1-INTRODUCTION

The contamination of the environment by toxic substances is linked both to industrialization and to agriculture. Toxic substances find their way into ecosystems from discharges and leaks of industrial products, consumer wastes and urban sewage, from farming and forestry runoff, and from accidental spills. Contaminants may be dispersed over great distances by winds and water currents. Some of these compounds (organochlorine pesticides) accumulate in animal tissues, particularly in predators that are at the top of the food chain. Organochlorine pesticides pose a serious threat to both the general environment and human health in particular, because it can take decades for them to decompose naturally. Indeed, although most organochlorine pesticides were banned worldwide from 1970s, onwards their effects persist today. These contaminants affect the ability of living organisms to reproduce, to develop, and to withstand the many other stress factors in their environment, by depressing their nervous, endocrine, and immune systems.

Persistent organic pollutants (POPs) have been linked to adverse effects on human health and animals, such as cancer, damage to the nervous system, reproductive disorders, and disruption of the immune system. Because they circulate globally via the atmosphere, oceans, and other pathways (**WHO, 1989),** POPs released in one part of the world can travel to regions far from their source of origin **(UNEP, 2005).**With mounting evidence, indicating the long-range transport potential of these substances to regions where they have never been used or produced and the consequent threats they pose to the environment. Organochlorine pesticides (OCPs), well known as typical persistent organic pollutants

(POPs), have adverse effects on humans and ecosystems, according to the Stockholm Convention of 2009 **(UNEP, 2009).**

Nanotechnology is the manipulation of matter on an atomic and molecular scale. Nanotechnology is defined as the manipulation of matter with at least on dimension sized from 1 to 100 nanometers **(Drexler, 1986).** In recent years, nanofiltration (NF) membranes have been extensively used for water and wastewater treatments as well as industrial purposes. Since they can perform the desire efficiencies for removal of target solutes with higher fluxes at low pressures and in many cases, nanofiltration processes have a lower capital and operating costs than typically high-pressure reverse osmosis (RO) processes. Moreover, the increasing interest in nanofiltration process is due to it can remove dissolved organic matter, color, heavy metal complexes, and some organic pollutants such as pesticides **(Kiso et al. 2000).**

To reduce the initial costs of pumps and piping equipments in a membrane process, it is necessary to operate the process in low operational pressure range. In addition, the running cost of such power consumption will be significantly reduced. As the solubility of pesticides in water is normally low, moreover, the operation of nanofiltration processes is possibly applied for treating pesticides contaminated in the water. In our study, consequently, it is worthwhile to focus on the treatment of agriculture wastewater containing pesticides by nanofiltration.

The objective of the present work is to survey pesticide residues in water samples collected from seven locations in Bahr El-Baqar drain at El- Sharqia governorate, Egypt. Moreover, this study focuses also on the

effectiveness of the nanofiltration process in the treatment of agricultural wastewater. Furthermore, the study also indicated the elimination performance of NF membranes (NF270 and NF90) for removing pesticides from water under different conditions such as high and low concentration, different temperature degrees, different pHs, and different types of water and interference effect between these conditions.

2-REVIEW OF LITERATURE

2.1. Monitoring of pesticide residues in waters:-

El-Kabbany et al. (2000) indicated that monitoring of pesticide residues were conducted at different locations in the El-Haram region Giza, Egypt. The water samples were collected from El-Haram Giza, canal water supplies (El-Zomor, Abd-el-aal land and seaside and El-Mansorya), in addition to El-Moheet drainage water. The residues of pesticides were varied between different locations. Also, organochlorine pesticide residues in El-Moheet drainage water were relatively higher than in the canal water. The concentrations of organophosphrous compounds i.e. chlorpyrifos, dimethoate and parathion seem to be low in water as compared to soil samples. Most findings were less than 1 $mgKg^{-1}$, which is considered a low-level finding. Sixteen organochlorine pesticides were detected in most of the water samples and the percent of positive samples followed the order drins> total BHC> total DDT >endosulfan > heptachlor epoxid > heptachlor. Pentachlorophenol PCP was detected only in El-Zomor and Abd-el-aal canal water. Results obtained confirm the presence of different pesticide residues representing different chemical classes in the canal waters. This means that the discharging of wastes in to the water supplies must be controlled. Drainage water was highly polluted andcontains much more pesticide residues than different canal waters.

De llasera and Bernal-gonza´lez (2001) studied the presence of carbamate pesticides, namely aldicarb, aldicarb sulfoxide, baygon, benthiocarb, carbofuran, 3-hydroxycarbofuran, carbaryl, desmedipham,

methiocarb, methomyl, thiodi-carb, oxamyl, and propham in ground and surface waters from an agricultural zone of the Yaqui Valley located in northwest of Mexico. Trace determinations were made by liquid chromatography (LC). Results indicated that the level of contamination with methiocarb was 5.4 μgL^{-1} in a groundwater sample and that for 3-hydroxycarbofuran was 18 μgL^{-1} in a surface water sample.

Rovedatti et al. (2001) Investigated that the analyses were performed on Reconquista River (Buenos Aires, Argentina) in three sampling stations (S_1, S_2 and S_3). Screening included the following pesticides:(a) Organochlorines: α, β and γ HCH; heptachlor, heptachlor epoxide; aldrin; endrin; dieldrin; *op'* and *pp'* DDT; *op'* and *pp'* DDE; α , γ chlordane and endosulphan II; (b) Organophosphates: ethyl and methyl parathion; chlorpyrifos and fenitrothion. From the 60 samples analyzed, 35% contained organochlorine pesticides in a concentration higher than the detection limit. Organophosphates were found in no case. Throughout the studied period, DDT and its metabolite DDE were only found in S1 and g chlordane in S_3; heptachlor was present in 50% of the samples of S_2 and in 35% of S_3, while HCH isomers were detected in 38% of S_2 and 45% of S_3 samples. Neither temporal nor spatial trends were found. No relationship between the time of samplings and the fumigation season was recorded for farming purposes. At all locations, pesticides levels were found to be between 40 and 400 times higher than the legal limits established for protection of aquatic life.

Sudo et al. (2002) investigated the concentrations and loading rates of pesticides used in paddy fields, Japan. Over a period of years in the seta river, which is the only natural outlet of Lake Biwa. Water samples, were collected from six rivers flowing into Biwa Lake in order

to compare the contamination level and concentration profile. The pesticides analyzed were four herbicides (molinate, simetryn, oxadiazon, and thiobencarb), one fungicide (isoprothiolane), and two insecticides (diazinon and fenitrothion). Molinate, simetryn, oxadiazon and isoprothiolane were found at the higher frequencies with maximum concentrations of 1.1, 0.4, 0.1 and 0.5 μgL^{-1} in the Effluent River, one or two order of magnitude higher than that of effluent in Influent Rivers. These peak concentrations were observed during the application period in Influent Rivers and two or three weeks after that in Effluent River. The frequency of occurrence of thiobencarb, diazinon, and fenitrothion was relatively low and their maximum concentrations in the effluent remained below 0.1 μgL^{-1}. The decrease of molinate, simetryn and oxadiazon concentrations in the Effluent River were approximated by two straight lines plotted on semilogarithmic scale.Increased loading was induced by intense rainfall, which took place during the application period. Simetryn and isoprothiolane persisted in relatively high concentrations through the year were also influenced on its loading by the heavy rainfall in the following months. The percentages of the total amount of pesticides released through Lake Biwa to the basin in downstream were estimated to be 1.3–2.9% for molinate, 5.4–10.0% for simetryn, 0.6–1.3% for oxadiazon,0.2–0.9% for thiobencarb, 1.8–6.6% for isoprothiolane, 0.3–2.1% for diazinon, and 0% for fenitrothion.

Zulin et al. (2002) indicated that seventeen organic phosphorus pesticides (OPs) and 18 organic chlorine pesticides (OCs) at water from Jiulong River Estuary (JLRE), China. were determined .The contents of the total Ops (17) ranged from 134.8 to 354.6 ngL^{-1} (the mean is227.2 ngL^{-1}) .Total OCs concentrations varied from 115.4 to 414.7 ngL^{-1} in

water (mean237.7 ngL^{-1}). The levels of total hexachlorocyclohexane in water varied from 31.95 to 129.8 ngL^{-1} (mean62.51 ngL^{-1}), and those of total DDTs were in the range 19.24–96.64 ngL^{-1} (mean48.69 ngL^{-1}). The distribution and behavior characteristics of Ops indicate that five main Ops (methamidophos, dichlorvos, Malathion, omethoateanddimethoate) occupied them ostpart of the total Ops, in addition, the sources of the Ops (mainly from current usage) are not stable. While the OCs mainly came from early application and were more stable. The Ops did not have obvious correlation with the dissolved organic carbon and suspended particulate matter at water from JLRE. It may be due to the complicated hydrological kinetics in the estuary, and the higher water solubility and weak absorption (with organic matter) action of Ops. When compared with other areas, the OP sand OCs level in JLRE were some moderate.

Feng el al. (2003) carried out a field survey during 1999–2000 in the Taihu Lake Region, China. Organo-chlorine pesticide (OCP) residues in soil, water, fish and sediment samples. In river water, DDT was detected in 10 out of 13 samples ranging from 0.2 to 9.3 μgL^{-1}, with an average of 1.0 μgL^{-1}. While HCH was detected in 12 out of 13 samples ranging from 0.02 to 36.1 μgL^{-1}, with an average 5.6 μgL^{-1} .DDT residues in sediment ranged from 0.1 to 8.8 μgKg^{-1}, while HCH ranged from 0.3 to 66.5 μgKg^{-1}. DDT residues in fish body ranged from 3.7 to 23.5l $mgKg^{-1}$ and HCH ranged from 3.7 to 132 μgL^{-1}.

Golfinopoulos et al. (2003) indicated that a survey undertaken in Northern Greece has shown that organochlorine pesticides were present in the surface waters. Surface water samples have been collected seasonally from four rivers and five lakes for a period of two years. The most commonly encountered organochlorine pesticides in surface waters

were the isomers of hexachlorocyclohexane, aldrin, dieldrin and endosulfan sulfate. In some cases, the concentrations detected were higher than the qualitative target levels set by the European Union, especially for hexachlorocyclohexane and aldrin. This is due to the possible transfer of organochlorine pesticides from activities in the neighbouring countries. Moreover, the presence of organochlorine pesticides in water is also attributed to intense agricultural activity in the area of Northern Greece.

Matthews et al. (2003) surveyed the applying pesticides in Cameroon, the survey considered those growing cocoa, coffee, oil palm, maize, cotton, tomatoes, groundnuts, plantains, bananas and various other crops. The main herbicides used by the growers were paraquat and glyphosate, while metalaxyl, maneb and copper were the principle fungicides. Cypermethrin and chlorpyrifos were the main insecticides.

Neumann et al. (2003) described a water-sampling device to monitor waters quality in temporary channels or point sources and its application to pesticides contamination in Germany. Seven in flow events were analyzed for 20 pesticide agents (insecticides, fungicides and herbicides). All three entry routes were remarkably contaminated. It was found parathion-ethyl concentrations of 0.3 $\mu gL^{-1,}$ diuron up to 17.3 μgL^{-1}, ethofumesate up to 51.1 μgL^{-1}, metamitron up to 92 μgL^{-1} and prosulfocarb up to130 μgL^{-1}.

Palma et al. (2004) surveyed residues of five pesticides in surface water during 2001 and 2003 in the Traiguén river basin in Southern Chile. Simazine, hexazinone, 2, 4-D, picloram herbicides and carbendazim fungicide were selected through a pesticide risk

classification index. Six sampling stations along the river were setup based on agricultural and forestry landuse. The water sampling was carried out before and after the pesticide application periods and in correspondence to some rain events. Pesticides were analyzed by HPLC with DAD detection in a multi residue analysis. During 2001, in the first sampling campaign (March), the highest concentrations of pesticides were 3.0l mgL^{-1} for simazine and hex-azinone and 1.8l mgL^{-1} for carbendazim. In the second sampling (September), the highest concentration were 9.7 mgL^{-1} for 2, 4-D, 0.3l mgL^{-1} for picloram and 0.4l mgL^{-1} for carbendazim. In the last sampling period (December), samples indicated contamination with carbendazim fungicide at levels of up to 1.2 mgL^{-1}. In sampling carried out on May 2003, no pesticides were detected. In October 2003, the highest concentrations of pesticides were 4.5l mgL^{-1} for carbendazimand 2.9l mgL^{-1} for 2, 4-D. Data are discussed in function of land use and application periods of the products, showing clear seasonal pattern pollution in the Traigue´n River. Risk assessment for these pesticides was calculated by using a risk quotient (RQ=PNEC/PEC). For picloram the calculated RQ < was 0, which indicates that no adverse effects may occur due to the exposure to this herbicide in the Traigue´n river basin. For 2, 4-D, simazine, hexazinone, carbendazim RQ > 1, meaning that adverse effects could occur and it is necessary to reduce pesticide exposure in surfacewaters.

Sankararamakrishnan et al. (2005) studied the organochlorine and organophosphorous in ground water surface waters of uttar Pradesh, India. Their results showed the presence of high concentrations of both organochlorine and organophosphorous pesticides in the surface and ground water samples. Among the various pesticides analyzed, high

concentrations of g-HCH (0.259 μgL^{-1}) and malathion (2.618 μgL^{-1}) were detected in the surfacewater samples collected from the River Gangesin Kanpur. In the ground water samples collected from the various hand pumps located in agricultural and industrial areas, apart from g-HCH and malathion, dieldrin was also detected.The maximum concentration values of g-HCH, malathion and dieldrin were 0.900, 29.835 and 16.227 μgL^{-1}, respectively. Especially, the concentration of malathion was found to be much higher than the EC water quality standards in the groundwater samples from industrial are aposing a high risk to the common people. Pesticides like DDE, DDT, aldrin, ethion, methylparathion and endosulfan were not detected in both the surface and groundwater samples.

Konstantinou et al. (2006) reviewed the status of pesticide pollution in surface water (rivers and lakes) of Greece. This review evaluates and summarizes the results of long-term research projects, monitoring programs and published papers concerning the pollution of surface waters (rivers and lakes) of Greece by pesticides. The pesticide classes mostly detected in Greek rivers involve herbicides used extensively in corn, cotton and rice production, organophosphorus insecticides as well as the banned organochlorines insecticides due to their persistence in the aquatic environment. The compounds most frequently detected were atrazine, simazine, alachlor, metolachlor and trifluralin of the herbicides, diazinon, parathion methyl of the insecticides and lindane, endosulfan and aldrin of the organochlorine pesticides.Rivers were found more polluted than lakes. The detected concentrations of most pesticides follow a seasonal variation, with maximum values occurring during the late spring and summer period

followed by a decrease during winter. Nationwide, in many cases the reported concentrations ranged in low ppb levels. However, elevated concentrations were recorded in areas of high pesticide use and intense agricultural practices. Generally, similar trends and levels of pesticides were found in Greek rivers compared to pesticide contamination in other European rivers. Monitoring of the Greek water resources for pesticide residues must continue, especially in agricultural regions, because the nationwide patterns of pesticide use are constantly changing. Moreover, emphasis should be placed on degradation products not sufficiently studied so far.

Rissato et al. (2006) reported a detailed analyses of persistece of organic pollutants (POPs) such as organochlorine pesticides (OCPs), hexachloro-cyclohexane (HCH) isomers (HCHs), dichloro-diphenyl-trichloroethane (DDT) and its metabolites (DDTs) and congeners of polychlorinated biphenyls (PCBs) in soil and surface water from the northeastern São Paulo, Brazil. These analyses can allow the evaluation of the contamination status, distribution and possible pollution sources. The pesticides and PCBs demonstrated markedly different distributions, reflecting different agricultural, domestic and industrial usage in each region studied. The ranges of HCH, DDT, and PCBs concentrations in the surface water samples were 0.02–0.6, 0.02–0.58 and 0.02–0.5ngL^{-1}, respectively. High ratios of metabolites of DDT to DDT isomers revealed the recent use of DDT in this environment. The sources of contamination were closely related to human activities, such as domestic and industrial discharge, street runoff, agricultural pesticides and soil erosion, due to deforestation as well as atmospheric transport.

Zhou et al. (2006) investigated the levels of 13 organochlorine pesticides (OCPs) in surface water and sediments from (Qiantang River in East China) to evaluate their potential pollution and risks. A total of 180 surface water samples at 45 sampling sites and 48 sediment samples at 19 sampling stations were collected along the river in four seasons of 2005. The total OCPs concentrations in surface water and sediments were 7.68–269.4 ngL^{-1} and 23.11–316.5 ngG^{-1}-dry weight (dw), respectively. The concentrations of OCPs in sediments were in the range of 8.22–152.1 ngG^{-1}-dw for HCHs (α, β, γ, δ-HCH), 1.14–100.2 ngG^{-1}-dw for DDTs (p,p' -DDD, p,p' -DDE, p,p' -DDT o,p' -DDD), 9.41–69.66 ngG^{-1}-dw for other OCPs (aldrin, diedrin, endrin, heptachlor, heptachlor epoxide).The total OCPs concentrations in soils and wet deposition were 5.04–214.9 ngG^{-1}-dw and 16.18–242.4 ngL^{-1}, respectively. Among the OCPs, HCHs, DDTs and heptachlor were the most dominant compounds in the sediments. The dominant OCPs in water were -HCH among HCHs, heptachlor among other OCPs and p,p -DDE among DDTs . Also, different contamination patterns among sampling seasons were found. The concentrations of OCPs in sediment collected in spring were higher than those in summer and autumn. In contrast, the concentrations of OCPs in surface water in summer and autumn were higher among four sampling seasons. Distribution of HCHs, DDTs and other OCPs were different indicating their different contamination sources. The notable contamination was found in Fuchun reservoir. Composition analyses in sediments indicated a recent usage or discharge of lindane into the river.

Xu et al. (2007) investigated the extent of organochlorine pesticides (OCPs) contamination in coastal waters around LaiZhou Bay and JiaoZhou Bay in Shandong Peninsula, northern China. The areas around the two bays are both densely populated, thrived with intensive

agriculture and industrial activities. including alpha, beta, gamma and delta isomers of hexachlorocyclohexane (HCH), pentachloronitrobenzene (PCNB), heptachlor, aldrin, endosulfan, p,p0-DDE, dieldrin, endrin, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT and methoxychlor. The survey results show that contaminations by OCP residues remain widespread in the areas, but the averaged concentration levels are all below the regulatory limits, e.g., CMC limits (acute criterion values) specified in US Environmental Protection Agency (USEPA) and China national standards. Average concentration of OCPs in water samples were from undetectable to 3.8 ngL^{-1} in LaiZhou Bay and from 0.1 to 3.9 ngL^{-1} in JiaoZhou Bay, respectively.

Darko et al. (2008) determined some organochlorine pesticides residues in tilapia fish, seditanments and water samples from Lake Bosomtwi (the largest natural lake in Ghana) to find out the extent of pesticide contamination and accumulation in the lake. The extracted residues were analyzed on a micro-capillary gas chromatograph equipped with electron capture detector. DDE (*p,p'*-1,1-dichloro-2,2-bis-(4-chloro-phenyl) ethylene) was the predominant residue in all the samples analyzed ; detected in 82% of water samples, 98% of sediment samples and 58% of fish samples at concentrations of 0.061 ±0.03 ngG^{-1} 1,8.342±2.96 ngG^{-1} and 5.232±1.30 ngG^{-1}, respectively. DDT (*p,p'*-1,1,1-trichloro-2,2-bis-(4-chloro-phenyl) ethane) was detected in 78% at a mean concentration 0.012±0.62 ngG^{-1} of water samples analyzed. The mean concentrations of DDT in sediments and fish were 4.41±1.54 ngG^{-1} and 3.645±1.81 ngG^{-1}, respectively. The detection of lower levels of DDT than its metabolite, DDE, in the samples implies that the presence

of these contaminants in the lake is as result of past usage of the pesticides.

Hildebrandt et al. (2008) carried out an environmental monitoring program to determine the impact of eight pesticides on the surface and groundwater quality of agricultural areas within the Ebro, Duero and Mino river basins, North Spain. Three triazines and their desethyl degradation products, metolachlor and metalaxyl, were monitored during 18 months in 63 sites . The frequency of detection of the studied compounds, considering all surface and ground water samples, was atrazine > desethylatrazine > simazine > desethylsimazine >metolachlor > desethylterbuthylazine > terbuthylazine > metalaxyl. Overall results and taking into consideration the European Union (EU) maximum residu allimit of pesticides in groundwater, only 12% of the results exceeded the 0.1 mgL^{-1} limit. However, sporadic high levels up to 2.46 mgL^{-1} in ground water and 0.63 mgL^{-1} in surface water were detected. PC a permitted to state that Duero and Ebro river basins were especially affected by a contamination pattern dominated by atrazine, the Ebro river basin being occasionally affected by a contamination pattern dominated by simazine. Only trace levels were rarely detected in the Mino river basin. Ground water levels were higher than surface water levels for the studied pesticides.

Jiawei et al. (2008) collected the water samples from the Wenyu, Beiyun, Yanqing, Fangshan, Changping, and Shunyi Rivers in the suburb of Beijing and the residues and characteristics of DDT and HCH. The results showed that the contents of DDTs and HCHs were ND–13.98 ngL^{-1} and 3.87–146.42 ngL^{-1}, respectively. According to the

indicators of the ratio values of (DDD + DDE) / DDT and α-HCH / β-HCH.

***Carvalho et al.* (2009)** investigated the coastal lagoon system of Laguna de Terminos, Campeche, Mexico, a natural reserve since 1994, for contamination by agricultural and industrial chemical residues. Water, sediment and biota samples were analyzed for a wide variety of organochlorine and organophosphorus compounds. Chlorpyrifos was detected in water in concentrations up to 72 pgL^{-1} and, amongst organochlorine compounds) PCB were measured averaging 1177 pgL^{-1} and) DDT 279 pgL^{-1}. Residues of chlorinated com pounds were present in sediments and in biota with) DDT averaging 190 pgG^{-1} and 5876 pgG^{-1} in sediment and oysters, respectively. Results show that the more wide spread contaminants in the Laguna were residues of chlorinated hydrocarbons, such as DDTs, PCBs, endosulfan, and lindane. Concentrations of residues were not at an alarming level and were even lower than reported for other costal lagoons of the region. Still there is a need to implement con troll measures on persistent and bio accumulative compounds that may reach the aquatic system of Laguna de Terminos.

Kim et al. (2009) investigated the contamination status of twelve persistent organic pollutants (POPs) on the Stockholm convention in the surface sediments of Han River, which is one of the largest river in the South Korea. Five organochlorine pesticides (OCPs) such as aldrin, dieldrin, endrin, mirex, and RCHLs (a-chlordane, c-chlordane, cis-nonachlor, trans-nonachlor, and heptachlor) were not detected in all sediment samples.The overall concentrations of DDTs, HCB, dioxin-like PCBs (DL-PCBs) and PCDD/Fs were in the range of 1.05–8.94 μgkg^{-1} (average value: 3.93 μgkg^{-1}), 0.485–3.73 μgkg^{-1} (1.48 μgkg^{-1}), 41.5–