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Radiation -Adsorption Treatment of Pesticides by Using Pulp Wood and Pulp Bagasse

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ABSTRACT

Alkaline pulping of pulp wood and bagasse using sodium hydroxide resulted in the reduction of lignin from the wood and bagasse fibers and consequently increasing adsorption of the pesticide pollutants in these fibers. Three different types of pesticides were used in this study namely, metalaxyl, dicloran and arelon, which were irradiated at a dose of 4 kGy before adsorption treatment.The results show that moderate adsorption was observed for all pesticides when adsorption was carried out without alkaline pulping and irradiation. This is due to the presence of lignin which retards the adsorption process. Batch sorption experiments at different pH values (3, 7, 9) for the retention of these pesticides by pulp wood and pulp bagasse fibers indicated that sorption is governed by the interaction of the ionized form of these compounds with the polyhydroxyl structure of cellulose. The study shows that alkaline pulping of pulpwood and bagasse improves their ability towards adsorption of the pesticide molecules degraded by radiation.

Key words: Radiation-Adsorption -Pulp wood- Pulp bagasse- Pesticides

INTRODUCTION

Alkaline pulping of pulp wood and bagasse at elevated temperatures liberates a phenolic hydroxyl group. Alkaline hydrolysis includes consumption of alkali in the reaction with lignin, carbohydrates and extractives. The degree of fragmentation of lignin observed in alkaline and kraft pulping is much lower than that indicated by hydrolysis. This is due to the condensation reaction of partly degraded lignin which competes with the nuclophiles supplied by the cooking liquor (S, SH and OH) for the reactive sites in the lignin generated during the pulping process, particularly for methylene- quinone intermediates. The role of additives in alkaline pulping (in case of bagasse) has been studied for several years.[1-3]

In the present study, an attempt is made to explain the degradation kinetics due to the irradiation of aqueous solutions of some active ingredient pesticides. A combined treatment by gamma irradiation and conventional methods was applied. Factors affecting the radiolysis of the pesticides such as irradiation dose, pH of the solutions were studied. The effect of different additives such as oxygen and ozone on the degradation process was investigated. Also, the equilibrium isotherms and the intraparticle diffusivities were investigated using batch experiments for determining the adsorption of aqueous solutions of pesticides onto pulp wood and pulp bagasse.

EXPERIMENTAL

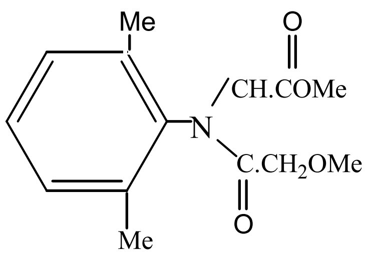
a - Pesticides :

Each of the following pesticides was prepared initially by dissolving 10 mg in 1 ml acetone and then diluted up to one liter of bi-distilled water. The concentration of the pesticide was measured and determined by UV- Spectrophotometry.

1- Acetylalaninate Group of Fungicide :

- Metalaxyl $C_{15}H_{21}NO_4$ (M.Wt: 279.3)

It was supplied by Ciba - Geigy Germany. It is a crystalline solid, m.p. 71-72^{0}C . Its solubility at 20^0 C is 7.1 g/L, soluble in most organic solvents.

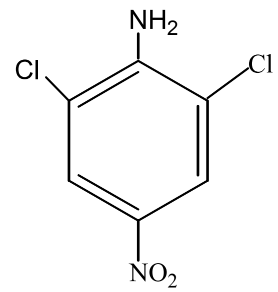


Metalaxyl

2-Nitroaniline fungicide : 2, 6- dichloro-4- nitroaniline

- Dicloran $C_6H_4CI_2N_2O_2$ (M.Wt: 208)

It was supplied by the Boots Co. Ltd. It is a brownish yellow powder and is practically insoluble in water, moderately soluble in polar organic solvents e.g., 34 g/kg acetone.

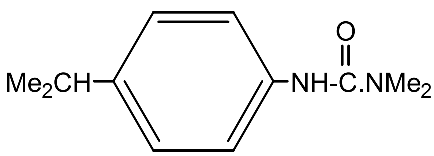


Dicloran

3-Phenyl Urea Group of Herbicide

- Arelon or Isoproturon $C_{12}H_{18}N_2O$ (M.Wt: 206.3)

It was obtained from Ciba Geigy Germany. It is a colourless powder, m.p. 155-156˚C. Its solubility at 200 is 55 mg/L water; soluble in most organic solvents.



Arelon

b- Adsorbents:

1 - Bagasse

The depithed bagasse used in this study was supplied by El- Nasr - Edfo Co. (Egypt) in a dry condition and cutting form. Average cut size as received was as follows: length 1.0 to 4.5 cm, width 0.4 to 5 mm and thickness 0.3 to 1 mm. Chemical pretreatment : 80 g of bagasse cuttings with a roughly 50% moisture content were mixed with 800 ml of solution of 32 g (NaOH) and 0.1% anthraquinone for each gm bagasse in a round flask fitted with condenser and the temperature required is controlled by a thermostate. Cooking was carried out for about 6 hr at 150^0C. After cooking, bagasse was washed with distilled water until free from excess NaOH , and subsequently refined, after being stored at room temperature.

2 - Pulp wood.

Pulp wood used in this study was supplied by National Research Centre, Cairo, Egypt. The samples were grinded by a laboratory grinder to 40-60 mesh. For each g pulp wood 5 g NaOH was pulped in a round flask fitted with condenser and the temperature required was controlled by a thermostate. Pulpping was carried out for about 6 hr. at 150^0C. After cooking, the pulp wood was washed with bi-distilled water until excess NaOH was completely removed, and subsequently refined, dried before being stored.

3 - U.V. Spectrophotometry.

The concentration of pesticide solutions was determined by measuring the absorbance at different wavelengths: 268, 464 and 242 nm for the compounds 1, 2, 3, respectively. Optical density measurements were carried out against blanks of the individual solvents at room temperature (25 ^{0}C). The instrument with a single beam U.V. visible spectrometer: Milton Roy spectronic 1201, U.S.A. was used.

RESULTS AND DISCUSSION

Irradiation of pesticides

a- Air-saturated solution

The effect of radiation dose on the different pesticide solutions at an initial concentration of 5 mg/L (pH7) was studied and the results are shown in Fig.(1). It can be seen that the radiation degradation of Dicloran (fungicide) is somewhat higher than that of Arelon (herbicide). Dicloran was 82% destroyed at a dose of 10 kGy, while Arelon showed a 75% destruction. This is in a good agreement with the results reported by **Cappadona et al.[(4)].** For chlorinated pesticides, hydrochloric acid was detected (pH of the pesticide solution decrease). Metalaxyl fungicide was degraded to a very low extent (5%) by gamma irradiation up to a dose of 10 kGy. The difference in behaviour of the pesticides (pollutants) may be attributed to the difference in their structure. It was reported by many authors[5,6] that low doses of gamma radiation has produced considerable destruction of pure parathion. **Cappadona et al.**[4] used commercial pesticides that are generally prepared with mixtures of active agents and different additives such as Lindane, Dieldrin and DDT, and found that the active agent was destroyed to 50, 79 and 49% at a dose of 3 kGy, respectively. This difference in behaviour of the different pesticides towards gamma -irradiation was also reported by **Shubin et al** [7] who attributed it to the difference in the structure of the different pesticides. Arelon was almost destroyed with the formation of hydrochloric acid which lead to a decrease in the pH of the pesticide solution, i.e. the chlorine atoms of the pollutants were very sensitive to gamma radiation. Metalaxyl which contains nitrogen showed high resistance to gamma irradiation than all the other pesticides studied.

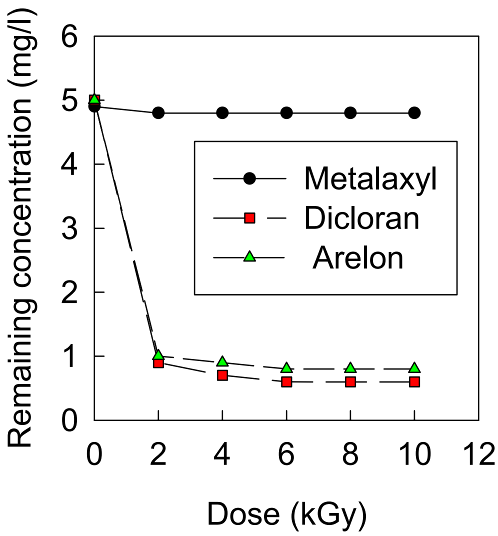


Fig.(1)Relationship between gamma-irradiation dose (kGy)and the remaining concentration (mg/l)at

b-Effect of pH

Figures (2-4) show the effect of the pesticide solution pH on the percent degradation at concentration of 5 mgL^{-1} as a function of irradiation dose (2, 4, 6, 8 and 10 kGy) carried out in air. The pH influence has proved to vary according to the type of the pesticide. The observed behaviour of the influence of pH on the degree of degradation should be expected, based on the acid base properties of the primary radical species and structure of the pesticide molecule[8]. It is known in fact that, the radiolysis of water in neutral range of pH leads to the efficient formation of e^-_{aq} , H and OH radicals and H_2 and H_2O_2 molecules.

In acidic aerated medium the following transformations occur:

$$e^-_{aq} + H \longleftrightarrow H^{\cdot} \quad (1)$$

$$O_2 + H \longleftrightarrow HO^-_2 \quad (2)$$

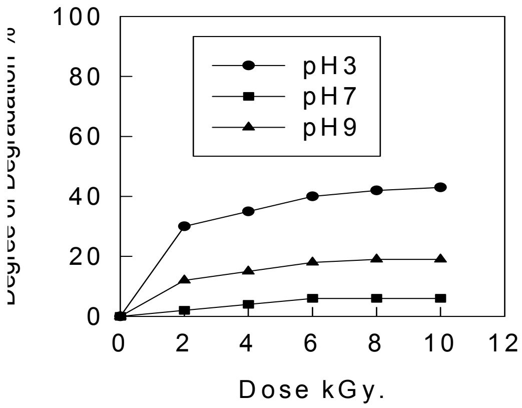
In basic aerated medium, the following transformations take place.

$$H^- + OH^- \longleftrightarrow H_2O\ ,\ e^-_{aq} \quad (3)$$

$$O_2 + e^-_{aq} \longleftrightarrow O^-_2 \quad (4)$$

The decrease in the degree of degradation over the pH range 7 to 9, suggests that O_2 radical is less reactive towards attack on pesticides than HO_2 radical as well as towards the dissociation of OH radical in basic solutions to O^- and H^+ . This suggests that the degradation in acidic medium (where HO_2 radical concentration increases) should be higher than that in neutral and alkaline media.

The pH value decreases as the irradiation dose increases. The drop in the pH value of the irradiated pesticide solutions suggests that the pesticide molecule is degraded to lowe molecular weight compounds, such as organic acids. [9] It was also observed that the pH of the pesticide solutions affectes its degradation without irradiation. Metalaxyl, Dicloran and Arelon showed a somewhat higher degradation ranging from (4-15%) in an alkaline medium.



(2): Effect of gamma irradiation dose on

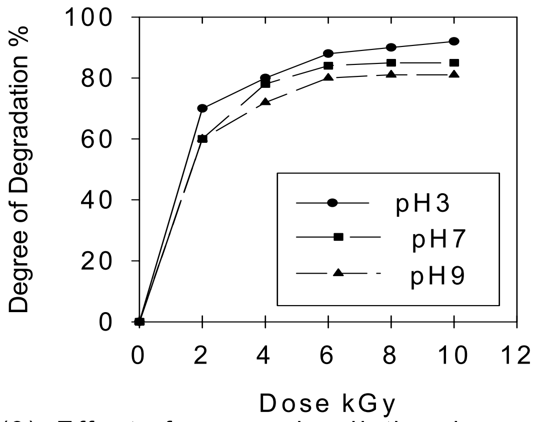


fig (3): Effect of gamma irradiation dose on

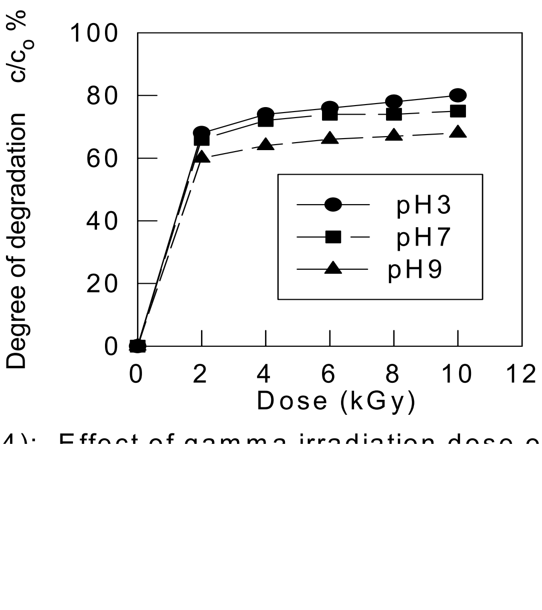


Fig (4): Effect of gamma irradiation dose on the

2- Oxygen addition

The degree of radiation degradation of the oxygen- saturated pesticide solutions was investigated at different pH values as a function of irradiation dose and the results are shown in Figs (5-7). The addition of oxygen resulted in an enhancement of the radiation degradation of the pesticide solutions. The extent of this degradation was different for the different types of pesticides. Metalaxyl suffered the highest degree of degradation due to the presence of oxygen, while Dicloran and Arelon showed a moderate enhancement in degradation. In most cases the radiation degradation of the pesticides was higher in the acidic medium followed by that in neutral medium and then that carried out in alkaline medium. The gamma irradiation of the pesticide solutions leads to the formation of radicals formed from the radiolysis of water:

$$H_2O \xrightarrow{\gamma\text{-rays}} HO,\ H,\ e^-_{aq},\ H_2O_2,\ H_2$$

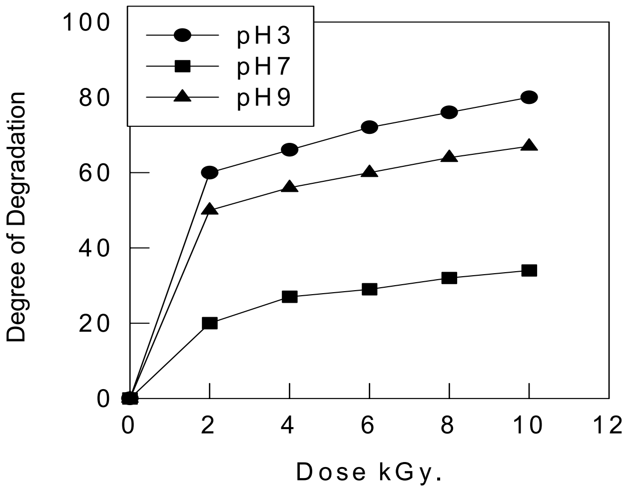
In the presence of oxygen, the hydrogen atoms react rapidly with oxygen, leading to the formation of the oxidizing HO_2 radical.

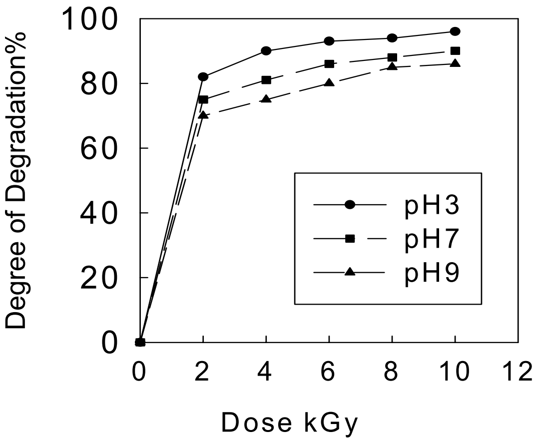
$$H + O_2 \longrightarrow HO_2$$

Also, the O_2 radical is formed according to the following equation.

$$e^-_{aq} + O_2 \longrightarrow O_2$$

According to **Suzuki et al.,** [9-10] in addition to the primary OH radicals, these species (HO_2 and O_2) contribute to the degradation process and this process in the presence of oxygen leads to the formation of peroxides which contribute also to the degradation reactions.





Fig(6): Effect of gamma irradiation coupled with

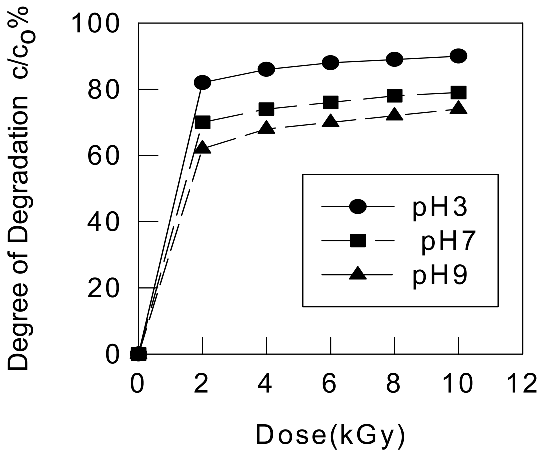


Fig.(7) Effect of gamma irradiation coupled with

3- Ozonolysis

It is well known that ozone is a powerful oxidant and it can react with organic and inorganic molecules in solution both directly and indirectly via its aqueous phase degradation products such as hydroperoxyl and hydroxyl radicals.[(11)] The ozone-saturated pesticide solutions were also studied : The degree of radiation degradation of these solutions was determined at various pH values as a function of radiation dose and the results are shown in Figs (8-10). The addition of ozone resulted in enhancement of the radiation degradation of the pesticide solutions. The extent of degradation depends on the type of the pesticide. Thus, in the presence of water in either the gas or aqueous phase, ozone will photolyze to produce hydroxyl radicals, which are stronger oxidizing agents. Therefore, the combined ozone- gamma irradiation process greatly enhances the degradation of organic compounds more than an ozone process alone. These results are in good agreement with previous results which showed an enhancement of the radiation- degradation process in the presence of oxygen as well as the presence of ozone[(13,14, 15)].

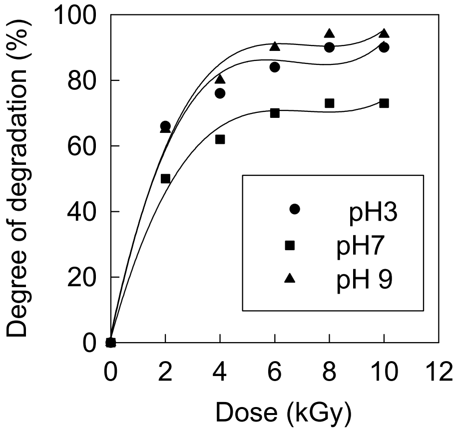


Fig.(8): Effect of gamma - irradiation coupled with ozone saturated solutions on the degree of degradation of metalaxyl at different pH values.

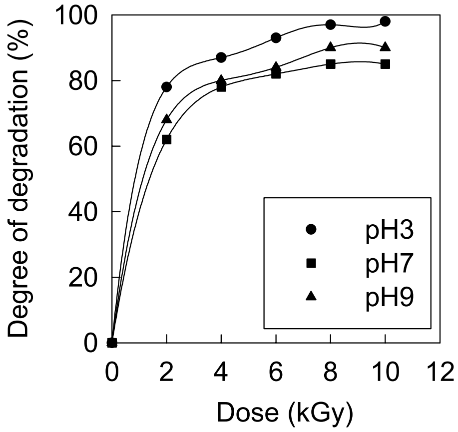


Fig.(9): Effect of gamma - irradiation coupled with ozone saturated solutions on the degree of degradation of dicloran at different pH values.

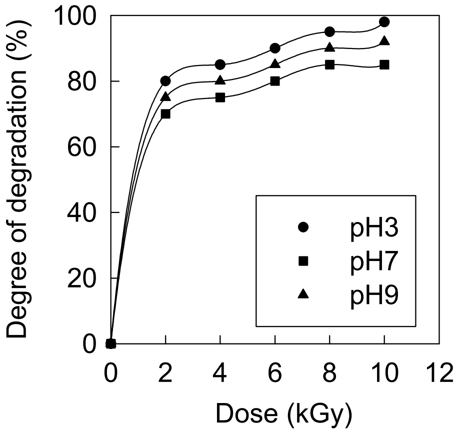
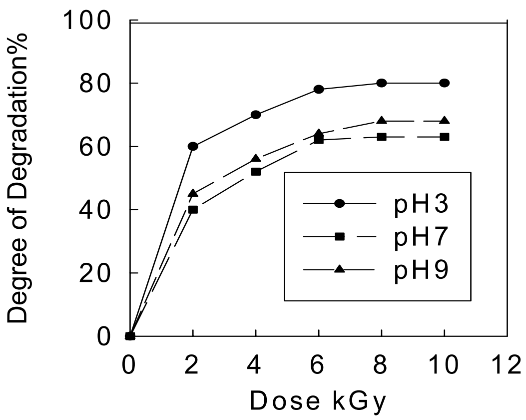


Fig.(10): Effect of gamma - irradiation coupled with ozone saturated solutions on the degree of degradation of arelon at different pH values.

- Electron beam irradiation :

Aqueous solutions containing pesticides at initial concentration of 5 mg/L and of different pH values were irradiated in air using an electron beam accelerator (1 MeV) to study the compounds degradation. The samples were irradiated with different doses ranging between 2 and 10 kGy. The electron beam irradiation treatment efficiency was evaluated by U.V. measurements of the samples before and after irradiation. Figs.(11-13) show the relationship between the electron beam irradiation dose and the degree of degradation of the three pesticides at various pH values. It can be seen that at a dose of 6 kGy Dicloran reached a maximum degradation of 86% which was a little higher than the value obtained when irradiation was carried out with gamma rays under the same conditions. In case of Arelon, high degradation was observed by electron beam (96%) ,whereas gamma radiation showed 80% degradation. However, electron beam irradiation proved to be more effective than gamma irradiation in case of Metalaxyl, in which the degree of degradation using gamma rays was 43% at a dose of 6 kGy, while by using electron beam irradiation it was raised to 80% at pH 3. The efficiency of electron beam irradiation is obviously greater than the degradation by gamma irradiation.



Fig(11): Effect of electron beam dose on the

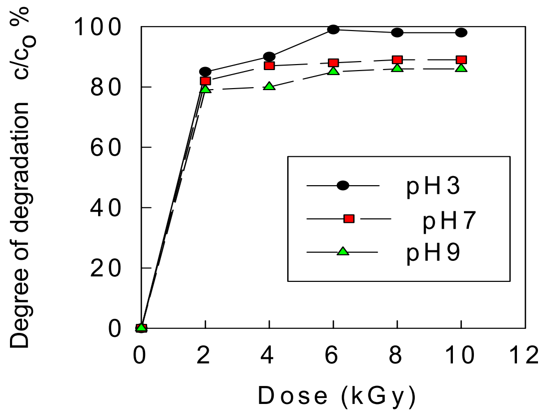


Fig.(12) Effect of electron beam irradiation dose on

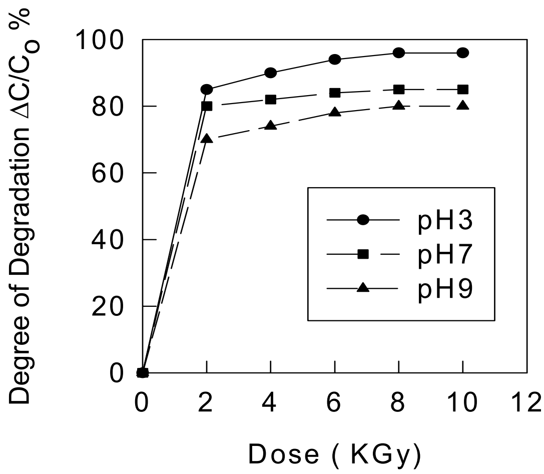


Fig (13) :Effect ofelectron beam dose on the

γ- Irradiation followed by adsorption purification

Aqueous pesticide solutions at different initial concentration (3, 4, 5, 6, 7 mg/L) were irradiated at a dose of 4 kGy and the remaining concentration after irradiation is shown in Table (1). Adsorption experiments were carried out with pulp wood and pulp bagasse after gamma-irradiation (4kGy) at different pH values to study the adsorption behaviour of the three pesticides. The results in Table (3) show that moderate adsorption was observed for all pesticides when adsorption was carried out without alkaline pulping and irradiation indicating that adsorption alone is not enough to achieve complete removal of these toxic pollutants. This is due to the presence of lignin which retards the adsorption process.

A processed wood fiber is a composite structure mainly from cellulose and lignin. The chemical differences between these components result in significant variability in their ability to interact with water. The polyhydroxyl structure of cellulose provides strong hydrogen bonding, while lignin's phenylpropane units produce relatively hydrophobic regions. There is evidences [15-16] that these variations in sorbent hydrophilicity strongly impact its retention of organic chemicals, significant reductions and even the elemination of sorption which occurs with increasing sorbent oxidation levels. Batch sorption experiments for the retention of the three pesticides by pulped wood fibers and bagasse indicated that sorption is governed by the interaction of the acid form of these compounds with lignin. Measurements also indicate that sorption is unaffected by fiber surface area and concentration, but it do show dependency on the concentration of colloidal materials. [17]

Comparison with cellulose and lignin model particles as sorbents demonstrate that aqueous toluene and trichloroethylene have a higher affinity for lignin. This indicates that lignin may dominate the sorption of non-polar organic species to pulp fibers and fiber solids. The presence of an ionizable group creates the potential for both hydrogen bonding and interaction between the compounds ionized form and fiber surfaces. It is generally noted that the hydrogen bonding can increase adsorption. [18-19]. Some studies report an increase of sorption with greater sorbent oxidation levels, while others report either no effect or a decrease. This may indicate that sorption enhancement due to the creation of specific bonding sites may be offset by the sorbents increased hydrophilicty.

Alkaline pulping results in fragmentation of lignin and an increase in the cellulose composition percent as shown in Table (2) according to Tappi standards, T222 50-54, where hydrogen bonding dominate and improves the adsorption process as shown in Table(3). The difference in the amount adsorbed depending on the physicochemical characteristics of the different pesticides, degraded pesticide molecules and the effect of the charged functional group on the sorption , are expected to be significant where ionized organic compounds are much more water soluble than their conjugate acids. Experiments on model compounds showed that the reducing additives in soda pulping act as antioxidants by preventing the formation of lignin oxidation intermediates, which take part in polymerization reaction.(17-20) It was found that the extent of inhibition of the process leading to an increase in the mass of lignin correlates to the redox potential of the additive. (21)

In agreement with these views, **Fleming et al.**(20) proposed a pathway for alkaline delignification with additives as a complex of oxidation reductions. **Fullerton** (21) reported that addition of anthraquinone produces an identical acceleration in the rate of pulping, which indicates that anthraquinone plays a vital role in the mechanism involved in anthraquinone pulping.

pH dependency and pesticide adsorption :

Table (3) shows the removal percentage of pesticides before and after radiation-adsorption treatment at different pH values. It can be seen that more adsorption took place at pH 3 than at pH 7, while in an alkaline medium it showed the lowest degree of adsorption (22).

This behaviour of the different pollutants and their dependence on the pH of the solutions was investigated by many authors, (22-23) who reported that more species were adsorbed in acidic medium which may be due to the fact that the uptake by changing the pH value is greatly affected by the ions of pesticide solutions since it helps the migration of these charged particles to be diffused or distributed within the pulp fibers.

It may be concluded that a combined treatment of radiation followed by alkaline pulping by pulp wood and bagasse improve the process of adsorption of pesticide molecules from wastewater and minimize their concentrations in surface water to a great extent.

Table(1):Remaining concentration of pesticides after irradiation at a dose of 4 kGy

Pesticides	Metalaxyl	Dicloran	Arelon
3 mg/L	2.88 mg/L	0.6 mg/L	0.84 mg/L
4 mg/L	3.80 mg/L	0.8 mg/L	1.12 mg/L
5 mg/L	4.80 mg/L	1.0 mg/L	1.40 mg/L
6 mg/L	5.70 mg/L	1.2 mg/L	1.68 mg/L
7 mg/L	6.70 mg/L	1.4 mg/L	1.96 mg/L

Table (2): Composition percent in dry base for pulp wood and bagasse before and after pulping

Composition Percentage	Lignin		α-Cellulose		Ash	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
Bagasse	**16.8%**	**6.8%**	**42.2%**	**75.2%**	**4.8%**	**0.5%**
Pulp wood	**24.6%**	**13.2%**	**48.5%**	**70.6%**	**9.4%**	**1.2%**

Table (3): Removal percentage of pesticides before and after radiation-adsorption treatment at different pH values.

Pesticide	*Removal % before treatment*						*Removal % after treatment*					
	pulp wood			*pulp bagasse*			*pulp wood*			*pulp bagasse*		
	pH3	*pH7*	*pH9*	*pH3*	*pH7*	*pH9*	*pH3*	*pH7*	*pH9*	*pH3*	*pH7*	*pH9*
Metalaxyl	*39%*	*36%*	*34%*	*44%*	*40%*	*33%*	*83%*	*81%*	*75%*	*88%*	*84%*	*80%*
Dicloran	*40%*	*38%*	*32%*	*42%*	*39%*	*35%*	*95%*	*93%*	*90%*	*96%*	*94%*	*92%*
Arelon	*44%*	*40%*	*38%*	*47%*	*43%*	*38%*	*90%*	*88%*	*84%*	*93%*	*89%*	*87%*

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