides in leachate water at pilot plant scale using ZnO/Na₂S₂O₈ tandem as photosensitizer / oxidant, and the addition of photosensitizer greatly improved pesticides removal compared to photolytic experiments. Thuy, *et al* [27] removed pesticides from surface water during coagulation-flocculation process followed by the use of aluminum sulfate as a method for the removal of four pesticides (aldrin, dieldrin, atrazine, bentazon) coagulant in different atmosphere, from no

high dosecoagulant (300mg/L). The removal of residues of fungicides applied directly to a racked white wine, elaborated from Airen variety grapes from the D.O. Region of Jumilla (Murcia, Spain) have been studied by Oliva, *et al* [28]. Vinod, *et al* [29] studied the removal of 2,4-dichlorophenoxyacetic acid (2,4-D) and carbofuran from aqueous solutions from wastes from fertilizer industry and steel industry (slag from blast furnace, dusts, and sludge) as an adsorbents in batch method. The carbonaceous adsorbent prepared from the carbon slurry exhibited the uptake capacity of 212 and 208 mg g⁻¹ for 2,4-D and carbofuran, respectively at 25 °C and pH 7.5. Adsorption of 2,4-D and carbofuran on carbon slurry at 25, 35, and 45 °C could be best fitted in the pseudo-second-order kinetic model. A variety of activated carbon materials have been used such as granular activated carbon (GAC) [30], powdered activated carbon (PAC) [31], carbon cloth [32], carbon fibers, black carbon, activated carbon composites and commercial activated carbon (CAC). Fatima Moscoso *et al* [33] were studied removal of pesticides from aqueous solution by adding salting out agent. The forms GAC and PAC are mostly used since they are considered very capable and effective materials for the adsorption of a variety of pesticides. Therefore, in recent years, many researchers have tried to produce activated carbons for removal of various pollutants using renewable and cheaper precursors, which were mainly industrial and agricultural byproducts.

A wide variety of carbons have been prepared from biomass and other wastes, such as date stone, wood, biochar, coconut shell, coconut fibers, bagasse, sal wood, green waste, peat moss, horseshoe sea crab shell, corn stillage, and oil palm fronds. Industrial wastes such as sludge, fly ash, and carbon slurry are classified as low-cost materials because of their low cost and local availability and can be used as adsorbents for pesticides removal.

N. Singh [34] reported that coal fly ash has significantly high retention capacity for metribuzin, metolachlors, and atrazine. Vinod, *et al* [35] reported the removal of endosulfan and methoxychlor from water on carbon slurry produced in generators of fuel-oil-based industrial generators as an effective and efficient adsorbent. Adsorption efficiencies of endosulfan and methoxychlor were 34.11 and 36.06 mg/g in batch processes. S. Ghosh, *et al*. [36] studied the adsorption behavior of lindane on *Rhizopusoryzae*biomass. They found that the adsorption process does not depend on the pH of the solution or incubation temperature. S. Chatterjee, *et al*. [37] showed the interaction of malathion, an organophosphorus pesticides with *Rhizopusoryzae*biomass. They found that the amine groups of chitosan are mainly responsible for chemical interaction between malathion and *Rhizopusoryzae*cell wall. Hydrophobic interaction is the main cause of physical interaction as adsorption of malathion decreased to a great extent after removing lipids from *Rhizopusoryzae*biomass. It may be used for the removal of malathion from potable water.

Activated charcoal is a versatile material that can be applied in many technological processes. Various books and research papers have been published on pesticide pollution of soil, water and air in India [38]. However, water pollution is due to pesticides is very common. In India, rivers are polluted due to the discharge of untreated sewage and industrial effluents. Abida, *et al* [39] analysed the pesticide residue in some Streams of the Cauvery River Karnatka. Beena, *et al* [40] studied the pesticide residues in rain water from Hisar.

Manjubala, *et al* [41] investigated a cluster of pesticide poisoning in Orissa. Naresh, *et al* [42] analysed the organochlorine pesticide residue from different sources like tanks, laks, rivers and ground water and found the concentration of Lindane and DDT are 0.01-0.43 µg/l and 0.03-0.65 µg/l respectively. Therefore, this study was carried out in view of the increasing pollution of water sources caused by pesticides.

EXPERIMENTAL SECTION:

2. MATERIAL AND METHODS:

All chemicals used in this study were of analytical grade and were obtained from Renkem, Merck, Germany or SD Fine Chem. Ltd. India. The carbofuran pesticide stock solution was prepared using carbofuran in purified water. The purified water was prepared in Millipore Milli-Q water treatment plant. The stock solution was diluted to obtain solutions with different concentrations. The pH was adjusted with standard solutions of acids and bases (0.5 M H₂SO₄ and 1 M NaOH).

2.1. EQUIPMENTS USED:

A pH meter is used for pH measurement, model CT No. CL46, Toshnival, India. Measurements of carbofuran pesticides were made using Agilent UV-Vis spectrophotometer (CARY 60) at a wavelength of 273 nm. IR Spectra were recorded using a Thermo Nicolet-Nexus FTIR spectrophotometer with KBr pellets. Carbon content was analyzed using an Elementar CHNS analyzer, model: Vario EL III autoanalyzer (Vario EL, Elementar Analyzer system, GmbH, Germany), scanning electron microscope (SEM) model Zeiss, EVO40 instrument operating at an accelerating voltage of 10 kV//. mA and a working distance of 1.0-50 µm. An energy dispersive X-ray analyzer (model Zeiss, EVO40) equipped with a SEM was used for elemental analysis. A wrist shaker (Popular Trade India), an electronic balance (Shimadzu model: TX423L), an automatic water dispenser and a manual water dispenser (Hach, USA) were used for the study.

2.2. ADSORBENTS PARTICLE SIZE:

All adsorbent powders were passed through various British Standard sieve (BSS) and fractions corresponding to 100-150, 150-200 and 200-250 mesh were collected. In order to understand the effect of adsorbent particle size, the adsorption of particles of various sizes was studied.

2.3. PREPARATION OF SAMPLE:

The pesticide used in this study was 99.9% technical purity carbofuran(C₁₂H₁₅NO₃) purchased from Sigma-Aldrich. The chemical structure of carbofuran is shown in Fig. 1. All solutions were prepared using deionized water.

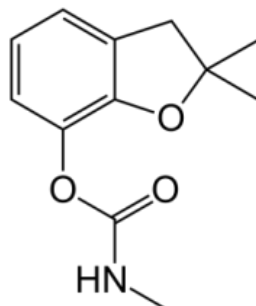


Fig 1. Chemical structure of Carbofuran

A stock solution of the pesticide carbofuran (500 mg/l) with a concentration of 1.0×10^{-3} M was prepared by dissolving the required amount of carbofuran in purified water.

2.4. PREPARATION OF INEXPENSIVE ADSORBENT:

CARBONACEOUS ADSORBENT:

The spent carbon slurry was collected from National Fertilizer Limited, Panipat (Haryana). It consists of fine, black, greasy granules. It is treated with hydrogen peroxide to oxidize the adhering organic matter, washed with water, and heated at 200 °C until the black carbon emission ceases. The dried material was then activated in air for 2 hours in a muffle furnace at a temperature of 500 °C. After the activation was completed, it was cooled, treated with 1M hydrochloric acid to remove ash, washed 3 to 4 times with distilled water, and dried. The dried sorbent was stored in a desiccator for further use. The final product was called carbon adsorbent.

2.5. BATCH STUDIES:

Batch sorption experiments were performed in 250 ml conical flasks at room temperature to obtain rate and equilibrium data; the solution was shaken with a hand shaker. The reaction mixture consisted of 50 ml of a carbofuran solution of known concentration to which 50 mg of a carbonaceous adsorbent was added. After the required reaction time had elapsed, each flask was removed and the solution poured onto a No. 2 Whatman filter paper. To investigate the effects of initial pH (2.0-12.0) on the uptake of carbofuran, experiments were conducted with an initial carbofuran concentration of 25 mg/L and an adsorbent capacity of 1 g/L at a fixed contact time of 150 min. Isothermal studies were performed at different carbofuran concentrations (25-250 mg/L), a fixed adsorbent volume of 1 g/L, and a contact time of 150 min at pH 4.0. The effect of contact time was studied by varying the contact time from 15 to 150 min at an initial carbofuran concentration of 200 mg/l and an adsorbent capacity of 1 g/l at pH 4.0. The behavior of the adsorbent was studied by varying the adsorbent capacity from 1 to 10 g/l at pH 4.0, initial carbofuran concentration (200 mg/l) and contact time of 150 minutes.

2.6. ADSORPTION ISOTHERMS:

Two isotherm models were used to test fit the experimental data, the Langmuir isotherm, the Freundlich isotherm [19-20].

Langmuir Isotherm:

For Langmuir isotherm the equation is given below:

$$q_e = \frac{bK_{eq}C_e}{1 + K_{eq}C_e}$$

Where b is the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent) and K_{eq} is the Langmuir constant related to energy of adsorption. The linear form can be used for linearization of experimental data by plotting C_e/q_e against C_e . The Langmuir constants b and K can be evaluated from the slope and intercept of the following linear equation.

$$\frac{C_e}{q_e} = \frac{1}{bK_{eq}} + \frac{C_e}{b}$$

The Langmuir isotherm equation is widely used as an adsorption isotherm model. When a graph plotted $1/q_e$ vs $1/C_e$, a straight line with a slope of $1/b$ was obtained, indicating that the adsorption of carbofuran onto carbonaceous adsorbent follows the Langmuir isotherm. The nature of the adsorption process can be assessed by determining the dimensionless equilibrium parameter (R_L) as follows:

$$R_L = \frac{1}{1 + K_{eq}C_0}$$

K_{eq} is the Langmuir constant

C_0 is the highest carbofuran concentration (mg/L)

In general, values of $0 < R_L < 1$, $R_L = 0$, $R_L = 1$ and $R_L > 1$ indicate favorable, irreversible, linear and unfavorable adsorption characteristics, respectively.

Freundlich Isotherm:

For Freundlich equation as stated in equation,

$$q_e = KC_e^{1/n}$$

where K and n are Freundlich constant.

A plot of $\log C_e$ versus $\log q_e$ yields a straight line which indicates the conformation of Freundlich isotherm for adsorption. The constant can be determined from the slope and intercept.

$$\log q_e = \log K + \frac{1}{n} \log C_e$$

3. RESULTS AND DISCUSSION:

3.1. CHARACTERIZATION OF THE PREPARED ADSORBENTS:

The FTIR spectra of carbonaceous adsorbent and adsorbent loaded with arsenic were recorded in dried KBr (0.1g). The FTIR spectra of carbonaceous adsorbent indicate the presence of prominent bands lying at 1400, 1616, and 3408 cm^{-1} . The first strong band (bending) at 1400 cm^{-1} may be assigned to the presence of methyl and methylene group. The strong band appearing at 1616 cm^{-1} might be attributed to C=O stretch whereas, the bands appearing at 3408 cm^{-1} may be assigned to the presence of the N-H stretching.

In the carbofuran-loaded activated carbon, an additional peak at 2917 cm^{-1} corresponds to C-H stretching vibrations. The peaks observed at 1616 cm^{-1} and 3408 cm^{-1} in the carbonaceous adsorbent can be assigned to C=O and N-H stretching vibrations, respectively, and these shifted to 1626 cm^{-1} and 3388 cm^{-1} in the carbofuran-loading activated carbon. These changes observed in the FT-IR spectra indicate the possible action of carbofuran on the surface of the activated carbon in the adsorption.

The surface area was determined by nitrogen gas adsorption and was found to be 360 m^2/g for carbonaceous adsorbent, the CHNS analytical data of carbonaceous adsorbent indicated that the carbon content as 84.2% whereas, after loading carbofuran pesticide on adsorbent surface the carbon content increased to 91.20%.

In addition, the SEM allowed direct observation of the surface microstructure of the activated carbon. Fig. 2 shows SEM microscopic images of the samples before and after adsorption of carbofuran. The activated adsorbent showed a well-developed pore structure for the adsorption of carbofuran. Activation created pores and removed a significant amount of inorganic materials from the raw material.

To determine the elemental composition on the surface of the carbonaceous adsorbent before and after adsorption, elemental analysis was performed using EDX analysis. The EDX analysis is shown in Fig. 4, which shows the presence of various elements along with a high percentage of carbon.

EDX analysis of selected sites on the surface of the adsorbent provided information on the distribution of elements before and after adsorption (Fig. 3). The weight percentages of each element in the different composites were calculated from the EDX plots (Table 1). The unloaded adsorbent consists mainly of carbon and Ca impurities.

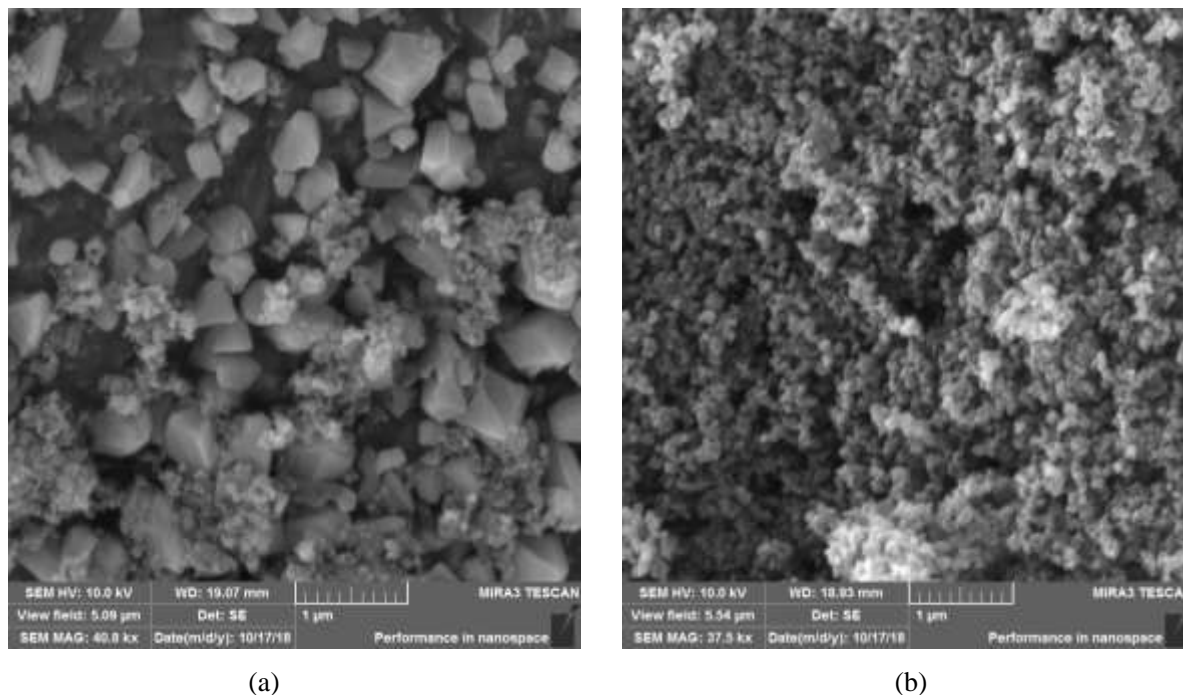


Fig.2. SEM micrograph (a) carbonaceous adsorbent before adsorption (b) carbonaceous adsorbent after adsorption of carbofuran pesticide.

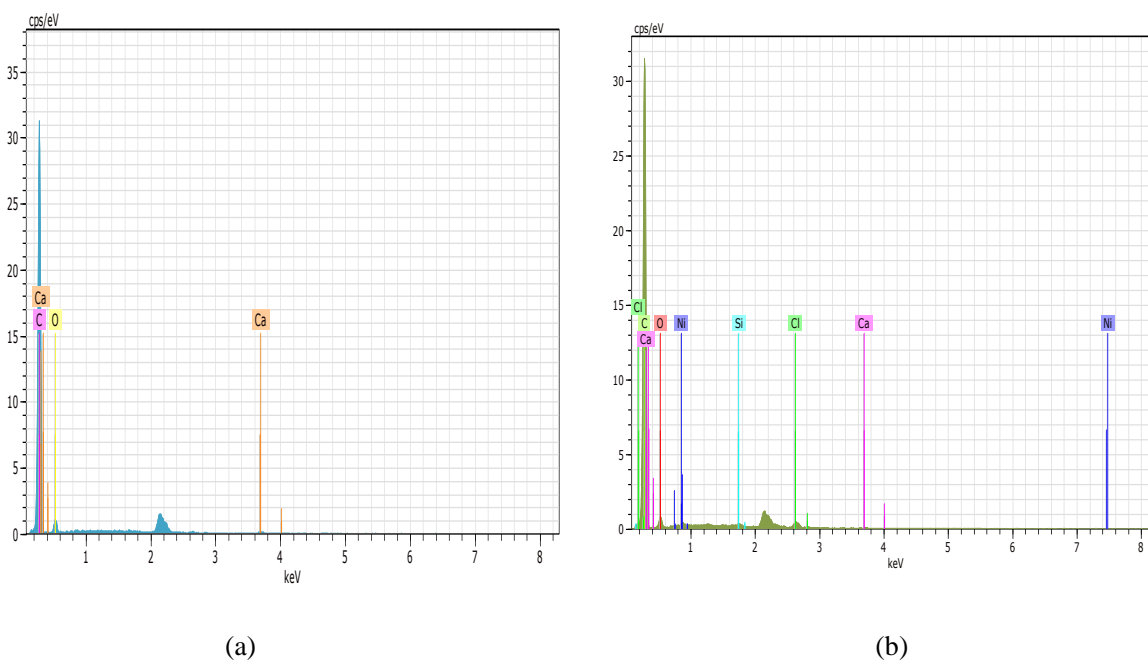


Fig.3. EDX analysis of carbonaceous adsorbent (a) before adsorption (b) after adsorption.

Table 1: Elemental analysis of carbonaceous adsorbent surface

Element	Atom (wt.%)	
	Carbonaceous adsorbent before adsorption	Carbonaceous adsorbent after adsorption
C	92.27	94.38
O	7.34	4.45
Ca	0.39	0.15
Cl	-	0.62
Ni	-	0.17
Si	-	0.22

After adsorption, the concentration of O and Ca decreased significantly, while the relative concentrations of Cl, Ni, and Si increased slightly compared to the untreated adsorbent. The value of the elemental analysis is not the absolute mass, but the relative weight percentage of the surface composition. Therefore, the increase or decrease in the relative amount of impurities is mainly due to the increase or decrease in the amount of carbon and oxygen on the adsorbent surface. The concentration of carbon on the adsorbent increased significantly after the adsorption process. The higher weight percentage of carbon in the adsorbent after the adsorption process indicates that the functional group containing carbon is higher on the surface. Remarkable variations in the relative amount of carbon and oxygen were observed during adsorption. Moreover, carbofuran contains nitrogen in its structure; the peak corresponding to nitrogen was not detected in the spectra. This suggests that the nitrogen is mineralized or converted to various forms during the process. It was found that the nitrogen from carbofuran was converted to either ammonium or nitrate and the remaining nitrogen was mineralized.

3.2. BATCH STUDIES:

3.2.1. EFFECT OF pH:

The influence of pH (2.0-12.0) on the adsorption of the pesticide carbofuran is shown in Fig. 4. The adsorption capacity for the pesticide carbofuran is almost constant in the acidic pH range from 2.0 to 5.0, while it decreases in the basic medium with an increase in pH from 7.0 to 12.0 and remains almost constant with a further increase in pH up to 14.0. The maximum adsorption capacity for the pesticide carbofuran is 82% at pH 2.0 to 4. The adsorption capacity decreases with increasing pH because the dependence of adsorption on pH values depends mainly on the types and ionic states of the functional groups present on the carbonaceous adsorbent and the types of compounds in the solution. At a low (acidic) pH of the solution, the carbon surface is predominantly positively charged, while at a strongly basic pH, negative charges appear on the surface due to dissociation of the functional groups. This results in a less positively charged carbon surface at higher pH values. However, the interaction of carbonaceous adsorbent surfaces with deprotonated carbofuran should be weaker than with its neutral molecular form.

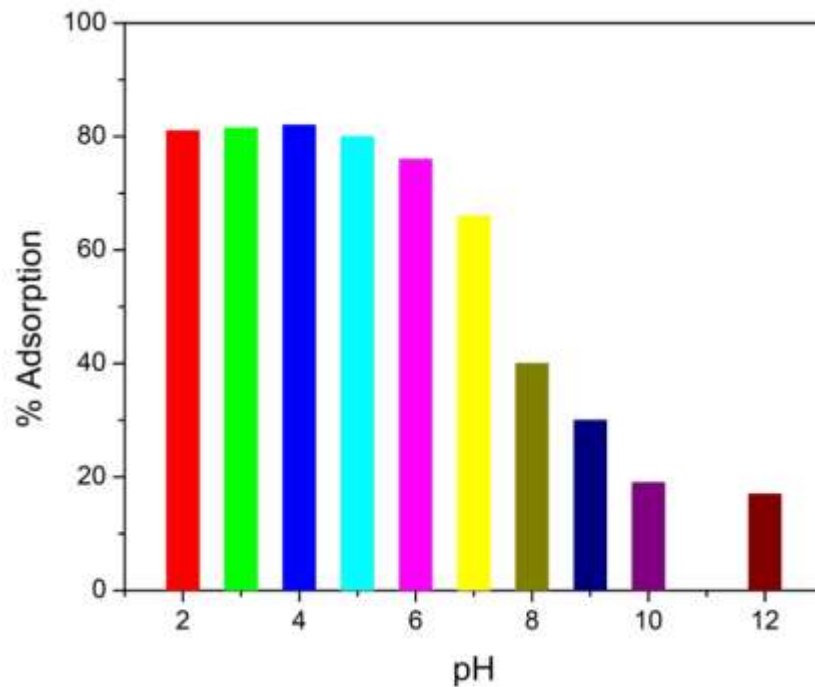


Fig.4: Effect of pH on carbofuran adsorption by low cost adsorbent.

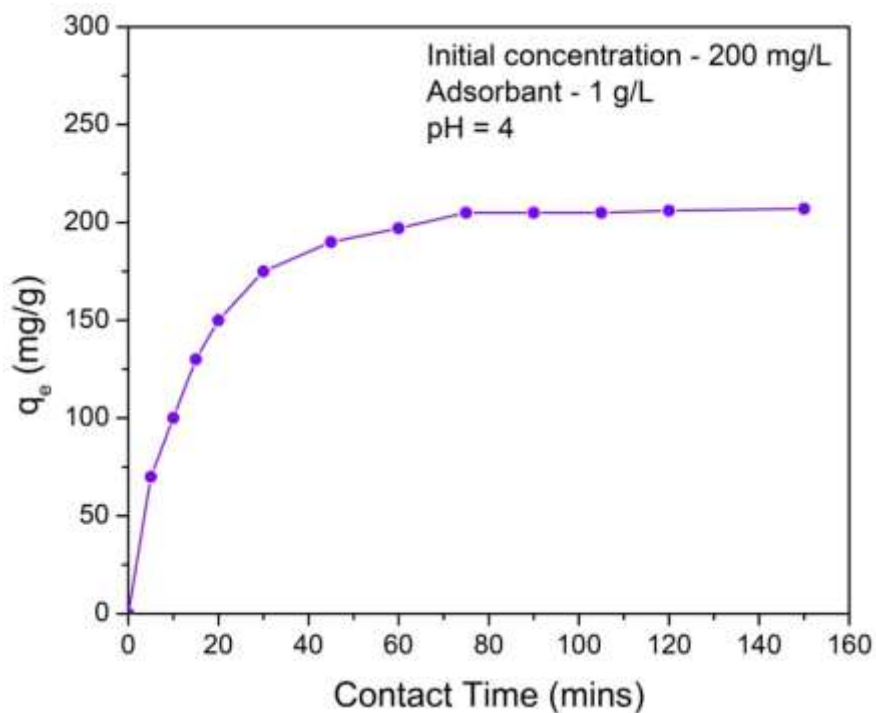


Fig.5: Effect of contact time of carbofuran adsorption on carbonaceous adsorbent (temperature, 25°C; particle size 200-250 mesh).

3.2.2. EFFECT OF CONTACT TIME:

Fig. 5 shows that the adsorption efficiency increases rapidly with increasing contact time and is as high as 75 minutes when a carbonaceous adsorbent with a particle size of 200-250 mesh is used. The maximum removal efficiency was 82% and remained almost constant until the end of the experiment. The data in Fig. 5 show that the time required for equilibrium adsorption is 75 minutes.

3.2.3. EFFECT OF INITIAL CARBOFURAN CONCENTRATION:

The studies were conducted with different initial concentrations and contact times to determine the equilibrium time for maximum uptake of carbofuran. As the initial concentration was increased from 200 mg/l to 600 mg/l, the adsorption capacity of the carbonaceous adsorbent increased and the removal rate decreased from 82% to 16%. The effect of the initial concentration of carbofuran (200-600 mg/l) on the carbonaceous adsorbent is shown in Fig. 6. This shows a higher removal efficiency (82.0%) at a lower initial concentration (200 mg/l) of the pesticide carbofuran. However, at higher carbofuran concentrations, the adsorption efficiency gradually decreases, and the maximum removal efficiency at carbofuran pesticide concentration (600 mg/l) was 16% for the carbonaceous adsorbent. The reason for the lower adsorption efficiency of carbofuran pesticide at higher initial concentrations could be due to the porous nature of the adsorbent, which leads to a large surface area and eventual saturation with adsorbed carbofuran, making it impossible to add more carbofuran pesticide to the solution. It was found that the adsorption uptake was initially high and depended on the initial pesticide concentration.

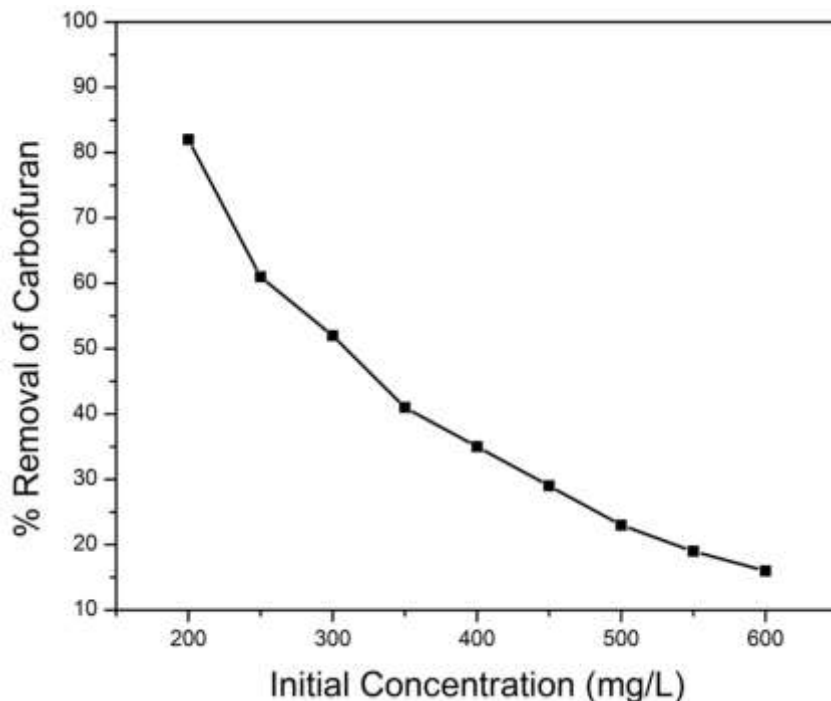


Fig.6: Effect of initial concentration of carbofuran adsorption on carbonaceous adsorbent (temperature, 25°C; particle size 200-250 mesh).

3.2.4. EFFECT OF TEMPERATURE:

The adsorption of carbofuran was studied at different temperatures (298, 308 and 318 K). It was found that the adsorption increases with increasing temperature from 298 to 318 K (Fig.7). This shows that the adsorption system is exothermic in nature and the thermodynamic parameters were estimated. The adsorption was compared with two adsorption models (Langmuir and Freundlich) to find out the appropriate model (Fig. 8).

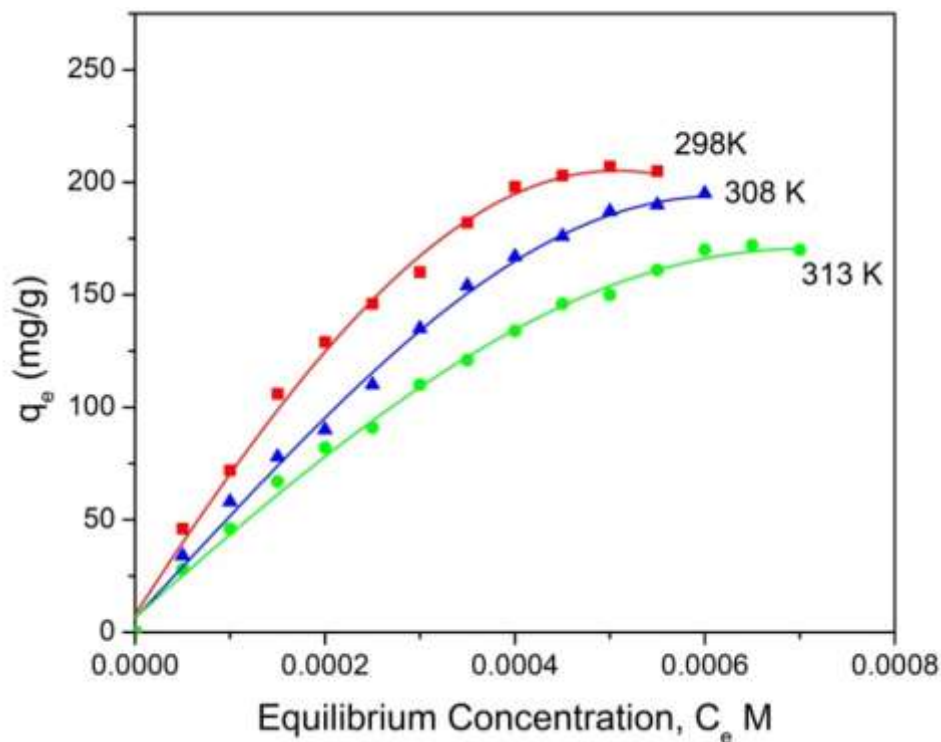


Fig.7: Effect of temperature of carbofuran adsorption on carbonaceous adsorbent (particle size 200-250 mesh). Fig.8 shows that the experimental data correspond to the Langmuir model and the Freundlich model. At a temperature of 298 K, the maximum adsorption capacity according to the Langmuir model is 321.54 mg/g, and the slope and intercept resulting from plotting $\ln q_e$ versus $\ln C_e$ in the Freundlich isotherm are the Freundlich constants (K_e and n) (data not shown). The larger the value of n , the higher the adsorption capacity. In general, n in the range of 2-10 is considered to indicate good adsorption performance; 1-2, moderate adsorption; and less than 1, poor adsorption. On the other hand, in the Langmuir model, values of $0 < RL < 1$ indicate good adsorption properties.

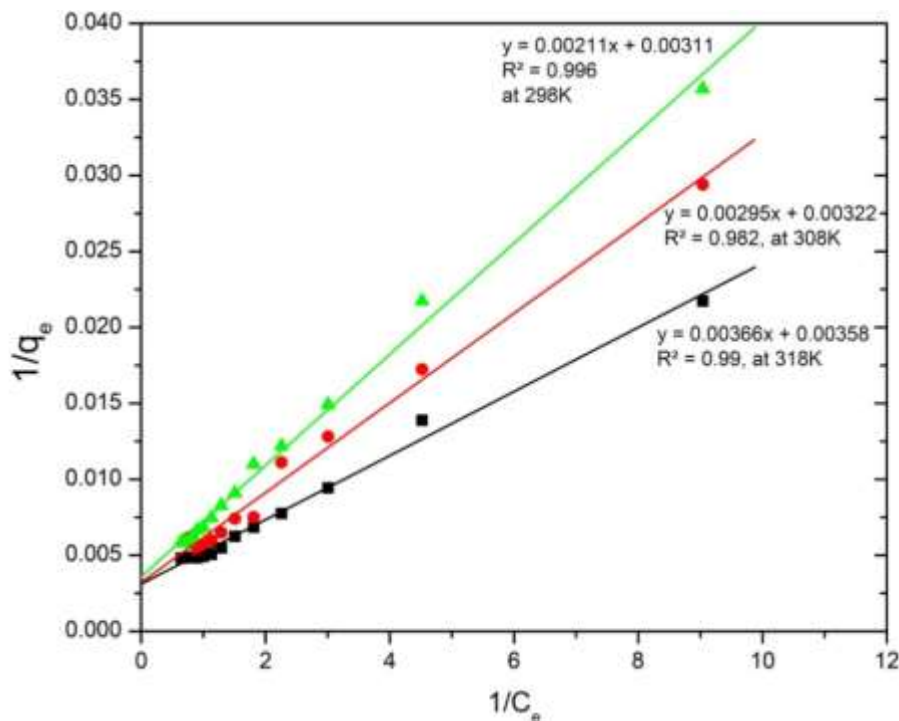


Fig.8: Langmuir model fit for adsorption of carbofuran at 298K, 308K and 318K (particle size 200-250 mesh). The data obtained with the Freundlich model are not favorable because the n values of the Freundlich constants ($n= 1.53, 1.37,$ and 1.41 at 298, 308, and 318 K, respectively) range from 1 to 2. However, the Langmuir model yields significant results. Comparing the average correlation coefficient R^2 of the two models, it can be seen that the value R^2 of the Langmuir model is more accurate than that of the Freundlich isotherm. The main assumption of the Langmuir isotherm is based on the monolayer adsorption of the adsorbent on the adsorbent surface by assuming that the adsorption of carbofuran on the carbonaceous adsorbent leads to the formation of a monolayer.

3.1.5. EFFECT OF ADSORBENT DOSAGE:

Adsorption experiments were also performed with different adsorbent dosages ranging from 0.1 to 10 g/l. A slight increase was observed when the adsorbent capacity was further increased to 10 g/l. Adsorption efficiency with increasing adsorbent dosage. The dosage of adsorbent increased the adsorption of the pesticide carbofuran and increased from 0.1 to 10 g/l. At a dosage of 10 g/l, the residual carbofuran was found to be below the limit of BIS. As the capacity of the adsorbent increases, the adsorption capacity also increases. The increase in removal efficiency can be explained by the fact that as the adsorbent becomes more loaded, a larger surface area of the adsorbent is available, resulting in an increase in the number of pores and solutes adsorbed on the surface.

3.1.6. EFFECT OF ADSORBENT PARTICLE SIZE:

Adsorption of the pesticide carbofuran was studied at different particle sizes. It was found that adsorption increases with decreasing particle size. This is mainly due to the fact that the surface area and the number of

active pores of an adsorbent increase with decreasing particle size. Adsorption to adsorbents depends on the pore size distribution and the number of pores in the structure. It was found that the adsorption ratio increased with increasing particle size of the adsorbent from 100-150 mesh to 200-250 mesh.

4. CONCLUSIONS:

The present study on the adsorption of carbofuran on carbonaceous adsorbents in batch experiments provides basic information on the equilibrium time, optimum pH and dosage of the adsorbent. The results show that the carbonaceous adsorbent can be used as an adsorbent to reduce the carbofuran concentration in water to less than 204.7 µg/l (at 1 g/l adsorbent capacity and an initial carbofuran pesticide concentration of 200 µg/l), which is suitable for use in small systems or domestic wastewater treatment plants. The current study has helped to achieve the required carbofuran concentration in drinking water as per Indian standards.

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REFERENCES:

- [1] Chen, S., Sun, D. Z., Chung, J. S.; Treatment of pesticide wastewater by moving-bed biofilm reactor combined with Fenton-coagulation pretreatment. **J. Hazard.Mater.**, 2007, 144 (1-2), 577-584.
- [2] Abdessalem, A. K., Bellakhal, N., Oturan, N., Dachraoui, M., Oturan, M. A.; Treatment of a mixture of three pesticides by photo- and electro-Fenton processes. **Desalination**, 2010, 250(1), 450-455.
- [3] Ma, Y. S., Sung, C. F., Lin, J. G.; Degradation of carbofuran in aqueous solution by ultrasound and Fenton processes: Effect of system parameters and kinetic study. **J. Hazard.Mater.**, 2010, 178(1-3), 320-325.
- [4] Jiang, J. D., Zhang, R. F., Li, R., Gu, J. D. Li, S.; Simultaneous biodegradation of methyl parathion and carbofuran by a genetically engineered microorganism constructed by mini-Tn5 transposon. **Biodegradation**, 2007, 18(4), 403-412.
- [5] Chu, W., Lau, T. K., Fung, S. C.; Effects of combined and sequential addition of dual oxidants ($H_2O_2/S_2O_8^{2-}$) on the aqueous carbofuranphotodegradation. **J.Agr. Food Chem.**, 2006, 54(26), 10047-10052.
- [6] Chang, K.-L., Chen, C.-C., Lin, J.-H., Hsien, J.-F., Wang, Y., Zhao, F., Chen, S.-T.; Rice straw-derived activated carbons for the removal of carbofuran from an aqueous solution. **New Carbon Materials**, 2014, 29(1), 47–54.
- [7] Salman, J. M., Hameed, B. H.; Adsorption of 2,4-dichlorophenoxyacetic acid and carbofuran pesticides onto granular activated carbon. **Desalination**, 2010, 256(1-3), 129-135.
- [8] Salman, J. M., Hameed, B. H.; Removal of insecticide carbofuran from aqueous solutions by banana stalks activated carbon. **J. Hazard.Mater.**, 2010, 176(1-3), 814-819.
- [9] Gupta, V.K., Carrott, P.J.M., Ribeiro Carrott, M.M.L., Suhas; Lowbcostadsorbents: growing approach to wastewater treatment e a review. **Crit. Rev. Environ. Sci. Technol.** 2009, 39, 783-842.
- [10] USEPA, <http://www.epa.gov/pesticides/factsheets/index.htm>.
- [11] Gupta, V.K., Imran, A.; Removal of DDD and DDE from wastewater using baggasse fly ash sugar industry waste. **Water Res.** 2001, 35, 33-40.
- [12] Gupta, V.K., Imran, A.; in: A. Hubbard (Ed.), Adsorbents for Water Treatment: Low Cost Alternatives to Carbon. **Encyclopedia of Surface and Colloid Science**, vol. 1, Dekker, New York, 2002, p. 136.
- [13] Singh, R. K., Philip, L., Sarathi, R.; Rapid Removal of Carbofuran from Aqueous Solution by Pulsed Corona Discharge Treatment: Kinetic Study, Oxidative, Reductive Degradation Pathway, and Toxicity Assay. **Ind. Eng. Chem. Res.**, 2016, 55 (26), 7201–7209.

- [14] Rama Krishna, K., Philip, L.; Adsorption and desorption characteristics of lindane, carbofuran and methyl parathion on various Indian soils. **J. Hazard. Mater.**, 2008, 160(2-3), 559-567.
- [15] Mohammad, S. G., Ahmed, S. M., & Badawi, A. F. M.; A comparative adsorption study with different agricultural waste adsorbents for removal of oxamyl pesticide. **Desalination and Water Treatment**, 2014, 55(8), 2109–2120.
- [16] Njoku, V. O., Islam, M. A., Asif, M., Hameed, B. H; Preparation of mesoporous activated carbon from coconut frond for the adsorption of carbofuran insecticide. **J. Anal. Appl. Pyroly.**, 2014, 110, 172-180.
- [17] Santana, G. M., Lelis, R. C. C., Jaguaribe, E. F., Morais, R. de M., Paes, J. B., & Trugilho, P. F.; Development of Activated Carbon from Bamboo (*bambusa vulgaris*) for Pesticide Removal from Aqueous Solutions. **Cerne**, 2017, 23(1), 123–132.
- [18] Remya, N., Lin, J.-G.; Microwave-granular activated carbon (MW-GAC) system for carbofuran degradation: Analysis of characteristics and recyclability of the spent GAC. **Desalination and Water Treatment**, 2013, 53(6), 1621–1631.
- [19] Langmuir, I.; The adsorption of gases on plane surfaces of glass, mica and platinum, **J. Amer. Chem. Soc.**, 1918, 40(9), 1361–1403.
- [20] Freundlich, H. M. F.; Over the adsorption in solution, **J. Phy. Chem.**, 1906, 57, 385–470.
- [21] Bruggen Van der, B., Everaert, K., Wilms, D., Vandecasteele, C.; Application of Nanofiltration for Removal of Pesticides, Nitrate and Hardness From Groundwater: Rejection Properties and Economic Evaluation, **J. Membr. Sci.**, 2001 15, 239.
- [22] Lu, Li C., Wang, C. I., Sye, W. F; Applications of chitosan beads and porous crab shell powder for the removal of 17 organochlorine pesticides (OCPs) in watersolution, **Carbohydr. Polym.**, 2011, 83(4), 1984.
- [23] Shawaqfeh, A. T.; Removal of Pesticides from Water Using Anaerobic-Aerobic Biological Treatment, **Chin. J. Chem. Eng.**, 2010, 18(4), 672.
- [24] Ormad, M. P., Miguel, N., Lanao, M., Mosteo, R., Ovelleiro, J. L.; Effect of application of ozone and ozone combined with hydrogen peroxide and titanium dioxide in the removal of pesticides from water, **Ozone Sci. Eng.**, 2010, 32, 25.
- [25] Rodriguez, A., Garcia, J., Sotelo, J. L., Ovejero, G., Mestanza, M., Removal of the pesticides diuron and carbofuran in aqueous solutions by activated carbon. **Fresenius Environ. Bull.**, 2009, 18(11), 2093.
- [26] Navarro, S., Fenoll, J., Vela, N., Ruiz, E., Navarro, G.; Photocatalytic degradation of eight pesticides in leaching water by use of ZnO under natural sunlight., **J Hazard Mater**, 2009, 72(2) 1303.
- [27] Thuy, P.T., Moons, K., van Dijk, J. C., Anh, N. V., Van der Bruggen, B.; **Water Environ. J.**, 2008, 22, 217.
- [28] Oliva, J., Cayuela, M., Paya, P., Martinez-Cacha, A., Cámara, M.A., Barba, A.; Influence of fungicides on grape yeast content and its evolution in the fermentation. **Commun. Agric. Appl. Biol. Sci.**, 2007, 72, 181–189.
- [29] Gupta, V. K., Ali, I., Suhas, Saini, V. K.; Adsorption of 2,4-D and carbofuran pesticides using fertilizer and steel industry wastes., **J. Colloid. Interface Sci.**, 2006, 2, 556.
- [30] Kitous, O., Cheikh, A., Lounici, H., Grib, H., Pauss, A., Mameri, N.; Application of the electrosorption technique to remove Metribuzin pesticide., **J. Hazard Mater.**, 2009, 161, 1035.
- [31] Ohno K., Minami T., Matsui Y., Magara Y.; Effect of chlorine on organophosphorus pesticides adsorbed on activated carbon: desorption and oxon formation. **Water Res**, 2008, 42, 1753.
- [32] Ayranci E., Hoda N.; Adsorption of bentazon and propanil from aqueous solutions at the high area activated carbon-cloth. **Chemosphere**. 2004, 57, 755.
- [33] Moscoso, F.; Deive, F.J.; Esperança, J.M.S.S.; Rodríguez, A. Pesticide removal from aqueous solutions by adding salting out agents., **Int. J. Mol. Sci.** 2013, 14, 20954.
- [34] Singh, N.; Adsorption of herbicides on coal fly ash from aqueous solutions., **J. Hazard. Mater.**, 2009, 168, 233.
- [35] Gupta, V.K. , Ali, I.; Removal of endosulfan and methoxychlor from water on carbon slurry'. **Environ. Sci. Technol.**, 2008, 42, 766.
- [36] Ghosh, S., Das, S. K., Guha, A. K., Sanyal, A. K.; Adsorption behavior of lindane on *Rhizopusoryzae* biomass: physicochemical studies, **J. Hazard. Mater.**, 2009, 172, 485.

- [37] Chatterjee, S., Das, S. K., Chakravarty, R., Chakrabarti, A., Ghosh, S., Guha, A. K.; Interaction of malathion, an organophosphorus pesticide with *Rhizopusoryzae* biomass, **J. Hazard. Mater.**, 2010, 174, 47.
- [38] Pillai, M. K.; Pesticide pollution of soil, water and air in Delhi area, India. **Sci. Total Environ.**, 1986, 55, 321.
- [39] Begum, A., Krishna, H., Khan, I.; A Survey of persistent organochlorine pesticide residues in some Streams of the Cauvery River, Karnataka, India, **Internat. J. Chem. Tech. Res.**, 2009, 2, 237.
- [40] Kumari, B., Madan, V. K., Kathpal, T.S.; Pesticide residues in rain water from Hisar, India. **Environ. Monitor. Assessm.**, 2011, 133, 467.
- [41] Panda M., Hutin Y.J., Ramachandran V., Murhekar M.; A Fatal Waterborne Outbreak of Pesticide Poisoning Caused by Damaged Pipelines, Sindhikela, Bolangir, Orissa, India. **J. Toxicol.** 2009, 1.
- [42] Ghose, N. C., Saha, D., Gupta, A., Synthetic detergents (surfactants) and organochlorine pesticide signatures in surface water and groundwater of greater Kolkata, India. **Water Resource Prot.**, 2009, 4, 290.