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Treatment of pesticides containing effluents using organoclays/nanofiltration systems: rational design and cost indicators

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ABSTRACT

Removal of hazardous pollutants from wastewater is an essential step for safe recovery and reuse. The immediate objective of this paper is to discuss functional requirements and design considerations of a nanofiltration (NF)-based system for the treatment of pesticide industry effluents and contaminated surface water. Techno-economic considerations for a 100 m^3/d membrane filtration plant for the treatment of pesticide industry effluents and contaminated agricultural drainage water are presented. Metolachlor has been selected as the model for pesticide removal. The proposed system comprises membrane ultrafiltration (UF), NF, and adsorption of pesticides using modified clays such as organoclays. This paper is concluded with design guidelines and indicators pertinent to the treatment of pesticide-containing wastewater using NF systems. The estimated capital cost of a 100 m^3/d treatment facility amounts to $ 240,850. Further, the treatment cost is about $1.77/$m^3$.

Keywords: Pesticide; Metolachlor; Nanofiltration; Organoclay; Design; Cost

1. Introduction

Removal of pesticides from surface or ground water is a multi-faceted problem. On one hand, pesticides manifest direct and severe health and environmental impact [1]; and on the other hand, pesticide removal and destruction mandate costly complex treatment. The author of this paper participated in the development of a multi-tier approach for pesticide destruction using a complex system comprising membrane separation, chemical oxidation, carbon adsorption and incineration [2]. This system is under evaluation through joint Egyptian/American cooperation [3]. To further optimize this system and also to focus on point source problems, a new modification is proposed to deal with pesticide industry effluents from the source, thus eliminating the need to deal with end of the pipe large volume effluents. With the possibility of recycling water and some active ingredients to upstream sections of the plant, the need for costly oxidation and incineration may be considerably reduced with consequent cost reduction. Also, taking into consideration the availability of low-cost adsorbent clays in Egypt and in many parts of the world, the need for activated carbon may be also elucidated through the use of modified clays. Thus, the new system modification will follow a separation, concentration and removal concept. The proposed new pesticide removal system is dedicated basically to the pesticide manufacturing sections in the plant. The following sections will focus on the techno-economic aspects of the proposed pesticide treatment system. The issue of water and chemicals recycling governs the new system design.

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2. Technology identification

Numerous technologies have been proposed, developed and tested for the removal of pesticides from surface and ground water [4,5]. Those technologies include physical, chemical and biological treatments. The scope of chemical treatment centers on chemical precipitation, oxidation by ozone, ozone/ultraviolet [5] and Fenton oxidation [6]. Further, physical separations include plain sedimentation, filtration, while membrane separation [7,8] and adsorption [9] represent physicochemical separations. Biological treatment of pesticides manifested significant progress comprising anaerobic and aerobic treatment in addition to modified acclimatized strains for the removal of specific pesticides.

Metolachlor is one of the most commonly produced and used pesticides. It is a non-ionizable substituted methoxy acetamide (molecular weight of 283.81) herbicide that controls grasses and broadleaf weeds in some crops. It is considered a hydrophobic herbicide, with relatively low solubility in water and good solubility in a number of solvents such as hexane, methanol, etc. It hinders elongation of roots and shoots. Metolachlor is considered moderately persistent in most soils, with slow microbial and anaerobic degradation, and stable in water under regular sunlight. Thus, metolachlor has the potential to contaminate groundwater and is widely found as a groundwater pollutant [10].

Metolachlor as a model pesticide has been treated by using chemical oxidation techniques and NF membrane separation [11]. Many researchers studied the adsorption of metolachlor on clay minerals and modified clays (formulations based on the interactions between clay minerals, organic chemicals and metolachlor) in order to reduce leaching or avoid decomposition [12–14].

2.1. Rationale for selected separation, concentration, adsorption and recycling scheme

Treatment of pesticide industry effluents from upstream sections of the plant enables considerable advantages including, but not limited to, a relatively high concentration of pesticides, relative homogeneity of streams through avoiding mixing with other conventional pollutants with consequent possibilities of water reuse and also recycling of some active ingredients. Moreover, it is logical to recycle separated streams with a quality fulfilling almost their primary functions to upstream sections of the plant. Targeting pesticide effluent separation and recovery will systematically eliminate or reduce the pesticide destruction stage. Thus, the tailored modified scheme will focus on effluent processing from metolachlor industry using UF, NF and adsorption using modified clays such as organoclays.

2.2. NF-based pesticide separation

NF is functionally positioned between UF and RO. Thus, it is possible to permit a water and low molecular weight solvent passage while retaining medium molecular weight dissolved matter including dissolved organic carbon such as pesticides. Typical performance indicators for the removal of some pesticides are depicted in Table 1 [7–9,11,15]. Typical removal percentages range from 61.4% to 99.8%. Comparative indicators for RO are also shown in Table 1. The NF type seems to manifest appropriate performance.

2.3. Modified clays for adsorption of pesticides

Natural adsorbents such as bentonites and clays are available in Egypt as well as other countries. It is perceived that activation of specific clays would enable sustainable availability of low-cost adsorbents. In this paper, organoclays have been selected in the process design stage for technology identification, development and evaluation. Performance indicators of modified clays including organoclays for the removal of specific pesticides are outlined in Table 2. The adsorption capacity of different pesticides varied considerably from 1 mg/g for atrazine to 85 mg/g for metolachlor. Thus, the latter pesticide has been selected as a model for pesticide removal in the combined membrane/organoclay adsorption system. In addition, metolachlor is within the pesticide matrix currently in use in the country [13,14, 16–20]. Several formulations were proposed for metolachlor which were based on the preparation of a complex with hydrophobic properties between an organic cation and the clay mineral The adsorption isotherm of metolachlor to organoclays can be interpreted as "C-type" with a maximum adsorption capacity of 65 mg/g [19].

3. Process design aspects and cost trend

The basic design concept integrates two types of membrane separations, namely ultrafiltration (UF) and NF with organoclay adsorption. UF will act as a pretreatment for removal of turbidity and minerals in addition to any colloidal matter. The following sections depict technical and preliminary cost indicators of the proposed system.

3.1. Proposed UF/NF/ organoclay system

For the recycling and recovery of liquid and solid components of pesticide effluent from metolachlor industry taken from a point source upstream of the plant, a system comprising UF, NF and organoclay has been selected. Typical pesticide effluent essentially comprises a concentration of metolachlor of 2 mg/l. and a hydrophobic solvent (chloroform).

Table 1
Typical performance indicators for pesticide rejection using NF and RO membranes

Pesticide	Membrane	Initial concentration (mg/l)	% rejection	Pressure (bar)	Reference
Alachlor	HNF-1	1.1	88.7	3	11
Atrazine	NF90[a]	20	98.9	6	9
	NF[b]	10	62.0	10	15
	NF-270[a]		81.4	6.9	7
	RO-CPA2[c]		95.9	10	7
	HNF -1	1.1	61.4	3	11
Chloroneb	HNF-1	0.102	88.4	3	8
Diazinon	NF-270[a]		93.1	6.9	7
Metolachlor	HNF- 1	1.1	93.9	3	11
Pirimicarb	HNF-1	0.85	89.9	3	11
Terbumetone	NF[b]	1	95	20	15
Triadimefon	NF-270[a]		99.8	6.9	7
	RO-CPA2[c]		78.3	10	7

[a]FilmTec, Dow; [b]Vladipor, Russia; [c]Hydranautics.

Table 2
Performance indicators for some pesticides treatment using organoclays

Pesticide	Organoclay	Initial conc. (mg/l)	Adsorption capacity (mg/g)	Ref.
Atrazine	Ca^{++}/saturated smectite clay		6	16
	Na^{++}/bentonite/quaterny ammonium salt	2.6	1	17
	Montmorillonite/octadecyl ammonium bromide	1.8	1	18
Linuron	Montmorillonite octadecyl trimetyl ammonium bromide	3–4	4.5	18
Metolachlor	Thermally activated bentonite(350–550°C)	Up to 400	Up to 85	13
	Montmorillonite/Ca^{++} or Al^{++} / benzyl trimethyl ammonium ions	Up to 400	Up to 80	14
	Montmorillonite/difenzoquat-DZ		Up to 65	19
Malathion	Kaolin/tetradecyltrimethyl ammonium bromide		5.85	
	Bentonite/acetyl pyridinium chloride	36–38.5	16.7	20

Elements of the proposed system are shown in Fig. 1. For system design purposes with metolachlor as a model pesticide, membrane rejection and recovery as well as adsorption capacity and removal efficiency of organoclays are selected as shown in Table 3 [11–13]. The functional design of this system projects the following features:

- Total dependence on physical separation without incorporation of chemical or biological treatments.
- The NF stages are preceded by UF to eliminate colloidal components which may be recycled or disposed off separately. Selection of UF permeation and rejection characteristics would enable excellent pretreatment prior to the NF stages. Membrane material should be selected based on the solvent characteristics associated with the pesticide effluent. An inorganic UF membrane would be a good candidate for the pretreatment stage (CARBOSEP with membrane active coat, ZrO_2-TiO_2 with cutoff 50,000 Dalton), while, FilmTec, Dow, NF90 was selected for NF membranes. The characteristics of the afore-mentioned membranes match the requirements of the proposed system.

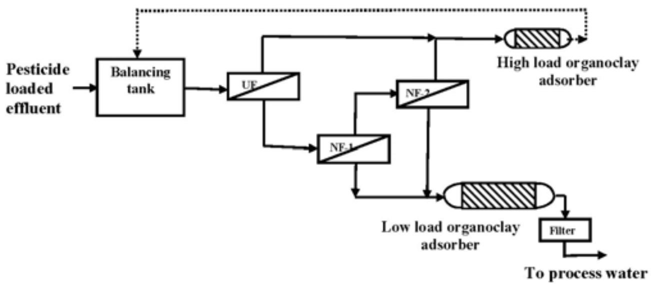

Fig. 1. Process flow diagram for the integrated membrane/organoclay treatment system.

- Effluents from the UF stage will be directed to the first NF stage (NF1) for maximum removal of pesticides. Solvent permeation will depend on the molecular weight and interaction with membrane surfaces. Solvent passage with permeate will not affect target

Table 3
Design basis for the selected treatment units

Item	UF	NF1	NF2	Organoclay	
				Low load	High load
Water recovery (%)	95	90	90	—	—
Metolachlor removal (%)	10	94	96	—	—
Pressure (bar)	3	15	15		
Membrane area (m^2)	26	73	7		
Adsorption capacity (mg/g)		—	—	6	30
Removal efficiency (%)				75	95

Table 4
Performance of the proposed membrane/organoclay system for pesticide treatment (100 m^3/d)

Separation stage	Flow rate (m^3/d)			Concentration (mg/l)		
	Influent	Concentrate	Permeate	Influent	Concentrate	Permeate
Membranes:						
UF	100	5	95	2	5.8	1.8
NF1	95	9.5	85.5	1.8	17.03	0.11
NF2	9.5	0.95	8.55	17.03	164.2	0.68
Organoclay adsorber:	Influent			Influent	Treated	
Low load	94.05			0.16	0.04	
High load	5.95			31.08	1.55	

stream function as recycled washing fluids. This type of permeate will be further refined using a low load organoclay adsorber.

- The concentrate from the NF1 stage is directed to a second NF stage (NF2) for further concentration and also for more water solvent recovery. The permeate from both NF1 and NF2 will be directed to a low load organoclay adsorber.
- Concentrate from the UF and NF2 stages will be directed to a high organoclay adsorber for maximum metolachlor removal. Effluents will be directed to the balancing tank.
- Two routes are proposed for the management of loaded organo clay adsorber depending on the quality of adsorbate and economics of desorption. The first route is the recycling of desorption products and the second route is to sell the loaded organoclays as a low-cost slow release pesticide (metolachlor).
- The predicted performance indicators of the different separation stages as pertinent to metolachlor treatment are shown in Table 4. The collected permeate streams directed to the low load organoclay adsorber (with an estimated adsorption capacity of 6 mg/g) is estimated to be about 94.05 m^3/d for reuse as a process water. The collected concentrate streams from UF and NF2 directed to the high load organoclay adsorber (with an estimated adsorption capacity of 30 mg/g) is estimated to be 5.95 m^3/d. These estimated values of the adsorption capacities are apparently lower than those shown in Table 2 to account for adsorption inhibitors (e.g., mineral oils and operational deviations).

3.2. Financial indicators

To determine an order of magnitude cost for the treatment/separation of metolachlor as a model pesticide, recent typical indicators for small-scale facilities have been used based on reported cost indicators, cost functions and the current Egyptian market prices [21]. Cost adjustments have been undertaken to account for some local considerations. The basis of cost estimates is shown in Table 5.

A theoretical requirement for organoclay approaches 8 kg/d. Taking into consideration the presence of detergents or cleaners, the adsorption efficiency is assumed to be 50% and the capacity is further increased by 30% (for peak flow requirements). Thus, the estimated daily organoclay requirement is about 21 kg/d. The price of recovered water, solvents or solid pesticide has not been included in this stage of the analysis. The capital and operating costs for a typical 100 m^3/d of UF/NF/ organoclay separation facility are shown in Table 6. Estimated cost indicators include:

- Total capital costs: $240,850
- Total operating costs: $58,513/y

Table 5
Basis of cost estimates for the adopted treatment scheme

Item	Basis
Capital costs:	
Plant capacity ,Q	100 m^3/d
Cost of UF (ceramic membranes)	\$940/m^3/d
Cost of NF1(polymeric membranes)	\$940/m^3/d
Cost of NF2 (polymeric membranes)	\$2250/m^3/d
Cost of organoclay adsorbers	
Low load and filter	\$300/m^3/d
High load	\$1160/m^3/d
Operating costs:	
Power consumption	Consumption of electric power, 3 kWh/m^3 at \$0.05/kWh
Labor	\$0.2/m^3
Membrane replacement	\$0.25/m^3
Maintenance and spare parts	3% of total capital costs
Chemicals	
Membrane system	\$0.02/m^3
Organoclay	\$1000/t
Other operating costs	10% of total operating costs
Amortization	10% of total capital costs/y

All cost bases are according to current Egyptian market prices; 330 operating d/y.

Table 6
Capital and operating cost estimates for the treatment units

Item/process	Capacity (m^3/d)	Cost
Capital cost (\$):		
UF membrane system	100	94,500
NF1 membrane system	95	89,775
NF2 membrane system	9.5	21,375
Total membrane costs		205,650
Organoclay adsorbers		
Low load	94.05	28,200
High load	5.95	7,000
Total capital costs (\$)		240,850
Operating costs (\$/y):		
Power consumption		4950
Labor		6600
Membrane replacement		8250
Maintenance and spare parts		7225.5
Chemicals		
Membranes		660
Organoclay		3300
Other operating costs		3442.83
Total operating costs		34428.3
Amortization:		24085
Total annual costs (\$/y)		58513.3
Unit cost (\$/m^3)		1.77

Thus, the average processing cost for 1 m^3 of pesticide effluents is estimated to be about \$1.77. The comparative cost with an earlier development of Shaalan et al [2] (\$5.33/m^3) manifests the financial advantage of this system.

3.3. Uncertainties and future directions

The proposed system has the advantage of by-passing biological or chemical treatment interventions. It enables almost complete recovery of the effluent components and, in particular, water and slow release pesticides. The latter product is a matter of numerous research endeavors to cut down the consumption of pesticides and also mitigate the risk of direct pesticide use. The efficiency of the system depends on a field optimization study which is currently under way through a joint Egyptian/American cooperation project.

There is also a limited range of uncertainty regarding the capital and operating cost items for the membrane separation stages due to inflation and fluctuating energy prices. However, the typical norms used for cost estimation reveals promising aspects of the proposed scheme, especially if the prices of recyclables have been included. It is important to stress the fact that in spite of targeting this endeavor for the management of pesticides industry effluents, this system holds a good promise for the treatment of other surface or ground water slightly contaminated with pesticides.

4. Conclusions and recommendations

Treatment of pesticide industry effluents is mandatory to mitigate environmental and health risks. Recent advances in membrane separation can be utilized in conjunction with a rational adsorption scheme to enable recycling of water and some active ingredients in the pesticide industry. A proposed scheme has been investigated for the removal of metolachlor as a model pesticide. The proposed scheme incorporates UF, two NF stages and an organoclay adsorber. Separation efficiencies for the two NF stages are 94% and 96%, respectively. Further, the adsorption capacities of the low and high load organoclay adsorbers are conservative at 6 and 30 mg/g, respectively. The latter values are significantly lower than the reported experimental values. Reasons for such low loading values include possible adsorption inhibitors in the effluents and possibilities of operational deviations. The estimated capital cost of a 100 m^3/d treatment facility amounts to \$ 240,850. Further, the treatment cost is about \$1.77/m^3. Additional work is currently underway to incorporate other pesticides and establishing performance indicators under varying pesticide loads using thermally activated bentonites.

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