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Elimination of Organophosphorus Pesticides from Wastewater on Fiber Cotton Waste: Kinetic Models Approach

Mourad Djeziri[1, 2] and Mohamed-Zine Messaoud-Boureghda[2*]

[1]*Center for scientific and technical research in Physico-Chemical Analysis (CRAPC); BP 384 Bouismail, Tipaza, Algeria*
[2]*Research Laboratory, Food Technology, Faculty of Technology, University M'hamed Bougara of Boumerdes 35000,Algeria*
**E-mail: mz.boureghdai@univ-boumerdes.dz*

Abstract: The objective of this work is therefore, to study the removal of three organophosphate pesticides (diazinon, fenthion and malathion), by their adsorption on waste cotton. The waste fiber cotton was characterized using FTIR, XRD, BET and SEM techniques. The effects of pH, contact time, adsorbent dose, initial concentration, temperature and ionic strength were evaluated and the removal efficiency of each parameter was established. The adsorption isotherms on waste cotton fibers, for concentrations of malathion and fenthion chosen for the initial experimental data, were interpreted by the Redlich-Peterson and Langmuir models. The Redlich-Peterson and Langmuir models for malathion retention for grafted cellulose. The results of the kinetic study for all pesticides showed that retention was extremely rapid. In fact, the linear regressions showed that the pseudo second order model monitors both the kinetics for diazinon and the pseudo first order model monitors fenthion, thus, malathion. This was clearly confirmed by the corresponding correlation factor values for each model.

Keywords: Solid waste, Cotton, Adsorption, Wastewater, Textile, Kinetics equilibrium, Pesticides, Organophosphorus

The reduction of pollution sources is, a major obligation for the environmental protection, this to encourage industrials for improving the development of new processes of anti-pollution and new control methods (Dubey et al 2015, Po-Hsing et al 2021). The use of water for human consumption, irrigation or discarded in the wild become major concern for all national and international organizations. The discharge of industrial wastewater containing toxic residues increasingly complex for the natural environment and threat the ecosystem and biotopes (Mhara et al 2021, Jill et al 2019, Theano et al 2021) and especially the human being. to preserve environment for future generations we must comply with international standards and regulations. Among these harmful chemicals, pesticides are used for control of weed. insects and diseases which are responsible for losses (Joop et al 2018, Rajveer et al 2019, Imran et al 2019, Hassaan et al 2020, Feng-Jiao et al 2020). Organophosphorus pesticides have replaced organochlorinated compounds this is due to their long-term stability (Bumbăcilă et al 2020). The removal of organophosphorus compounds at low concentration levels from water always constitute a technological and environmental problem, Because these pesticides contain different ratios of carbon , nitrogen, sulfur, and oxygen atoms in their structure and they are connected to a central phosphorus atom. Among the methods tested are oxide surface catalyzed hydrolysis (Sinar et al 2020). Many techniques have been developed for pollutant removal, such as electrochemistry (Sughosh et al 2018), biodegradation (Purbasha et al 2020) membrane techniques (Saravanann et al 2021), photocatalysis (Thien et al 2020), oxidation (Harald et al 2019) and adsorption (Cosgroveet al 2019, Costantino et al 2020, Iman et al 2020). Among these removal methods, the adsorption has been recently considered a highly attractive technique for the removal of organophosphorus pesticides, as it is easy, low-cost and ecologically friendly. In a standardized atmosphere has high capillarity, cellulose in various physical forms can absorb up to 10% moisture, has a great absorbency. The cellulose has a high affinity for water (hydrophilic) and is the most abundant organic substance in nature (Lei et al 2019). The homopolysaccharide composed of β-D-glucopyranose units linked together by a glycosidic bond β- (1- 4) (substitution of a hydroxyl group (OH) monovalent radical) of the hemiacetal of a sugar with a hydroxyl group of an alcohol of another sugar (Algarra et al 2019, Ibrahim et al 2019). Pesticides are highly toxic, hazardous to the environment and human health when they are transport-ted by sewage (Shalaby et al 2019, Sabran et al 2021) and currently, their separation is the subject of very serious concern. In this study, on absorption and retention of organic pollutants, mainly organophosphorus pesticides malathion (Ma), diazinon (Di) and fenthion (Fe), which are used now, because they are less harmful environment, the influence of physicochemical parameters on the adsorption capacity of pesticides .this according to the spatial chemical structure and physicochemical characteristics (weight-mass-dimensions-volume etc.) of our biomaterial. In addition, tested the material under real conditions after physico-chemical characterization of wastewater (STEP Reghaia-Algeria).

MATERIAL AND METHODS

Adsorbents: Malathion [Ma] [O,O-dimethyl-S-(1,2-dicarbethoxy) ethyl phosphorodithioate] is a widely used non-systemic insecticide and acaricide that exhibits low mammalian toxicity is an pesticide with a molecular formula of $C_{10}H_{19}O_6PS_2$, and is a derivative of phosphor-di-tuning acid (Ravindran 2019), 31(Rani and al 2017) (Fig. 1 and Table 1).

Diazinon [Di] [O, O-diethyl O-(2-isopropyl-4-methyl-6-pyrimiinyl) phosphorothioate] is a moderately persistent organophosphorus pesticide largely used in agriculture (Eunseon and al 2016a). Fenthion [Fe] O, O-dimethyl O-[3-methyl-4-(methyl-thio) - phenyl] phosphorothioate is one of OP insecticides. It is also moderately toxic to mammals (Wismer 2018) (Eunseon 2016b)

Adsorbent: The choice of cotton is also motivated as raw cotton contains about 87% cellulose, but after treatment it rises to 98-99%, and it has a very high quality hydropyle and material available and inexpensive (Pelegrini and al 2019, Ortega. and al 2019). Pesticides have a linear structure and planar synthesized with sulfonic groups to increase their solubility in water, they are particularly valued for dyeing cellulosic fibers (Fig. 2), this behavior allows the dye to bind on cellulose chains in cotton fiber, often by intermolecular bonding (including hydrogen). The specific area of cotton is 10-3 $km^2.kg^{-1}$- 13, 4.10-3 km^2. Kg^{-1} (Sudong and al 2019, Mäkelä. and al 2019)

For our study, used waste fiber cotton (WFC) from the textile factory DBK (Algeria). They are recovered at the beginning of the process of manufacture l (raw cotton) and after cutting the fabric, in the raw state, among the waste recovered at the unit DBK (carding waste, waste willow) as they contain less impurities, about 10 percent.

Cotton surface structure: The surface of the structure of cotton (Fig. 3), seen under an electronic microscope Dotopon Electronic, 5 MP USB 8), shows that the material has a certain porosity of different sizes, especially mesopores and micropores distributed unequally And which denotes its capacity to adsorb medium and large diameter molecules, which facilitates the flattened physical adsorption and

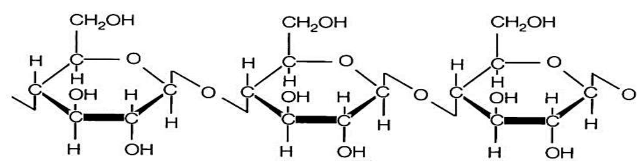

Fig. 2. Structural formula of cellulose

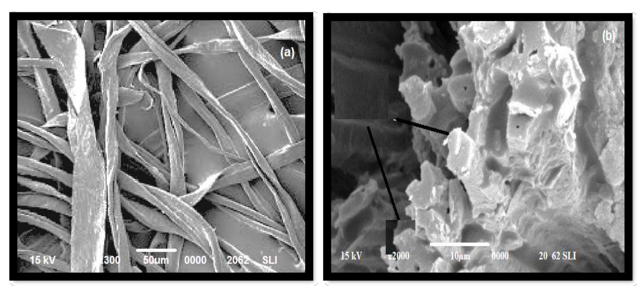

Fig. 3. Micrographics of fibers waste cellulose

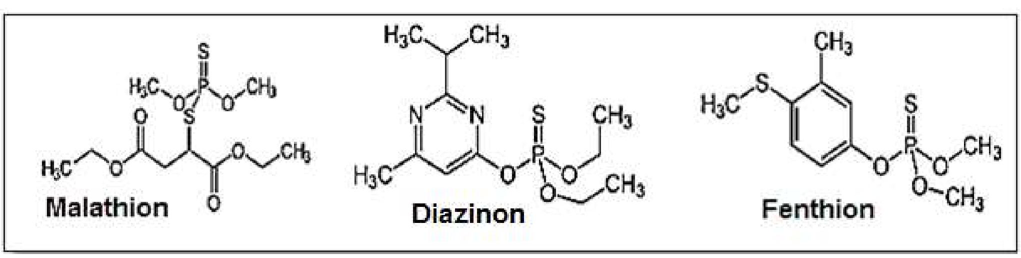

Fig. 1. Chemical formula of studied pesticides

Table 1. Characteristics of the three pesticides

Pesticides	Principal characteristics of pesticides				Topological polar
	Formule	Masse molaire	Masse volumique	Apparence	
Malathion	$C_{10}H_{18}O_6PS_2$	330.338	1.2	Liquid limpid –yellow to brown	128
Diazinon	$C_{12}H_{21}N_2O_3S_2$	304.346	1.1	Liquid colorless -oily	85.6
Fenthion	$C_{10}H_{15}O_3PS_2$	278.328	1.25	Liquidcolorless pur	85.1

exhibits a great increase in the area available for adsorption. This is probably due to the increase of porosity and the number of active sites leading to a slight swelling, allowing optimum permeability. This approach is confirmed by Lei Yang and Ferrero (Ferreira 2020, Jakob et al 2021, Mikko et al 2021a), without any real increase in the volume polymer used in the case where the adsorption is used in fixed bed.

Waste water characteristics: The raw wastewater was processed directly by adsorption with cotton waste. The TOC and COD and the Hydrocarbons largely decreased, without, reduction of the dissolved salts, a negligible decrease of the turbidity, probably due to the presence of very fine solids particles or oil drops (Table 2). The removal of pesticides in raw water and noted their concentrations before and after treatment (Table 3).

Determination of Zeta potential: To estimate the consequences of the modification of the interfacial properties of cellulose (surface tension) caused by the grafting agent "acrylic acid", Measurements of the zeta potential were carried out using Zetameter "Malvern Instruments", which measures the speed movement of a particle in a liquid within an electric field.

Determination of specific surface area: It was measured with a micromeritics ASAP 2420. Approximately 100 mg of WFC was kept at 105°C for minimum of 12 hours. The nitrogen adsorption method was conducted using a Perkin Elmer Sorptometer Model 21 2 C. Nitrogen adsorption and desorption were conducted at -196°C. The analysis of the specific surface area was calculated with the Brunauer, Emmett, Teller (BET) method (Mikko et al 2021b)

Effect of physicochemical parameters on the three pesticides: All the chemicals used for analysis were have an analytical grade with absolute purity (99.9%). To study the retention of pesticides by adsorption on FPC and GC, the experimental parameters studied are:

- Influence of physicochemical parameters (contact time, pH, the initial concentration, ionic strength of the retention of the three pesticides by varying one parameter at a time).
- Determination of the nature of the adsorption isotherm.
- Determination of the adsorption kinetics.
- The kinetics of adsorption was carried out by repeating the equilibrium study described previously, differing time of contact. The knowledge of equilibrium time was necessary for establishment of kinetic for adsorption models.

Table 2. Characteristics of wastewater (STEP of Reghaia-Algeria)

Parameters	Units	Values before treatment	Values after treatment
Temperature	°C	23.56	23.55
pH		6.55	6.99
COD	Mg/L	33500	201.23
TOC	Mg/L	1288	71.45
Hydrocarbons	Mg/L	54.56	28.12
Dissolve salts	Mg/L	897.23	895.12
Turbidity	NTU	721	87.56
Conductivity	u.s/cm	189.65	172.25

RESULTS AND DISCUSSION

Zeta potential: Zeta potential of pure cellulose is -24.34 mV. In addition, the effective charge of the cellulose fibers has gone from (−24.34 mV originally) to (+28.53 mV).

Specific surface area: The specific surface area measurements give a surface area varying from 25 to 28 g/m²

Characterization of WFC with Fourier Transformed Infrared Ray (FTIR): The results were confirmed by spectrophotometry infrared (Perkin Elmer 225) ,with the pelletizing technique in "KBr". Characteristic bands of the studied monomers for our samples confirmed the measurements (Fig. 1) confirmed these results. The absorption "peaks" (or bands), present in the transmission diagram, for our WCF is characterized by the common molecular bonding types and functional groups shown below. The WCF has cyclic bonds (weak acid) and unsaturated groups (double bonds) which are very suitable for the attachment of foreign elements to the structure.

The peaks are listed and detailed below.

3330- OH characteristic of the hydroxyl (OH) groups of

Table 3. Pesticides concentration before and after treatment on fiber waste cellulose with and without extraction and without settle able solids

Pesticides (mg/l)	Units	Before treatment	PA after treatment on cotton fiber waste				
			Percent	With settleable solids and extraction	Percent	Without settleable solids and extraction	Percent
Di	mg/l	75.821	68,45	20..801	91,52	2,256	97,02
Fe	mg/l	45.80	62,98	20.74	80,87	8,564	96,52
Ma	mg/l	41.256	39,81	14.5	52,15	0,076	93,95

cellulose, lignin (Deng 2022)

2897-CH_2- , =CH_2,methyl stretching vibration of C-H in cellulose and hemicellulose(Elisa 2020)

1621-The presence of water in the fibers at the band (Juntao and al 2018)

1428 -CH_2 symmetric bending of the cellulose

1364 bending vibrations of the C-H and C-O groups, respectively, of the aromatic rings in polysaccharides cellulose (Ornaghi 2020)

1315 -Hydrophobic alkyl radical

1033 -Primary alcohols the (CO) and (OH) stretching vibrations

895 -The presence of β-glycosidic linkages between monosaccharides (Balaji et al 2017)

X-ray diffraction analysis of WFC: X-ray diffractometer (D500 Siemens, Germany)was used in this study, operated at 40 kV and 40 mA at a scanning rate of 0.2°/min at ambient temperature (20°C). Figure 5 shows that for XRD plots, the maximum intensity peak is obtained at 22.7 of the 2h, which relates to the cellulose structure (Lizandro et al 2017, Orrabalisa et al 2019). The peaks at 14-16 and 34.4 are characteristics of cellulose (Kargarzadeh et al 2017,Tanpichai et al 2019),which corresponds to the (110), (0 0 2) and (0 0 4) diffraction patterns, these are characteristic of peaks of the Iβ form of cellulose 4 (Jankowska et al 2019, French et al 2020).

Effect of Physicochemical Parameters on the Three Pesticides

Effect of contact time on adsorption: The results presented in Figure 6, show that the retention of the three pesticides occurs in two distinct steps, the first step is slow, second is faster. The adsorption of Diazinon is fast, higher and reaches, Qe ranges, respectively, of 40 and 95 mg/g of retention, then it becomes stable when the equilibrium state is reached in 190 mn, For Fenthion , the retention is practically linear with a very low gradient and the rate of retention is really very low and does not exceed 45 mg/g after 200 mn.The retention rate for malathion is extremely low (10 mg/g), then a desorption process is observed. The spatial chemical structure and dimensions of the pesticides are probably responsible for this behaviour

Effect of initial concentration on adsorption: The initial concentration of pollutant has an important influence on the removal capacity of the solid matrix (De Gisi et al 2016, Aliyeh et al 2018). Forstudy, used concentrations of 5, 10, 20, 30, 40, 50, 60 and 100 mg/l.Ma,Fe and Diretention follows a same pattern, showing three steps adsorption, the first is very fast there , almost instantaneous (from 0 to 1 mg/g), the second step is parabolic and the third shows a saturation ,there is no substantial difference and seems to stabilize for malathion and fenthion (4.5 and 14 mg/g) and decreases appreciably for diazinon (Fig. 7). This can be attributed to the number of active sites of the adsorbent, which is constant (saturated pores) in increase in the number of molecules of polluting pesticides , except for malathion whose chemical structure presents very weak chemical bonds. This is due to molecules and the mode of attachment of the molecules which is "plane" by vertical by bonds (-O-, OH, ester,) at first

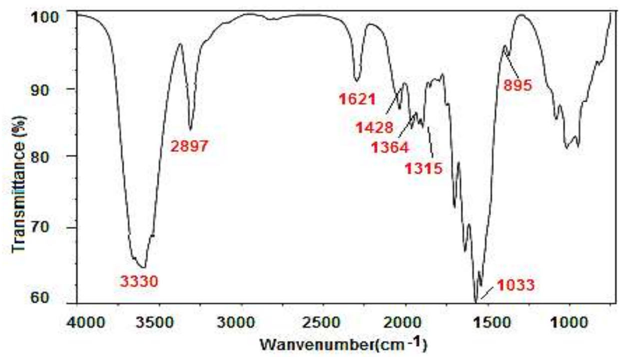

Fig. 4. Fourier Transformed Infrared Ray (FTIR) of fiber waste cotton

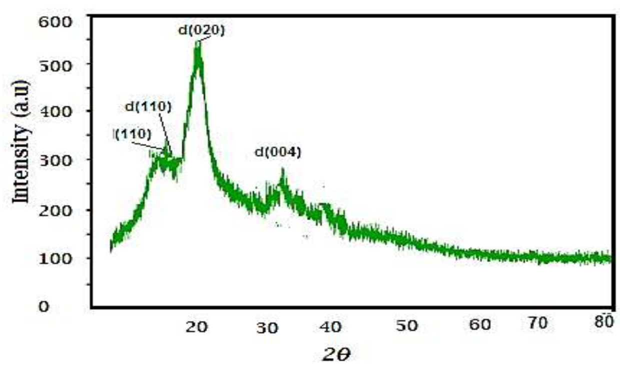

Fig. 5. XRD diffraction patterns of waste fiber cotton

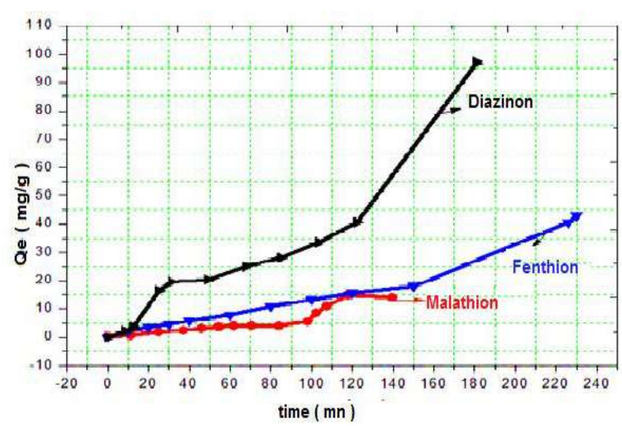

Fig. 6. Effect of contact time on the retention of Ma; Di, FeT ° = 20 ± 2 ° C, V agitation = 350 ; rpm, V = 25 ml, Time = 60 min, pH = 5.33

and in a second phase binds by double bonds and releases carboxylic ions; C-O, in the structure of the carboxylate and OH.(Brian et al 2017, Jiusheng et al 2017).

Influence of pH on the adsorption: The pH has a major influence on the removal process of pesticides from aqueous solutions, as it directly influences both the charge of the ionic species of the adsorbents and the nature of the surface (Fig. 8). The Figure 5, shows that in general the adsorption of pesticides is optimum at pH5 and diazinon is most influenced by pH, compared to the other two pesticides. The equilibrium removal capacity of diazinon increases with pH from 2 to 4.5, peaking at pH 4 and decreasing linearly to pH of 8. This is favoured by the presence of amide groups and protonation of the hydroxyl group on the adsorbent and the protonation of nitrogen atoms on the diazinon pyrimidine groups (Malakootian etal2021). In two other pesticides the influence of pH is very slight, the adsorption is between 2, 4 and 4.5 mg/g for fenthion and for malathion was 1.5 and 3.5 mg/g, showing a very low rate of elimination regardless of pH.It seems that the affinity of the studied organophosphorus pesticides towards the examined FWC decreases in the order diazinon- fenthion-malathion, this is due to their different physico-chemical characteristics (amide groups, surface-area) and this behaviour is influenced by the interference of chemical bonds in the active sites of the adsorber pore .

Influence of ionic strength on the adsorption : The efficiency of pesticide retention under the effect of ionic strength was studied as a function of the dose of sodium chloride salt (NaCl: 10, 30, 60, 120, and 180mg/l) added to solutions of three different ionic strengths (1, 2 and 3 Mole/l).The increase in ionic strength led to a decrease in the number of adsorbed pesticide molecules resulting from the competition between these pesticides and salt ions(Yong-Gu et al 2021, Magdalena et al 2021). The reduction in uptake is probably due to the activity of Na+ ions, which inhibit the approach of Ma, Fe, and Di, to the active sites and the affinity of the WFC adsorbent for Na+ ,as the electrical charge of sodium favours its fixation in microspores (Fig. 9).

Effect of temperature on adsorption : The adsorption of the three pesticides as a function of temperature (Figure 10)shows, that when varying the temperature in the interval 30-36°C at a concentration of 10 mg/L, for each pesticide, the adsorption initially increases, then decreases with increasing

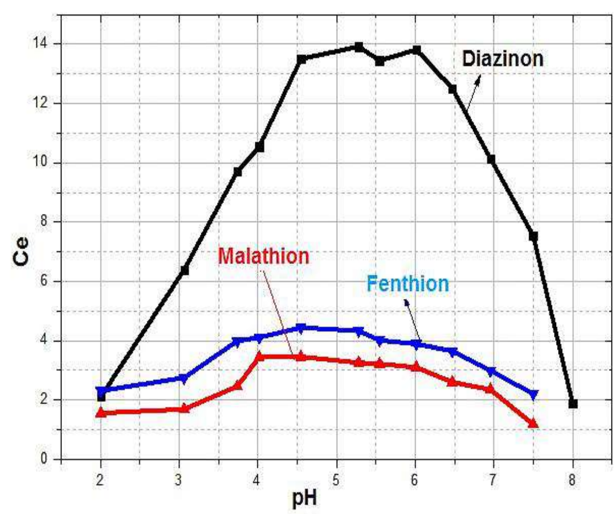

Fig. 8. Effect of the pH of the retention of pesticides (Ma, Di, and Fe). T ° = 20 ± 2 ° C, V agitation = 350 ; rpm, V = 25 ml, Time = 60 min, the retention of Copper ions: T ° = 20 ± 2 ° C, V agitation = 350

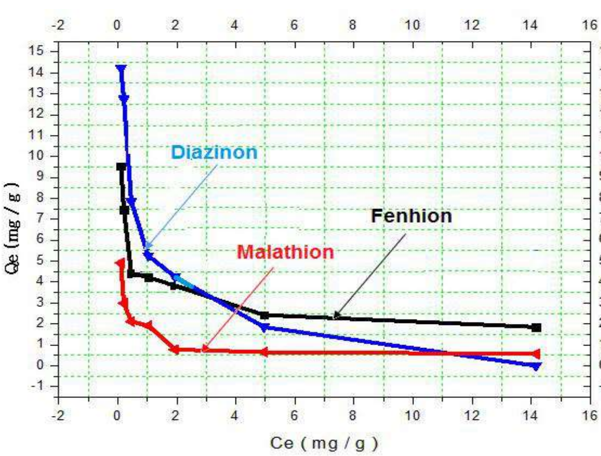

Fig. 7. The effect of concentation on the retention of (Ma, Di, Fe). T ° = 20 ± 2 ° C, V agitation = 350 ; rpm, V = 25 ml, Time = 60 min, pH = 5.33 the retention of Copper ions: T ° = 20 ± 2 ° C, V agitation = 350

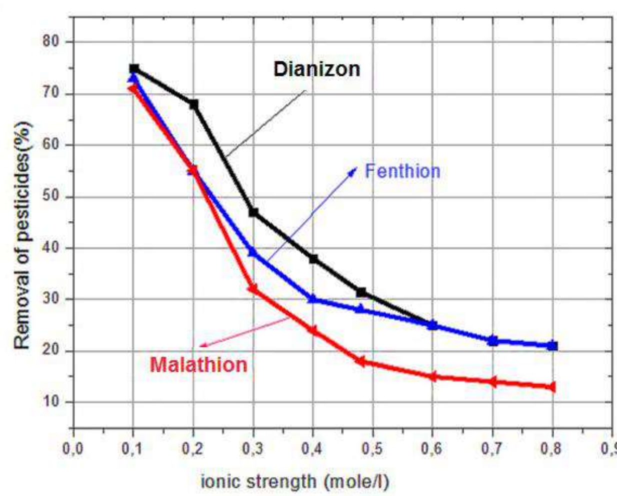

Fig. 9. Effect of pesticides rétention (Ma, Di, Fe). T ° = 20 ± 2 ° C, V agitation = 350 rpm, V = 25 ml, Time = 60 min, pH = 5.33

temperature, which suggests that their adsorption is an exothermic process. The followed by fention are the most adsorbed as temperature increases (35°C) and this may be due to their Topological Polar Surface Area Å² (85.1 , 85.6 and 128) (Table 1).

Validation of kinetic models: Kinetic data obtained for the adsorption process were analyzed based on the three most used models. In order to identify the retention mechanism for initial concentrations (C0 = 5 to 100 mg / L). The equilibrium concentrations of pesticides solutions were measured spectrophotometrically. The amount of pesticide adsorbed per unit mass of carbon-cloth, « qe », was calculated by Eq. (1),

$$q_e = V.\frac{C_0 - C_e}{m} \quad eq1$$

Where «V» is the volume of pesticide solution in l, «C_0» and Ce» are the initial and equilibrium concentrations, respectively, of the pesticide solutions in mg l^{-1} and m is the mass of the carbon-cloth in g. Eq. (1) gives «qe» in mg pesticide adsorbed per g carbon-cloth.

In order to make a detailed analysis for the adsorption data of the present work, some probable kinetic models were applied. These models include intraparticle diffusion, which can be formulated as.

$$q_t = k_i - t_2^1 \ eq2$$

Pseudo-first order, which can be formulated as

$$\ln c - \ln c_0 = k_1 t \quad eq3$$

and pseudo-second order which can be formulated as

$$\left(\frac{1}{C}\right) - \frac{1}{C_0} = k2.t \quad eq4$$

Where qt is the amount of adsorbate adsorbed at any time, «C_0» is the initial concentration of adsorbate, «C» is the concentration of adsorbate at any time, « it» is time and «ki, k_1 and k_2»are rate constants for diffusion, pseudo-first order and pseudo-second order models, respectively. «q_t» is obtained from «c_0» -and «c» values by the following equation:

$$qt = \frac{(C_0 - C).V}{m} \quad eq5$$

The kinetic data obtained for the adsorption process was analyzed for the six models in Table 4

- **First-order pseudo model:** The validity of the Lagergren equation is first tested by plotting ln (qe -qt) against t. The results obtained follow perfectly the linear variation given by the equation for pseudo first order kinetics, and the k1 constant for cellulose
- **Pseudo second-order kinetics model:** Based on the characteristic equation of pseudo second order kinetics and its linear form, the K2 value can be plotted by qt /t as a function of t.
- **Intra-particle diffusion model:** The use of the intra-particle diffusion model, plotting qt as a function of t0.5, indicates the application of the intra-particle diffusion model to the experimental data, controlling the adsorption kinetics. .

The D–R isotherm model was developed to account for the effect of the porous structure of the adsorbents (Qili et al 2018) and was based on the adsorption potential theory and assumed that the adsorption process was related to micropore volume filling as opposed to layer-by layer adsorption on pore walls (Dan et al 2022). The D–R isotherm model was superior to the Langmuir isotherm since it did not consider a homogeneous surface or constant adsorption potential (Kaur et al 2015). All isotherm curves pass through the one point (Cs, q_{max}) and the maximum adsorption capacity q_{max} was obtained when the equilibrium concentration is equal to the solubility. Freundlich isotherm is applicable to adsorption processes that occur on heterogonous surfaces which defines the surface heterogeneity and the exponential distribution of active sites and their energies (Ayawei et al 2015a, 2015b). The Freundlich and Langmuir adsorption isotherm models are used for acceptable error ranges. The shape of isotherms in this study, indicates, that fenthion and malathion are adsorbed as a monolayer, as the pesticides contaminants.

Adsorption isotherms of the three pesticides (Ma-Di-Fe): There was strong affinity of adsorbent for adsorbate, which is often observed when adsorbing in nanometer pore; type I observed for microporous adsorbents such as our WFC for which the porosity consists mainly of pore smaller than 2-5 nanometers, followed by a very significant reduction in the diffusion rate of adsorbate molecules towards the solid surface (Inglezakis et al 2020,Saraswati et al 2020). This is due to the mode of attachment of pesticide molecules which appears to be segmental at the first level (hydrogen bonding) and planar at the end of the process (Kärger et al 2016, Sang and al 2021).

Diazinon isotherms adsorption: The adsorption isotherms of diazinon on WFC (Table 4, Fig. 11) indicates that the

Table 4. Parameters of kinetic models studied fordiazinon

Kinetic models	Constants	Values
Kinetics of the first order	K1 (min^{-1})	1.,022
	Qe (mg/g)	6,8829
	R²	0,9724
Kinetics of the 2nd order	K2 (min^{-1})	0,01749
	Qe (mg/g)	8,2027
	R²	0,9531
Diffusion intra particle	kint (mg/g.$min^{0.5}$)	0,062
	R²	0.784

cellulose support has a very high affinity for Da and capacity of which increases with the initial concentration where two distinct zones are noted: for the first, the adsorption is very quickly, Qe increase from 0 to (4.5 and 5 mg/l) when Ce reached 50 mg/l ,This is explained by the formation of a monolayer segmentaire fixation (vertical) and the second zone the retention is too low(saturation) the adsorption is plane this is due to physical property (surface area of Diazinon, the isotherms obtained are similar to the L type according to Gill classification of isotherms.

Fenthion isotherms adsorption: The adsorption isotherm of fenthion on the cellulose (Table 5, Fig. 11) shows good affinity for. However, the curve seems at first sight to be linear or parabolic and the adsorption capacity increases with the initial concentration from 0 to 100 mg/g, until a level is reached corresponding to a saturation of the adsorption sites, which corresponds to a mono-layer adsorption resulting from the fixation mode of the fenthion molecules on the solid matrix. The isotherms obtained are similar to the L type, in accordance with the Gills classification of isotherms.

Malathion adsorption isotherms: The adsorption isotherm of malathion had a good affinity on the cellulose substrate, where can see a linear curve shaped by two distinct zones: the first, adsorption capacity increased very quickly, with the initial concentration and the second, linear, again, but with a very low gradient and the saturation plateau is reached very rapidly corresponding to saturation of the adsorption sites (Table 6 , Fig. 11). The adsorption operates in a double monolayer, the first one seems to show a plane adsorption in the macro-pores and the second stage is segmental (hydrogen bond and those due to the breaks of the double bonds). The isotherms obtained are similar to the C type

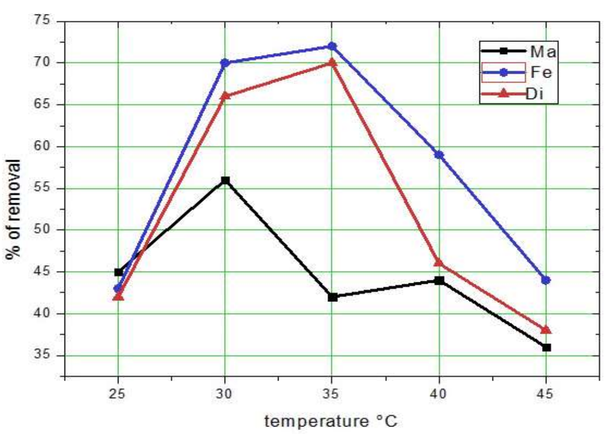

Fig. 10. Effect of temperature of retention of pesticides (Ma, Di, and Fe). C, V agitation = 350 rpm, V = 25 ml, Time = 60 min, the retention of Copper ions: T ° = 20 ± 2 ° C, V agitation = 350

Table 5. Parameters of kinetic models studied for fenthion

Kinetic models	Constants	Value
Kinetics of the first order	K1 (min^{-1})	1.,022
	Qe (mg/g)	6,8829
	R^2	0,9724
Kinetics of the 2nd order	K2 (min^{-1})	0,01749
	Qe (mg/g)	8,2027
	R^2	0,9531
Intra particle	kint ($mg/g.min^{0.5}$)	0,062
	R^2	0.784

Table 6. Parameters of kinetic models studied for malathion

Kinetic models	Constants	Values
Kinetics of the first order	K1 (min^{-1})	0..0153
	Qe (mg/g)	06.43904
	R^2	0.77774
Kinetics of the 2nd order	K2 (min^{-1})	0.00606
	Qe (mg/g)	5.11644
	R^2	0.3362
Diffusion intra particles	kint $mg/g.min^{0.5}$)	1.3911
	R^2	0.9421

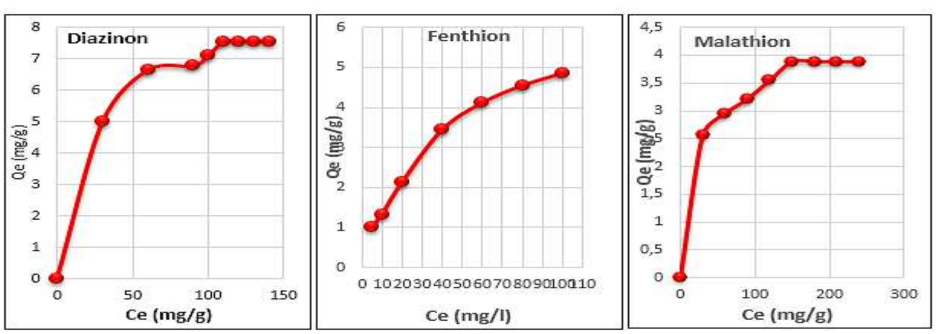

Fig. 11. Isotherm of adsorption ofdiazinon fenthion and malathion. T°= 20±2°C, V agitation= 350 tr/min, V= 25 ml, Time =60 min, pH =5.33

according to the classification of Gills classification of isotherms.

Kinetic studies adsorption: To identify the mechanism retention of pesticides on waste fiber cotton, by varying the initial concentration "C_0"=5 to "C_f" =100 mg/l), six theoretical models were tested (Freundlich, Langmuir, Temkin, Elovich ,Dubinin-Radushkevich (D-R) and Redlich-Peterson. For dianizon follows from the theory of Langmuir and Redlich-Peterson that in formation of more than a monolayer adsorption on the surface of the solid matrix. May be possible and sites are heterogeneous with differing mounting energy (Table 7). The shape of the isotherms indicates, that fenthion and, malathion are adsorbed as a monolayer, as the pesticides contaminants. In recent years, the analysis of linear regression, has been one of the most frequently used methods, to identify, the most, adequate adsorption models, as it can quantify the adsorbate distribution, estimate the adsorption process and test the theoretical assumptions of the adsorption isotherm model The Langmuir equation can be expressed in the form of a linear equation (Sang et al 2017).

$$\frac{C_e}{q_e} = \frac{1}{qmK \backslash E} + \frac{C_e}{q_m} \quad eq6$$

Where Ce is concentration of adsorbate at equilibrium (mg. g^{-1}).

K_L is Langmuir constant related to adsorption capacity (mg. g^{-1}), which can be correlated with the variation of the suitable area and porosity of the adsorbent which implies that large surface area and pore volume will result in higher adsorption capacity. The essential characteristics of the Langmuir isotherm is expressed by a dimension less constant called the separation factor (Somaia et al 2020).

$$R_L = \frac{1}{1+KL+CO} \quad eq7$$

Where C_0 is initial concentration of adsorbate (mg g^{-1}). R_L values indicate the adsorption to be unfavorable when $R_L>1$, linear when $R_L= 1$, favourable when $0<R_L<1$, and irreversible when $R_L = 0$.

Freundlich isotherm is applicable to adsorption processes that occur on heterogonous surfaces. This isotherm gives an expression, which defines the surface heterogeneity and the exponential distribution of active sites and their energies.

$$log_{qe} = log_{CF} + 1/n \ logC_e \quad eq8$$

The linear form of the Freundlich isotherm is as follows: where KF (L/mg) is adsorption capacity and 1/n is adsorption intensity; it also indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites.

Dubinin-Radushkevich isotherm model is an empirical adsorption model that is generally applied to express adsorption mechanism with Gaussian energy distribution onto heterogeneous surfaces. It is usually applied to differentiate between physical and chemical adsorption, Dubinin-Radushkevich isotherm (Agustín et al 2021).

$$lnq_e = lnq_m + \beta E_2 \quad eq\ 9$$

$$e = RT\ln\left(1+\frac{1}{C_E}\right) \quad eq10$$

$$E = \frac{1}{\sqrt{2B}} \quad eq11$$

Table 7. Correlation coefficients of isotherms adsorption of the three pesticides

Type d'isotherme	Constantes	Diazinon	Fenthion	Malathion
Langmuir	q_m (mg/g)	19,8019	11,0619	2,003205
	K_L (L/mg)	0,246101	0,53937	0,920014
	R²	0,997	0.8117	0.948
Freundlich	K_f (mg^{1-n}. l^n. g^{-1})	4,81193	3,735568	0,84806
	$1/n_f$	0,4521	0,7165	0,3071
	R²	0,897	0.966	0,917
Dubinin-Radushkevich	q_{mDR} (mg/g)	11,01105	1,5666	1,30343
	β	0,59696	6,4215	1,8623
	R²	0,7245	0,751	0,8024
Redlich-Peterson	n	1.999	2.525	1. 692
	ln (K_L^{-n}/q_m)	-2,86749	9,859.10^{-02}	-0,5347
	R²	0,895	0,7473	0,9956
	β	1.605	1,232	1,142
Temkin	B_T (mg/g)	2,6043	3,2423	2,9043
	K_T (L/mg)	0,7894	0,3524	0,3764

Where ϵ is Polanyi potential, β is Dubinin-Radushkevich constant R, is gas constant (8.31 $Jmol^{-1} k^{-1}$), is absolute temperature T, and E is mean adsorption energy.

The Redlich-Peterson isotherm is a mix of the Langmuir and Freundlich isotherms. The numerator is from the Langmuir isotherm and has the benefit of approaching the Henry region at infinite dilution (Mohammad et al 2020). This model is defined by the following expression:

$$q_e = \frac{AC_e}{1+BC_e^B} \quad eq12$$

Where A is Redlich-Peterson isotherm constant (Lg−1), *B* is constant (Lmg^{-1}), β is exponent that lies between 0 and 1, is equilibrium liquid-phase concentration of the adsorbent (mgl^{-1}), and qe is equilibrium adsorbate loading on the adsorbent ($mg\ g^{-1}$).

The linear form of the Redlich-Peterson isotherm is expressed as follows (Abdoulaye Demba and al 2019).

$$\ln\frac{C_e}{q_e} = \beta \ln C_e - \ln A \quad eq13$$

A plot of Ce/qe versus Ce enables the determination of Redlich-Peterson constants, whereβ is slope and A is intercept.

The Temkin isotherm is valid only for an intermediate range of ion concentrations. The linear form of Temkin isotherm model is given by the following:

$$q_e = \frac{Rt}{b}\ln K_T + \frac{Rt}{b}\ln C_e \quad eq14$$

Where b is Temkin constant which is related to the heat of sorption (J). The linear forms of the Elovich model are expressed as $mole^{-1}$ and K_T is Temkin isotherm constant.

Elovich isotherm. The equation that defines this model is based on a kinetic principle, which assumes that adsorption sites increase exponentially with adsorption and this implies a multilayer adsorption. The equation was first developed to describe the kinetics of chemisorption of gas onto solids.

$$\frac{qe}{qm} = Ke.Ce.e\frac{qe}{qe} \quad eq15$$

However, the linear form is expressed as follows

$$\ln\frac{qe}{Ce} = \ln Ke.qm - \frac{qe}{qn} \quad eq16$$

Elovich maximum adsorption capacity and Elovich constant can be calculated from the slope and intercept of the plot of lg (qe/Ce) versus Ce.

The adsorption isotherms of diazinon were studied, and the experimental data follow the Langmuir isotherm. Adsorption of diazinon could be well described by pseudo-first and second order kinetic models, the (R^2 = 0.997) of the Langmuir isotherm is higher than the Freundlich and D-R isotherms respectively (R^2 = 0,897 and 0,895). The removal of diazinon by the cotton waste showed the favourable and spontaneous nature of the adsorption process. This adsorbent can be considered, therefore, as a potentially efficacious adsorbent for the elimination of diazinon from aqueous solutions. For fenthion, The Langmuir constants are in relation with the adsorption capacity and the affinity of the binding areas. The correlation coefficient value (R^2 = 0.966) shows that the Freundlich isotherm fits the experimental data better than the Langmuir R^2 = 0.8117 and Temkin models. The maximal adsorption capacity of fenthion in all conditions), and is occurred on KT. The factor 1/n accounts for the non-linearity of the adsorption isotherm. When the Freundlich coefficient 'n' is around one, the adsorption would be linearly proportional to the equilibrium solution concentration and this would be used as the 'kf' distribution coefficient. The values of the distribution coefficient were not as high as those of Freundlich constant and was observed that the values of 'n' varied from 1.10 to 2.06 for cotton waste. For malathion, the linear regression approaches to determining the isotherm data appear to lead to acceptable fits to the analytical data with good coefficient of regression values (R^2). The linearized Redlich-Peterson and Langmuir, isotherms should also provide a better fit to the experimental data than the linearized Freundlich and Tempkin isotherms. Additionally, the value of the Redlich-Peterson exponent being higher than 1 (β > 1) at 25 ◦C suggests that no strain was fixed on the Redlich-Peterson exponent (Table 9) .The kinetic analysis using varying concentrations indicated that the pseudo-second order model.

CONCLUSION

Material's (cotton fibre waste) primary physiochemical characterizations were used to evaluate its absorbent properties. The infrared fourier transform spectroscopy validates the cellulose-specific bands. Under a scanning electron microscope, an extremely porous morphology of the fibre was observed, which assisted in the aqueous solution's flow. This promotes the growth of more amorphous, less structured areas for higher absorption. The retention of metallic ions on cellulose occurred relatively quickly; equilibrium was reached for copper after 60 minutes and for cadmium and chromium after 120 to 150 minutes for each (unbleached and grafted).The range between pH 4.5. and 6.5 of the organic matter removal rate is a function of pH. The effect of initial concentration, as well as the solid/liquid ratio for pesticides, was also examined, and diazinon was still the most affected. The binding mechanism with a high probability of adsorption is due to the formation of a water bridge by H-bonding between the surface of the biomaterial and the charged electronic side of the examined pesticide molecules, containing O and P. The adsorption isotherms of cotton fiber waste, for the selected malathion and fenthion concentrations, were interpreted by Redlich-Peterson and Langmuir models. Redlich-Peterson and Langmuir models are chosen for retention of malathion on grafted cellulose kinetics for all pesticides showed retention to be extremely rapid. The values of the linear regression factors for each showed that the pseudo second order model monitors both diazinon kinetics and the pseudo first order model monitors fenthion, and malathion. This was clearly confirmed by the corresponding correlation model.

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