International Journal of Innovation in Science and Mathematics
Volume 6, Issue 4, ISSN (Online): 2347–9051

Removal of Selected Pesticides from Aqueous Solution using Cost Effective Soft Drink Bottles

Maryam S. Abdulrahman, Hassan T. Abdulsahib and Salah S. Al-Luaibi
Department of Chemistry Science College University of Basrah, Basrah , Iraq

***Abstract* – A low cost soft drink bottle after chemical and thermal treatment are used to remove chlorpyrifos, dichlorovos, abamectin pesticides from aqueous solutions. The adsorption parameters i.e. PH, contact time and temperature have been studied. The adsorption efficiency of prepared polymers poly (bis (2 - hydroxy ethylene) terephthal) amide (PHETA) was found to be 86%, 79%, 87% for chlorpyrifos, dichlorovos and abamectin respectively within 8hrs at PH 2. The prepared polymer was characterized by FTIR, SEM, TG and XRD. Batch experiments were performed to recover the adsorbed pesticides from the adsorbent surface. The proposed adsorption method was utilized to remove chlorpyrifos, dichlorovos, abamectin pesticides from environmental water samples.**

***Keywords* – Bottle, PET, Pesticides, Adsorption.**

I. Introduction

Surface water bodies are subject to pollution by pesticides which can cause potential adverse public and environmental health effects [(1)]. Some pesticides are endocrine disrupting compounds [(2-3)]. Developed countries have become very strict for water treatment especially regarding pesticides compounds (levels, 0.1 mgl^{-1}) [(4)]. Techniques generally employed to reduce pesticides from effluents include adsorption, photocatalytic degradation [(5)] electrochemical degradation [(6)], oxidation [(7)], membrane filtration [(8)], nanofiltration [(9)]. Adsorption has advantages over other methods because of simple design with a sludge free environment and can involve low investment in term of both initial cost and land required [(10)]. Polymeric materials have been widely investigated for removal of pesticides from aqueous solution, because it require lower energy and consequently, lower costs for regeneration or renewal of adsorbents in comparison with other adsorbent [(11)]. In this work, the PHETA has been investigated for the analytical purpose. The polymer properties as adsorbent towards several pesticides such as chlorpyrifos, dichlorovos and abamectin, were studied.

II. Experimental

2.1. *Materials and Methods*

2.1.1. *Materials*

All the chemicals used were of analytical grade which were used without further purification : Chloropyrofos, Dichlorvos, Abamactine from (GHARD), Monoethanolam--ine (MEA) and sodium acetate were obtained from Aldrich Chemical CO., Poly (ethylene terephthalate) (PET) waste after removing caps and labels were washed, dried and chips with an average size of (0.5*0.5 cm^2) All pesticides solutions used in this study were prepared by dilution appropriate volumes of pesticides in distilled water.

2.1.2. *Methods*

2.1.2.1. *Synthesis of Poly (Bis (2 - Hydroxy Ethylene) Terephthal) Amide (PHETA)*

PET was reacted with MEA at weight ratio PET to MEA 1:1. The sodium acetate using 1.0% as catalyst (by weight based on weight of Polymer). The reaction mixture in round flask on the refluxed with mechanical stirrer, at temperature about 170 – 190 C^0 for 7 h. temperature of the reaction was then lowered to 100 C^0 for 1h. The end of reaction cooled to room temperature and added distilled water to the reaction mixture with stirrer to precipitate the product, poly (bis (2 - hydroxy ethylene) terephthal) amide (PHETA). White crystalline powder of was confirmed from their SEM, TGA, X-ray and IR spectra. The reaction of PET with MEA is illustrated in Figure (1).

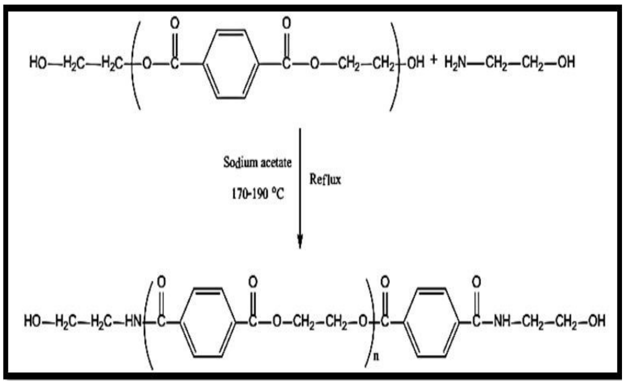

Fig. 1. Aminolysis Poly (ethylene terephthalate) by Monoethanolamine

2.2 *Characterization Techniques and Instruments*

Four methods were used for the characterization of the polymer :

Fourier transform infrared (FTIR) spectra were obtained (JASCO, FT – IR 4200, Japan) with samples incorporated into KBr discs in the range of 400 - 4000cm^{-1}. The Scanning Electronic Microscope images were taken by FESEM using supra 55 vp (ZEISS) (Germany). Thermogravimetric analysis (TGA) measurements were performed using a TA Instruments (TGA - Q50, USA). X – ray diffraction spectra were obtained PAN alytical Xpert PROMOD.

2.3 *Batch Adsorption Experiments:*

Batch equilibrium adsorption experiments were carried out in 100 ml flasks containing pesticides aqueous solutions (100 mg/l) at different pH (2, 4, 6, 8), (the pH of solution was adjusted to desired values with 0.1 N HCl or 0.1 N $NaHCO_3$). Adsorption experiment are developed by placing 0.1 gm of dry polymer and 100 ml of pesticides solution in 100 ml flask. The mixture is shaken at 200 rpm for different mixing time (0.25-24) hrs using a thermoseated shaker at different temperature (25, 35, 45, 55^{0}C). Samples are filtered at equilibrium and the remaining concentration of pesticides was determined using UV. Visible spectro photo--metr.

III. Results and Discussion

3.1. *Fourier Transformer Spectroscopy (FTIR):*

Fourier transform infrared spectroscopy (FTIR) was used to determine the vibration frequency of functional groups in the polymer. The spectra were measured by an FTIR spectrometer within the range of 400-4000 cm^{-1} wave number. The dry amount of polymer. (About 0.1 g) was thoroughly mixed with KBr and pressed into a pellet and the FTIR spectrum was then recorded.

3.2. *FTIR of Poly Ethylene Terephthalate with Monoethanolamine*

The characteristic IR absorption peaks of PET with monoethanolamine were observed Fig. (2) the presence of strong band at 1057and 3289 cm^{-1} indicating the presence of primary alcohol (CH_2OH-). The peaks for secondary amide stretching are observed at 1311, 1555 and 3363 cm^{-1} and the band observed at 878 cm^{-1} for (PHETA) is assigned to – CH - out - of – plane bending of P- substituted phenyl .

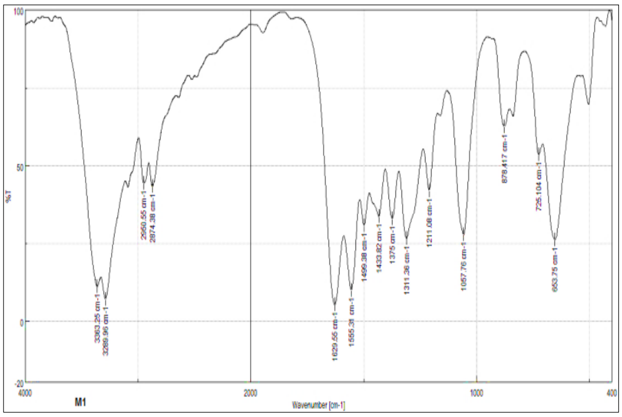

Fig. 2. FTIR of PHETA.

3.3. *The Thermal Stability Study of the Polymer:*

In the present study the thermal stability characteristics of the polymer was investigated by TG and DTG technique. TG is one of the familiar techniques for systematic assessment of polymers thermal stability. It is very useful tool and help to indicate the relative order of stability of various polymers. TG is defined as a continuous measurement of sample weight as a function of time or temperature at a programmed rate of heating. The resulting weight change v.s. temperature (or time) curve gives information about the thermal stability and decomposition of the materials.

The thermal decomposition of polymers initialed by homo cleavage of C-C or C-N bands to formation radical intermediate and then produce volatile compounds such as, ammonia (NH_3), carbondioxide CO_2 and benzene (C_6H_6). The TGA thermogram of (PHETA) in Figure (3) and shows that the three decomposition stages, the decomposition temperature (DT), half decomposition temperature $T_{50\%}$, cher contant, Rale of decomposition and activation energy ΔE were evaluated from TG curve and listed in table (3-1).

Table (3-1). TG curve of the PHETA.

polymer	Opt. Decomposition Temp.												T 50%	Char content.%	Rate of decomp . % min	ΔE Kj/Mole
	1st decomposition			2nd decomposition			3rd decomposition			4th decomposition						
	T_i	T_{op}	T_f	T_i	T_{op}	T_f	T_i	T_{op}	T_f	T_i	T_{op}	T_f				
PHETA	105	150	225	240	375	400	410	465	568	-	-	-	480	40	Min=28	81 Kg/mol

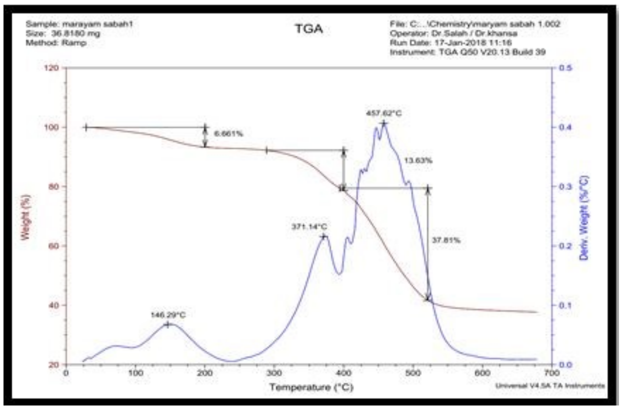

Fig. 3. Thermogravimetric diagram of PHETA.

3.4. *Scanning Electronic Microscope Study of the polymer :*

The Scanning Electronic Microscope is a very useful imaging technique that utilized abeam of electrons to acquire high magnification images of specimens Fig (4). Showed the SEM images of PET and PHETA. It can be seen that PET has relatively smooth surface, the surface become rougher after reacting with monoethanolamine. This change was possibly explained by the change of chemical structure in PET after reaction and introduced a functional groups from monoethanolamine to the surface and also increased the surface area of the PET particles.

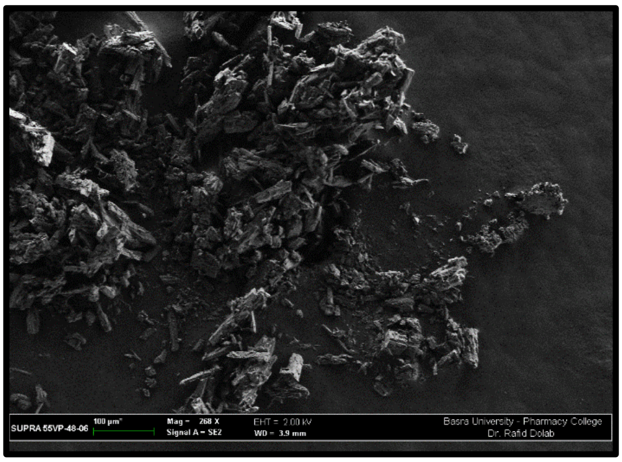

Fig. 4. SEM of PHETA and PET.

3.5. *X-ray Diffractometry :*

X-ray spectroscopy is a powerful and flexible tool and an excellent complement to many structural analysis techniques. The properties of polymers depended mostly on the molecular weight, polydispersity and crystallinity. XRD Commonly used to measure crystallinity,

The crystallinity index (CI) can be calculated on the basis of X-ray diffractograms. Postulating the following equation for determining the crystallinity index (CI):

$$CI\ (\%) = [(Im - I\ am) / I\ m]\ X\ 100$$

Where : Im (arbitrary unite) is the maximum intensity of the crystalline peak at around (2θ), and Iam (arbitrary unite) is the amorphous diffraction at (2θ). In most cases, CI provides information about the crystal state. The typical diffraction pattern is given in angle form. Fig (5) showed sharp peak 2θ = 23^0 which due to strong reflections at this angle, however, differently indexed crystalline peaks (72%), the chans form hydrogen bonded sheets linked by C = O …H - N bonds approxametly parallel to the axis, and each chain is stabilized by an O-H….O = C intramolecular hydrogen bond.

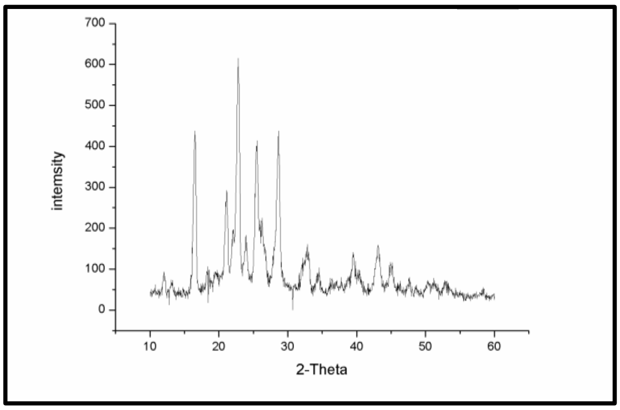

Fig. 5. X-ray Spectra of PHETA.

3.6. *Analytical Study*

We investigated the effect of parameters such as pH, contact time and temperature on the adsorption efficiency of PHETA polymer. By quantifying the pesticides concentration before and after adsorption, the efficiency of adsorption of pesticides by (poly (bis (2 - hydroxy ethylene) terephthal) amide) was calculated by using the following equation :-

$$Adsorption\ (\%) = \frac{C0 - Ce}{C0}\ X\ 100$$

Where :- C0: Initial concentration (mg/L) of pesticides, Ce : equilibrium concentration (mg/L) of the pesticides.

3.7. *Maximum Absorption Wavelength (λ max)*

For the determining the wavelength at which the maximum absorption occurs, the (chlorpyrifos, dichorovos, abamectin) absorbent are recorded by UV spectra using quartz cell of thickness (1cm) and with a concentration of (100 ppm) of pesticide. The result showed that maximum absorption of chlorpyrifos obtained at 290 nm and maximnm absorption of dichorovos obtained λ max 242 nm while maximum absorption of abamectin obtained 244 nm as shown in Fig(6). Table (3-2): demonstrate a comparison of obtained λ max of pesticides in this study and Literature.

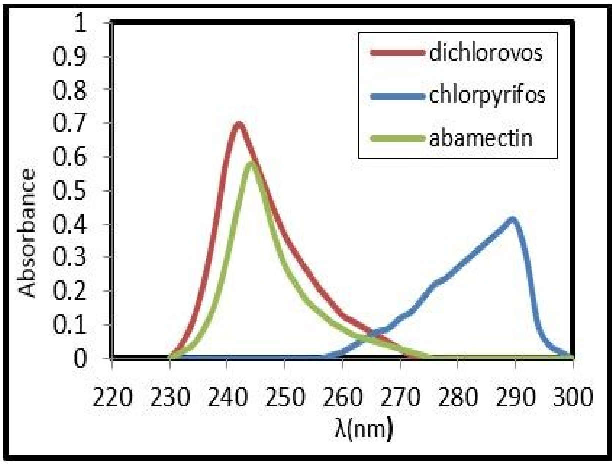

Fig. 6. UV- Visible Spectra of (chlorpyrifos, dichlorovos, abamect *in).*

Table (3-2). A comparison of obtained λ max of pesticides in this study and Literature.

Pesticide	Present study	Literature
Chlorpyrifos	290	230
Dichlorovos	242	216
Abamectin	244	239

3.8. *Effect of pH*

Since hydrogen ions affect the surface charge of the adsorbents and the adsorbate species, the sorption is greatly affected by the variation of solution pH. In order to investigate the effect of pH on adsorption of pesticides onto PHETA, experiments were performed with 100 ppm initial concentration of pesticides between pH 2 and 8 at 25 ^{0}C. As it seen from Figure (7, 8, 9) adsorption decreased with increasing pH. It was observed that the adsorption is highly dependent on pH since it has strong influence on the surface charge of the adsorbent. Attraction forces between more positively charged surface and pesticides are responsible for increasing adsorption with decreasing pH, the optimal pH value was determine as 2, this is due to the increase in the number of positive ions in the acid medium, which increase in the number the probability of hydrogen bonds between

International Journal of Innovation in Science and Mathematics
Volume 6, Issue 4, ISSN (Online): 2347–9051

the charged groups and hydrogen on the polymer surface more than tendency to the solvent molecules. According to surface chemistry theory, polymer particles and pesticide molecules are both surrounded by an electric double layer due to electrostatic interactions. In the other hand, electrons functional groups performs mesomeric effect (-M) due to nitrogen and oxygen atom hydrogen sp3, and Inductive effect (-I) caused by methyl group. Additionally all this has proven affinity between positive surface of PHETA and pesticides.

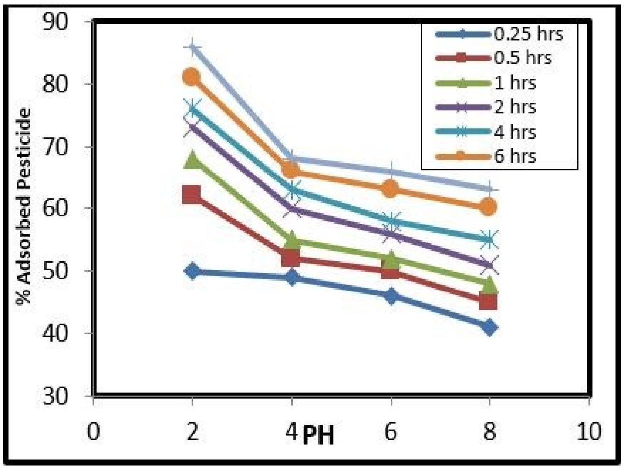

Fig. 7. Effect of pH on the chlorpyifos removal efficiency.

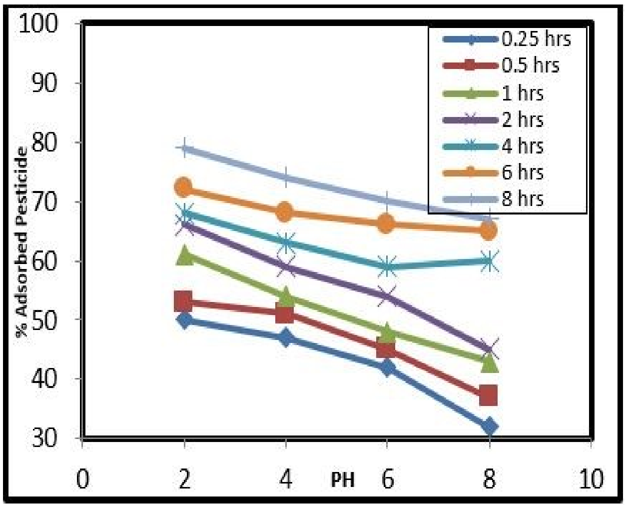

Fig. 8. Effect of pH on the dichlorvos removal efficiency.

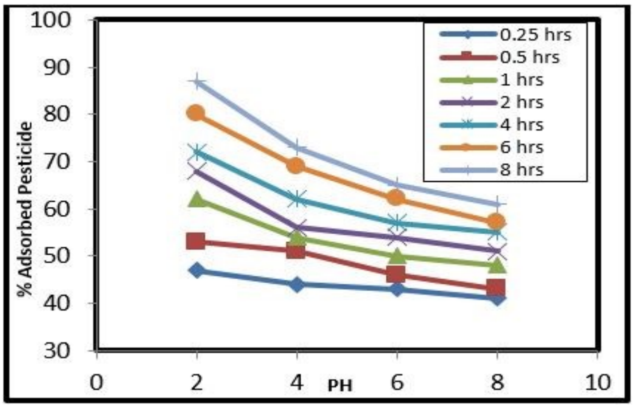

Fig. 9. Effect of pH on the abamactine removal efficiency.

3.9. *Effect of Contact Time*

The optimum period for the adsorption of (chlorpyifos, dichlorvos, abamectin) on PHETA can be observed by looking for the behavior of adsorption of pesticides solution after adding PHETA. Fig (10, 11, 12) shows the effect of contact time on the adsorption of pesticides using PHETA. The adsorption of (chlorpyifos, dichlorvos, abamectin) increases with increasing of contact time and attains equilibrium at about 8 h /200 rpm for an initial concentration 100 ppm of pesticides at pH 6. This behavior due to the availability of the active surfaces for adsorption. Initially, the number of active sites available for adsorption on the adsorbent surface is high but this number starts to decrease with the progress of adsorption. Finally, adsorption will stop when all active surfaces are covered with pesticides.

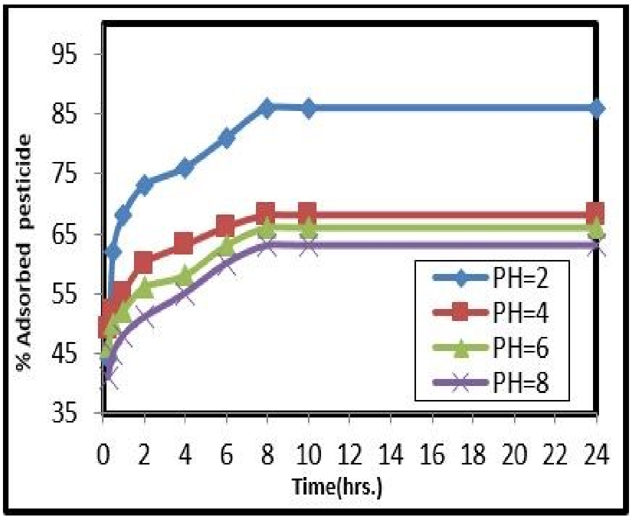

Fig. 10. Effect of treatment time on the chlorpyifos removal efficiency.

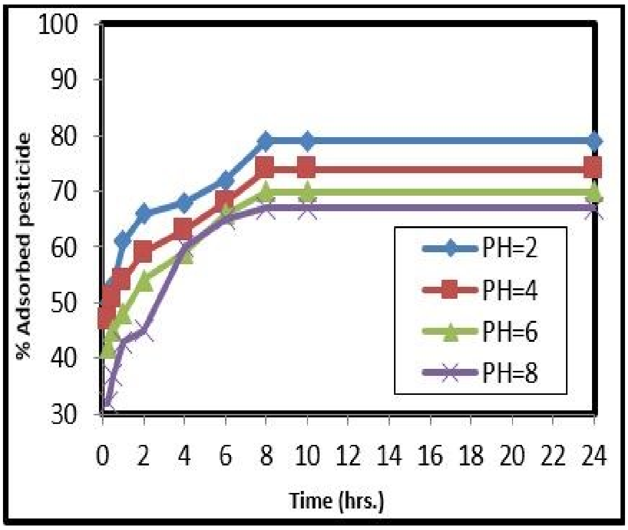

Fig. 11. Effect of treatment time on the dichlorvos removal efficiency.

International Journal of Innovation in Science and Mathematics
Volume 6, Issue 4, ISSN (Online): 2347–9051

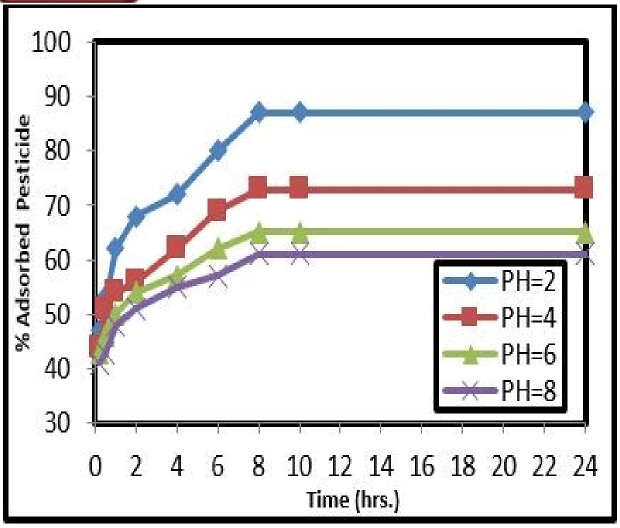

Fig. 12. Effect of treatment time on the abamactine removal efficiency.

3.10. *Effect of Temperature*

The effect of temperature on the removal of (chlorpyifos, dichlorvos, abamectin) in aqueous solution by PHETA was studied by varying the temperatures between 25 and 55C^0. The data presented in Figures (13) showed that adsorption efficiency of pesticides by the PHETA increased with increase in temperature with increasing temperature between 25 to 55 ^{0}C, however, the magnitude of such increase continues to decline as temperatures are increased above 55^{0}C. This can attributed to the increasing of pesticides spread inside the pores of PHETA with the temperature increasing between 25 to 55^{0}C and the saturation of PHETA surface with pesticides seems to be reached at 55^{0}C, after that most of the pesticides were removed at temperature above 55^{0}C because with increasing temperature, the attractive forces between PHETA surface and pesticides are weakened and the adsorption decreases.

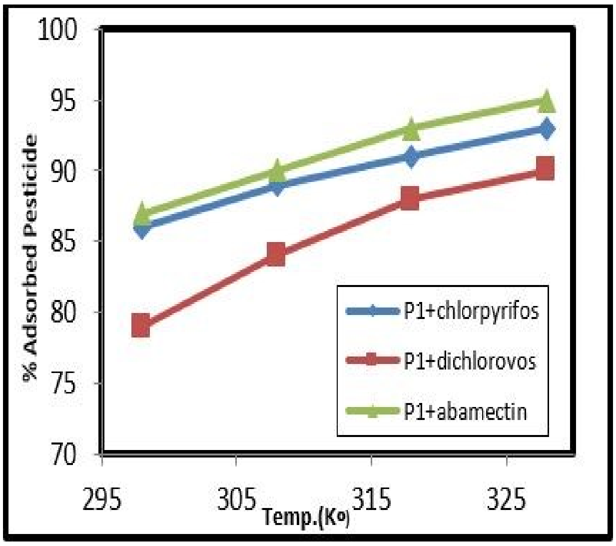

Fig. 13. Effect of temperature on the (chlorpyifos, dichlorvos, abamectin) removal efficiency.

3.11. *Desorption Study PHETA Polymer*

The desorption experiments were performed by suspending 0.1 gm of loaded polymer in 10 ml of ethylacetate and shaking on shaker at 200 rpm at 55^{0}C . After constant time intervals (0.5 – 24 hrs) the samples were filtered (Whatman filter paper No.42) and the filterate was analyzed by UV. visible spectrophotometer. Figure (14) shows the recovery percentage of the pesticides from the synthesized polymer PHETA as a function of the contact time with (ethylacetate). The obtained results show that the orders of recovery percentage of metal ions was in sequence:

Chlorpyifos > Dichlorvos > Abamectin

This could be related to the strong binding between polymer and pesticides.

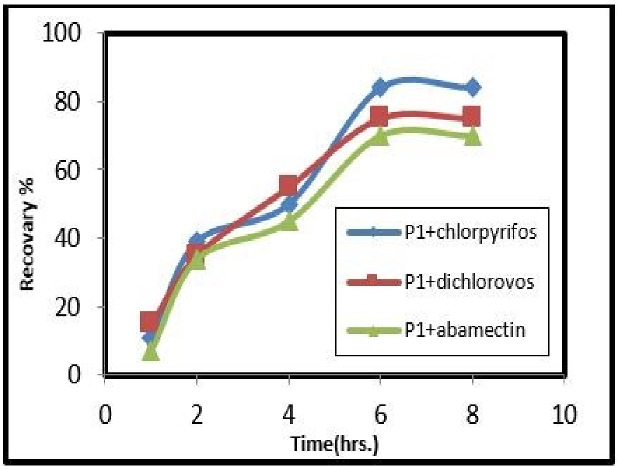

Fig. 14. Effect of time on pesticides recovery (chlorpyifos, dichlorvos, abamectin).

IV. Acknowledgment

The authors gratefully acknowledge the technical staff at chemistry department, college of science, university of Basra for their help with this work.

V. Conclusion

In the this study, effort is made to cultivate a simplified adsorption method to remove toxic pesticides from aqueous solution, Present study inspected local, cost effective and adsorbent i.e., soft drink bottles after aminplysis with monoethanolamine as a substitute of cheap adsorbent for the rejection of pesticides. The effectiveness of the adsorbent was analyzed by the conditions of pH, contact time and temperature. The suggested method was successfully engaged to remove investigated pesticides i.e. chlorpyifos, dichlorvos and abamectin from aqueous solution. Ethyl acetate was suitable solvent to recover the adsorbed pesticides from the surface of adsorbent. The adsorption efficiency of adsorbent was found practically constant after recurrent use of more than 5 times. It is, therefore, endorsed that costly synthetic adsorbent may be returning by these inexpensive and profuse adsorbent for the removal of toxic pesticides from water.

REFERENCES

[1] World Resources, "The Urban Environment", New York, Oxford University Press, p.128 (1997).

[2] Kluwe W M. Acute toxicity of 1, 2 – dibromo – 3 chloropropane in the F344 male rat. l. Dose response relationships and difference in routes of exposure, J Agric Food Chem, 59 (1981a) 71-83.

[3] Kluwe W M .Acute toxicity of 1, 2 – dibromo - 3 chloropropane in the F344 male rat. ll. Development and repair of the renal, epididymal, testicular. And hepatic lesions, J Agric Food Chem, 59(1981b) 84 -95.

[4] Face diffusivities using simple batch experiments. Fr Adsorption, 6(2000) 219 – 228.

[5] Ballesteros Martin M M. Sanchez perez J A. Garcia Sanchez J L, Montes de Oca L, Casas Lopez J L, Oller I & Malato Rodriguez S, Degradation of alachlor and pyrimethanil by combined photo – Fenton and biological oxidation J Hazard Mat. 155 (2008) 342 - 349.

[6] Miwa D W, Malpass G R P. Machado SAS & Motheo AJ, Electrochemical degradation of carbaryl on oxide electrodes, Water Res, 40(2006) 3281 -3289.

[7] Cristina S, Claudio Z, Mansilla H D & Mondaca M A, Imidacloprid oxidation by photo - Fenton reaction, J Hazard Mat, 150(2008) 679 – 686.

[8] Bonne P A C, Beerendonk E F, Van der Hoek J P & Hofman J A M H, Retention of herbicides and pesticides in relation to aging of RO membranes, Desalination,132(2000)189 –193.

[9] Ahmad A L, Tan L S & Shukor S R A, Dimethoate and atrazine retention from aqueous solution by nanofiltration membrances, J Hazard Mat,151 (2008) 71 -77.

[10] Viraraghavan T , Dronamrajum, Removal of copper , nickel and zinc from wastewater by adsorption using peat, J Environ Sci Health ,28(1993) 1261.

[11] Frimmel F H, Assemn macher M Sorensen M, Abbt – Braun G & Grabe G, Removal of hydrophilic pollutants from water with organic adsorption polymers – part I. Adsorption behavior of selected model compouns, Chem Eng process, 38 (1999), 601 - 609.