Preliminary Study on Nanotechnology-Based Process (Electrocoagulation) for Pesticide Wastewater Treatment Prior to Reuse in Agricultural Irrigation

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Abstract: The farmers interest in the use of this innovation is responsive to the development of innovative combined system which will be presented to water sector decision markers of the Arab Ministerial Water Council to include in their national water strategies and also within the Arab Water Strategy 2010-2030. No work has been carried out to date using nanomaterials as an additive to remove pesticide for comparison to the conventional electrocoagulation system. Tthe percentage of sludge less than 5%. The impacts of these system willsustain clean ground water, prevent land degradation and sustain human health through having safe food products when reusing treated wastewater in agricultural. This work provides new results on the electrocoagulation degradation of pesticide and lead to the following conclusion such as, after 90 days. For all pesticide studied by electrocoagulation the removal of pesticide wastewater is between 96% to 98%.

Key words: Pesticide wastewaters · Electrocoagulation · Nanotechnology

INTRODUCTION

It's predicted that word population will double in the next 50 years. In response, a greater yieds must be extracted from the current agricultural areas. In the MENA region, agriculture is the largest consumer of fresh water, accounting for more than 80% of water consumption. Futher, the irrigation schedule is mainly conventional based on the farmer experience.

This conventional irrigation approach cause inefficient use of water which can reduce the crops yield. Recycled wastewater presents a risk to human health and the environment due to presence of contaminants of emerging concern (CECs). Amongst the possible methods of treatment of pesticides, ozonation [1], oxidation with Fenton's reagent [2], photodegradation [3] and photocatalysis with TiO_2 have been investigated for a wide variety of pesticides [4]. Since the 1990s, electrochemical methods have been widely studied for the removal of organic substances and a number of reviews are available in the literature [5-7]. The adaptation of highly advanced nanotechnology to these traditional engineering processes offers new opportunities for development of advanced wastewater technology processes. Nanomaterials have unique size-dependent properties related to their high specific surface area (fast dissolution, high reactivity, strong sorption) and discontinuous properties (such as superp aramagnetism, localized surface plasmon resonance and quantum confinement effect). These specific nano based characteristics allow the development of novel high-tech materials for more efficient use of physical, chemical and biological wastewater treatment processes. The principal research issue of this project is the use of nanomaterials as analytical tools, for their use in innovative adsorption, electrocoagulation agricultural waste treatment processes. Our idea was developed for small and medium-sized company that or will be affected by climate change.

MATERIALS AND METHODS

Chemicals: Pesticide of technical grade (97%) was obtained from Rallis India. Analytical grade Na_2SO_4 (99.9%) used for the electrocoagulation process. Distilled water was used for preparing the pesticide stock solution. Tap water was used for diluting the stock solution to produce the artificially simulated wastewater.

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Fig. 1: Conception of unit pilot electrocoagulation

Instruments: Analysis of pesticide was carried out with a Hewlett–Packard 6890 gas chromatograph equipped with an ECD Detector, on-colum injection port and HP-5 column (5% diphenyl copolymer/95% dimethylpolysiloxane) (25 m × 0.32 mm ID, 0.52 μm film thickness). The temperature programme applied in GC/ECD was as follows: 80-250°C at 15°C/min, 80°C (1.00 min). The injection volume was 1 μl. The temperature of the detector was 300°C.

Extraction: The method used for the extraction of pesticide was adapted from Charles and Raymond [16]. For each 2 ml of the sample, 100 ml of acetone was added and the mixture was stirred for 2 hours. The extraction was carried out respectively with 100 ml and 50 ml of acetone. After filtration, the residues in acetone were partitioned with saturated aqueous sodium chloride (30 ml) and dichloromethane (70 ml) in a separating funnel. The dichloromethane fraction was collected and the separation process with (70 ml) dichloromethane were combined and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure at 40°C and the residues were dissolved in an acetone-hexane (1:9) mixture (10 ml). Samples were analysed by gas chromatography.

Preparation of Magnetic Particles: $FeSO_4$ and $CoCl_2$ with a molar ration of $[Fe]/[Co] = 2$ were immersed in 200 mL of aqueous solution. The systems were heated to 90 °C for 3 hours to promote further transformation of soluble initial ion/cobalt hydroxides to insoluble iron/cobalt oxyhydroxide complexes. The solution network was then transferred into 200 mL of a 1.32 mol/L NaOH solution with KNO_3 $[Fe^{2+}]/[NO^{3-}] = 0.44$) at 90 °C for 8 hours. The particle was then washed thoroughly and dried in order to generate magnetic particles [27].

Unit Pilot Design: A unit pilot was made using 32 aluminium electrodes (16 anodes and 16 cathodes) of total surface area 487 cm2 . Monopolar configuration of electrodes was adopted. The DC supply was capable of giving in the range 10- 30A. The set-up is as shown in Fig. 1.

To characterize the toxicity removal, the global parameter, the chemical oxygen demand (COD) is measured according to the standard methods for examination of water and wastewater [8]. All measurements were repeated in triplicate and all results were observed to be repeatable within a 5% margin of experimental error.

Statistical Treatments: The theoretical limit of detection, defined as the concentration of analyte that gives a signal equivalent to the blank signal plus three times its standard deviation, was calculated for each individual pesticide. In this work, the limit of detection (LOD) was taken to be the amount of analyte that gave a signal that was clearly distinguishable from the background noise of the instrument [26]. The theoretical limit of quantification (LOQ) was defined as the concentration of analyte that gave a signal equivalent to the blank signal plus ten times its standard deviation [9]. The comparison between the experimental results for unprocessed/edible and processed/inedible part of peppers was performed using the statistical *t*-student test with 0.05 as the significant level of the mean experimental values obtained in the determination of azoxystrobin and chlorothalonil [9]. The Student's t value was calculated using equation (I). For a population (unprocessed or edible parts of peppers) whose means have a values of (X), to have a high probability of belonging to the population (processed/inedible part of peppers), with a mean values

of (Y), the t-value calculated according to the above equation must be lower than the appropriate value listed in the Student's t-distribution table with the total number of degrees of freedom $n_1 + n_2 - 2$.

$$t_{cal} = \frac{\left|\overline{X} - \overline{Y}\right|}{s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \qquad (I) \qquad Where: \quad s = \sqrt{\frac{s_1^2 + s_2^2}{2}}$$

where n_1 and n_2 are the numbers of each group of samples and s is the unbiased estimator of the variance for the two groups of samples.

RESULTS AND DISCUSSIONS

Nanotechnology-based Process (Electrocoagulation) for Pesticide Wastewater Treatment
Performance of the Analytical Method: The use of method consisting in combined GC-ECD with liquid-liquid extraction (LLE) and solid phase extraction (SPE) seemed to be an excellent way to determine the types and levels of pesticides in water and in soil samples in a highly selective and sensitive manner. This method was previously validated before its use in our laboratory, according to the International Union of Pure and Applied Chemistry (IUPAC) criterions [10]. The linear dynamic range, precision (as relative standard deviation) and sensitivity (as limit of detection) values for determination of pesticide are reported in Table 1.

Linear Range: Individual calibration graphs were run with mixtures of pesticide at concentrations in the range 10–200 ng mL^{-1}. Each solution was injected five times.

The linear range, intercept and slope of the curve are given in Table 1 along with the regression coefficient for each pesticide.

Sensitivity: The LDs calculated in this way were 0.390 ng mL^{-1} to 1.297 ng mL^{-1} for pesticide. The limits of quantification (LQ) were 0.604 ng mL^{-1} to 2.324 ng mL^{-1} for each pesticide.

Precision: Untreated samples were fortified by the addition of an intermediate pesticide mixture solution. Samples were allowed to equilibrate for 2 h prior to extraction and were processed according to the procedure described above. The precision values for the method, expressed as relative standard deviation (RSD), were 2.6 to 5.5% (n = 5) for each pesticide.

Electrocoagulation Treatment System for Pesticide Using a Magnetic Particle: The first part of this work concerns the optimization of the different experimental parameters in order to mineralize pesticide, those parameters are initial concentration of compounds, concentration of the electrolyte support, temperature and the density of the current imposed. This mineralization has been done by a electrocoagulation through the electrodes of the iron. The degradation process has been followed by the DCO analyzes and the gas chromatography. It has been shown that the rate of mineralization exceeds 97 % and the concentration level of pesticide is less then limit of detection when added the magnetic particles in the system process. (Table 2). The optimum condition to treatment system for pesticide are the flow of unit pilot 100 L/h, the electrode is iron (36), current is 20 A and the temperature is 25°C.

Table 1: Figures of merit obtained for the used method (for details, see the text).

Analyte	Linear range (ng mL^{-1})	Y = a X + b	R^2	S$_{y/x}$	LD (ng mL^{-1})	LQ (ng mL^{-1})	RSD (%) (n=5)
Dicofol	25-200	(15.498±0.194)X–(46.272±2.088)	0.9995	26.310	0.404	1.348	4.4
Difenoconazol	25-200	(9.368±0.1653)X–(4.413±1.781)	0.9991	22.435	0.570	1.901	5.1
pyrimicarb	20-200	(27.797±0.511)X–(84.826±5.527)	0.9990	71.749	0.597	1.989	5.5
L. Cyhalothrin	10-100	(20.421±0.220)X–(70.490±1.340)	0.9997	17.068	0.197	0.6563	5.3
Fenzaquin	50-500	(9.878±0.137)X–(68.827±4.271)	0.9994	52.578	1.297	2.324	5.3
Deltamethrin	25-200	(18.38±0.222)X+(60.334±2.387)	0.9996	30.071	0.390	1.299	5.0
Azoxystrobin	20-200	(27.798±0.511)X–(84.826±5.527)	0.9990	71.7491	0.597	1.989	5.2
Bifenthrin	25-200	(9.374±0.167)X+(0.875±1.796)	0.9991	22.616	0.575	1.915	4.7
cypermethrin	25-200	(15.498±0.194)X–(40.2721±2.088)	0.9995	26.310	0.404	1.348	2.6
Cyprodinil	10-100	(52.120±0.517)X-(292.263±3.146)	0.9997	40.058	0.181	0.604	4.8

a; slope a; b, Intercept; *R*, regression coefficient; S$_{y/x}$, standard deviation of residuals; LD, limit of detection; LQ, limit of quantification, RSD, relative standard deviation.

Table 2: % COD reduction for pesticide wastewater treatment

	Pesticide	pH	Conductivity (µS/cm)	COD_i (mg/L)	COD_f(mg/L)	% COD	Concentrations mg. kg $^{-1}$
Without magnetic particle	Cypermethrin	7.7	780	2300	80	96	1.89
	Difenoconazol	7.4	756	4300	100	98	1.53
	Fenzaquin	7.6	710	2506	90	96	1.26
	Deltamethrin	7.8	685	3250	120	96	1.98
	Dicofol	7.7	890	3560	110	97	2.01
	Azoxystrobin	7.5	900	8500	120	98	1.52
	Bifenthrin	6.7	786	6520	110	98	1.23
	L. cyhalothrin	7.5	1000	3590	90	97	1.36
	Cyprodinil	6.8	950	3250	100	97	1.20
	Pyrimicarb	6.7	789	2560	100	96	1.36
With magnetic particle	Cypermethrin						< LD
	Difenoconazol						< LD
	Fenzaquin						< LD
	Deltamethrin						< LD
	Dicofol						< LD
	Azoxystrobin						< LD
	Bifenthrin						< LD
	L. cyhalothrin						< LD
	Cyprodinil						< LD
	Pyrimicarb						< LD

$$\%COD = \frac{CODi - CODf}{CODi} \text{ x } 100; \text{ COD : Chemical Oxygen Demand}$$

CONCLUSION

Nanotechnology-based process for pesticide wastewater treatment presented here has proved be very efficient for the cleaning of water contaminated with pesticides. The degradation rate of the pesticides in these system was fast. Therefore these system proposed could help in reducing the pesticide point contamination at farm level.

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