New perspectives for the application of diatomaceous earth to the remediation of polluted waters and soils

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RESUMEN. Se realizaron investigaciones acerca de la remediación de aguas residuales para prevenir daños, tanto de las reservas de aguas subterráneas como superficiales. Con este propósito, las tierras de diatomeas, un barato, disponible y no contaminante material, fue ensayado para la retención de contaminantes persistentes, tales como los metales pesados (cadmio) y pesticidas (antracita y cloropirifos). Esto ha sido utilizado en la prevención de la contaminación de aguas subterráneas debido a su gran movilidad reportada y a la irrigación y limpieza de suelos destinados a la agricultura. Variables tales como profundidad, espesor, etc. de los suelos quedaron cuidadosamente establecidos para simular una explotación casi real de suelos potencialmente contaminados. Los resultados preliminares presentados aquí muestran porcentajes de retención de cadmio mayores del 75 % y del 50 % para la antracita. Estos enfatizan el potencial uso como limpiador y remediador de las tierras de diatomea para contaminantes persistentes, tales como los metales pesados y los pesticidas, en particular, los utilizados en este estudio. La adsorción por las tierras de diatomeas es válida para todos los suelos ensayados. Luego, existe la posibilidad de prevenir la contaminación por cadmio en aguas subterráneas por deposición de una capa de las tierras de diatomeas bajo la superficie de los suelos.

ABSTRACT. Research effort dealing with the remediation of leaching waters polluted to prevent further damage of surface and ground water reserves are needed. For this purpose, diatomaceous earth, an inexpensive, available and no pollutant material, has been tested for retention of persistent pollutants, such as heavy metals (cadmium) and pesticides (atrazina and chlorpirifos). It has been used as underground water pollution prevention because of their high mobility reported, and for cleaning irrigation waters of a soil destined to agriculture purposes. There are parameters, such as depth, thickness, etc. that should be carefully established in order to respect the exploitation use of the potential polluted soil. The results obtained shown percentages retention for cadmium higher than 75 %, and 50 % for atrazina. This emphasises the potential of diatomaceous earth with remediation and cleaning purposes for persistent pollutants, such as heavy metals and pesticides used for this purpose. This DE adsorption is valid for all soils tested. The possibility to prevent cadmium underground water pollution by placing a diatomite earth layer under the surface of the soils exists then.

INTRODUCTION

During the last decades, industrial and other anthropogenic processes led to natural waters and soils pollution by persistent contaminants, both organic compounds (pesticides, PAH's...), and inorganic species (heavy metals). Among the organic pollutants, triazines pesticides are considered as priority pollutants since they are harmful to organisms even at low levels (µg . L^{-1}).[1] On the other side, cadmium has been considered one of the most toxic elements due to its high accumulation in the aquatic and biological systems.[2]

The increasing and undiscriminating use of pesticides and metal-containing fertilizers in agriculture means that the mechanisms and magnitude of these pollutants movement after their application continue to be an active research area.[3,4] The mobility of those compounds is highly dependent on their physicochemical properties and the soil characteristics. In the soils, for instance, cadmium is present as ionic soluble forms (hydroxides, chlorides, and other soluble chelates) or

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as precipitate (colloidal sulphurs, sulphates, carbonates, etc.). Soil composition (sand and mineral content, micro-organisms, humus) and environmental factors such as pH, moisture, redox conditions, etc. seriously affect the transport of this element favouring leaching phenomena (increasing water contamination risks), or rise the bio-availability that imply bio-accumulation and toxicity.[5] A similar behaviour can be expected for the pesticides cited above. Many pesticides, such as triazines, can disappear from the soil by physico-chemical processes including volatilisation, photolytic and/or microbial degradation, leaching, etc. Their high solubility in the aquatic systems makes them quite mobile into the environment.[6]

When the potential level of exposure to contaminants in an area is unacceptable for human health or for ecological reasons, remediation strategies become necessary. The total cleaning and contaminant removal from contaminated waters or soils are preferred rather than pollutants immobilisation or reduction of their toxic effect. However, very often there is an important fraction that remains linked to the substrate and to the components of the matrix.

Different methods for contaminated waters and soils recuperation have been employed, based on three main principles.[5]: i) immobilisation-stabilisation, by applying physical treatment (addition of adsorbents in order to increase the adsorbent power of the soil) or chemical treatment (pH or redox conditions modification, addition of complexing agents, etc.); ii) separation, by precipitating the contaminant and posterior separation, or by removal of the contaminated soil and replacement by a clean one; iii) destruction or transformation of the contaminant by its conversion to harmless species, or by growing high accumulating plants that assimilate the toxic compounds.

Within the remediation procedures, there are two main purposes for that.[7]: i) underground waters preservation, and ii) immobilisation of contaminants to reduce their bioavailability for plants. The main treatments used for recuperation of polluted areas have been focused on the reduction of the bioavailability and uptake of the contaminants by plants. With this purpose, some adsorbents have been used like zeolites, manganese oxides, activated carbon, etc.[8,9] To date, it has not been reported in the literature a direct analytical application of the diatomaceous earth (DE) with remediation purposes.

In this paper, DE substrate has been used with soil and water decontamination purposes. The studies have been focused in different analytes:

- inorganic cadmium: firstly, for the preservation of underground waters sited in the proximity of polluted soils; and a second study for the immobilisation of ionic cadmium in order to reduce its bio-availability for plants;
- pesticides: stabilisation of the organic analytes and cleaning of contaminated irrigation waters and then prevention of pesticides mobility to underground waters

In previous works, high retention capacity of these analytes by the DE was clearly demonstrated.[10] The necessity to know if the retention was permanent and reliable at natural conditions as well as the stability of such retention is presented in this work. Schemes and procedures for contaminated areas are proposed. A final discussion of the main advantages and drawbacks of this substrate has been included.

MATERIALS AND METHODS

Reagents and instrumentation

All reagents and solutions used were of analytical-reagent grade. Hydrochloric acid was purchased from Merck (Darmstad, Germany). Ethyl acetate was from Sharlau (Barcelona, Spain). Ultra-pure water from Milli-Q system (Millipore) was used throughout. A 1 000 mg/L atomic absorption standard solution of Cd^{2+} (purchased from Sigma) was used to prepare the stocks standard solutions, and stored at 4 °C . Atrazina, was purchased from Riedel de Haen (Hannover, Germany). Stock standard solutions (1 000 mg/L) were prepared in ethyl acetate and stored at –20 °C in the dark.

Working solutions were freshly prepared by diluting appropriate aliquots of the stock solutions.

Natural DE from Morocco (Ras-Traf , Nador, Morocco) was used as adsorbent material. It was screened to obtain powder with granulometry (d < 65 µm) and dried at 110 °C for 24 h before use. The chemical composition of these DE revealed a major content on SiO_2 (72 %), Al_2O_3 (7 %), CaO (10 %), Fe_2O_3 (4.5 %) and other minor components. This analysis has shown a typical composition for such material.

A Perkin-Elmer 2380 atomic absorption spectrometer was used for Cd elemental measurements. A wavelength of 228.8 nm was used and a spectral band-pass of 0.7 nm . A Cd hallow cathode lamp was used as the spectral source.

An electronic screening microscope JEOL JSM 6400 provided with a Dispersion Ray X Spectrometer LINK EXL has been used for the qualitative cadmium analysis in soils.

Pesticides detection was performed by using a gas chromatograph equipped with a nitrogen-phosphorus detector (GC-NPD, HP5890-II Hewlett Packard) with a 30 m X 0.32 mm id fused silica capillary column SPB-50 (Supelco, USA) with He carrier gas (1.8 mL/min) and N_2 make-up gas (30.7 mL/min) (Table 1).

Soil samples

Five different soils were obtained at the Chemistry and Agriculture Analysis Department, Agriculture Engineers School at the Universidad Politécnica (Madrid, SPAIN) (Table 2). There are significant differences in the contents of some characteristic components, such as sand clay, $CaCO_3$, which make them adequate for their study.

Experimental procedure

Cadmium removal from soil leaching: The figure 1 represents the experimental procedure followed for cadmium retention in DE to prevent leaching to underground waters. This scheme proceeds firstly with soil contamination by adding 100 times the Cd limit value established by the legislation (1 mg/kg) (Royal Decreto). That means addition of 5 mg Cd (as ionic Cd^{2+}) to 50 g of soil. The soil is then completely covered by tap water, stirring and left over 48 h for soil-pollutants exchange. Then, two strategies were adopted:

- Evaluation of the Cd retained and not retained by soils: the Cd not retained is dragged and collected as fraction 1 and analysed by FAAS. By using HCl at pH = 0.1, the Cd retained is quantitatively eluted (fraction 2) and measured by the same analytical technique. Both fractions represented the total Cd added.
- Retention of the labile Cd by DE: fraction 1 is mixed with 20 g DE substrate, stirred and filtered. Retention by DE was evaluated after elution with HCl at pH = 0.1 (fraction 3) and analysis by FAAS. Fraction 1 was used as a reference

(100 % Cd content) to evaluate the amount retained by DE.

Table 1. Chromatographic conditions for pesticides detection.

Detector temperature program	Initial T (°C)	Ramp (°C/min)	Final T (°C)	Holding time (min)
First step	60	50	180	1
Second step		15	225	3
Third step		2	280	1.5
Injector temperature	3° C over track			
Injection volume	1 µL			

Table 2. Characteristics of the soils used for the remediation studies employing DE.

Composition	A	B	C	D	E
(%)			(%)		
Sand	38	28	57	55	92
Mud	46	12	17	23	8
Clay	13	11	26	22	0,3
$CaCO_3$	3	42	—	—	—
pH	8	8	8	8	6

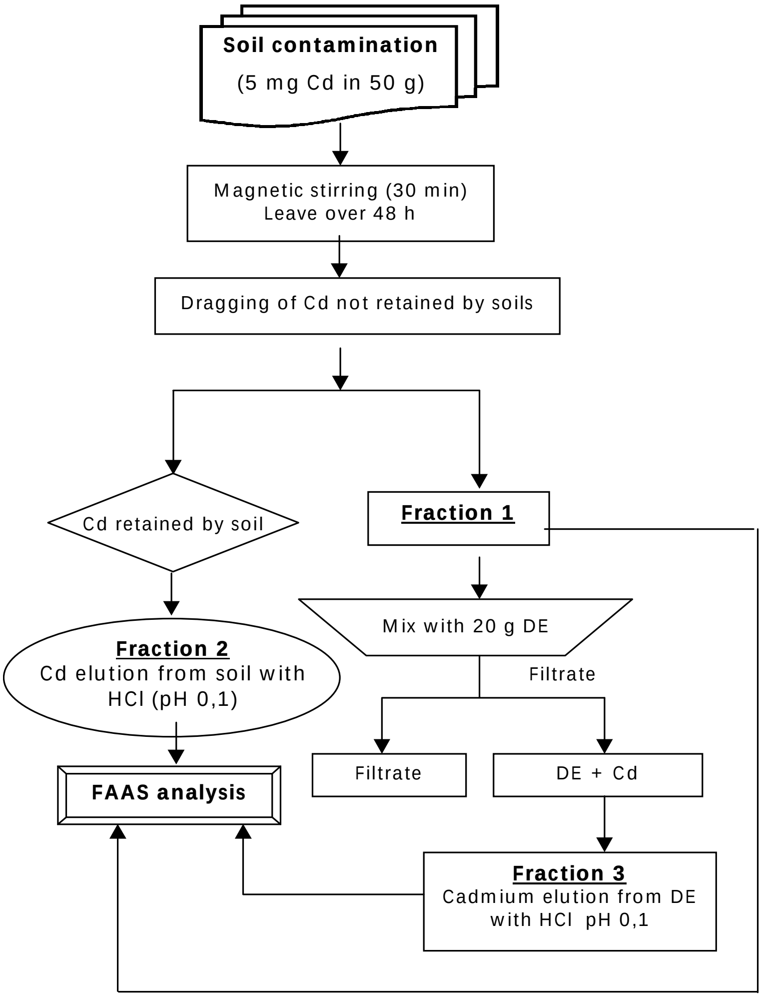

***Fig. 1**. Evaluation of cadmium retention by DE from polluted soils to protect underground waters.*

Stability of pesticides in DE: Initially, 12 µg of atrazina and chlorpirifos were added to 3 g of DE and 20 mL of methanol to increase the adsorption. The final concentration of each pesticide was 4 µg/g of DE. The mixture was mechanically shacked for 10 min . Then, methanol was allowed to evaporate overnight. DE containing the adsorbed pesticides was distributed in amber glass bottles and stored at –20 °C, 4 °C and 25 °C (as room temperature) for stability study over three months. Pesticides were extracted from DE at different dates by using 1 : 1 hexane/acetone in an ultrasonic bath for 25 min . Extracts analysis was carried out by GC-NPD.

Pesticides cleaning from irrigation waters: The first step, as for cadmium, is the contamination of the soil by adding 250 µg of atrazina, to 125 g of soil saturated with water (Fig. 2). Then, irrigation of the soil with 13 mL 0.01 % $CaCl_2$ was performed during 60 d . The liquid obtained from this experiment was collected after 48 h, waiting for equilibration of the system, and used with different purposes:

- measured by GC-NPD to know the mobility or retention of atrazina by the soils.
- filtrated through a Buchner funnel containing DE (0.5 g), and the filtrate was analysed by GC-NPD for evaluation of DE capacity retention. The leaching liquid was used as reference (100 % atrazina content) to evaluate the amount retained by this substrate.

In all cases, blanks were run to prove leaching and retention by soils and DE.

RESULTS AND DISCUSSION

Underground waters contamination is mainly due to filtration and adsorption of the contaminants through the soil profile. There are classical methods to evaluate this pollution by calculating the soil-water partition and adsorption coefficients of the contaminants to predict their mobility. However, this modelling is still a challenge in the case of the contaminants concerned. This lack of information has stimulated the experiments designed to rise the knowledge of these contaminants behaviour.

Cadmium retention by DE to prevent underground water contamination

Cadmium retention capacity by soils was evaluated as explained in the experimental procedure. Results showed a 25 % as minimum amount of cadmium retained by all soils

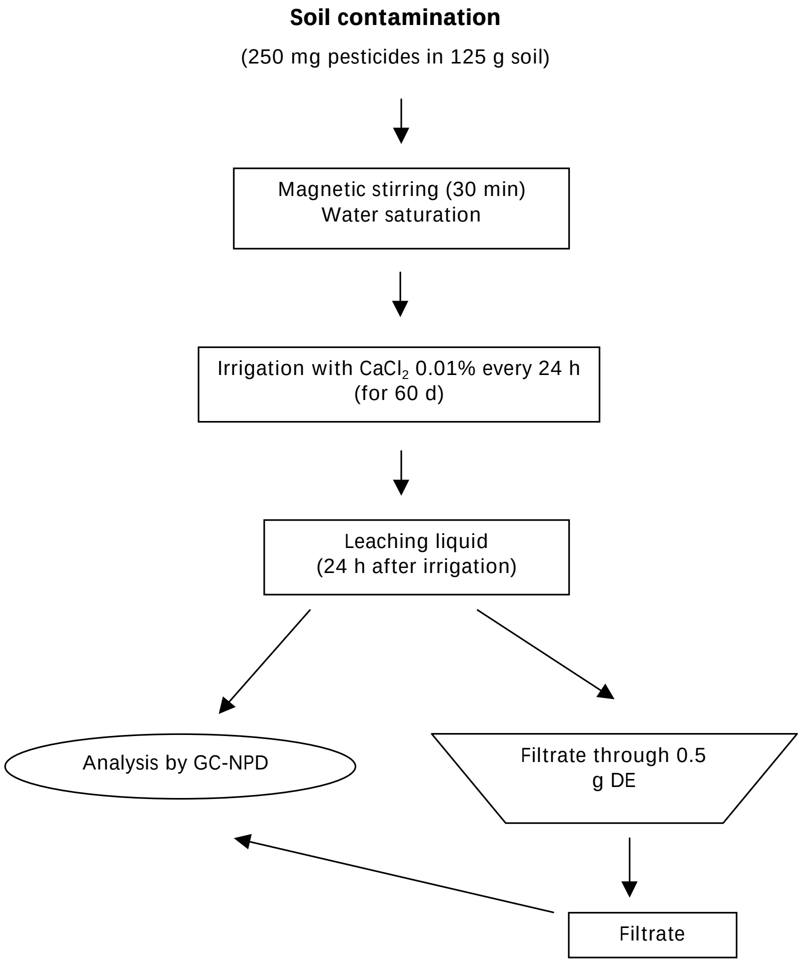

***Fig. 2**. Evaluation of pesticides (atrazina) retention by DE from polluted soils to protect underground waters.*

tested. The highest retention corresponded to soil B with major content of $CaCO_3$ (Table 2), by favouring the formation of the insoluble $CdCO_3$. On the other hand, the lowest retention capacity was observed in soil E, with 92 % sand content contrarily to the expected in a soil with this component. This may be due to the low clay and mud contents of this soil, which eventually could contribute to the immobilisation of this analyte. It can be concluded as a general remark, that an important percentage of the Cd added (at least 75 %) is leached through the soil layer, with the potential risk of underground water pollution.

Then, the experimental design for DE cadmium retention (Fig. 1) was tested in order to evaluate the DE capabilities to retain the cadmium migrated through the soil. HCl at pH = 0.1 was the eluent used to extract the Cd retained by DE substrate. Filtrate 1 (cadmium not retained by soils) was used as the reference (100 % Cd content) to evaluate the amount retained by DE. The analysis was performed by FAAS. Results (Fig. 3) show practically the total cadmium present in the soil leaching. This DE adsorption is valid for all soils tested. It exists then the possibility to prevent cadmium underground waters contamination by placing a diatomite earth layer under the surface. There are parameters, such as depth, thickness, etc. that should be carefully established in order to respect the exploitation use of the potential contaminated soil. This study is therefore a multidiscipline task that should be accomplished with agriculture, ecology, and other concerning field experts.

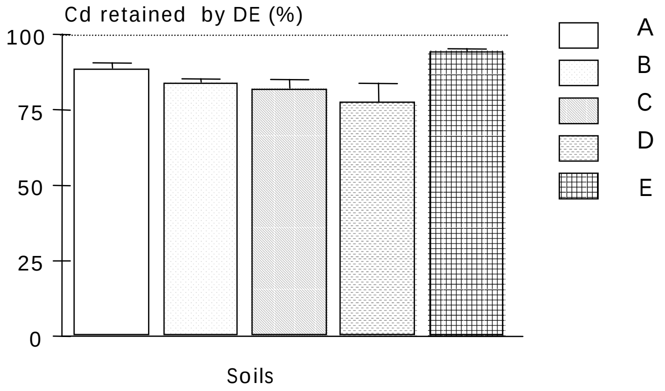

***Fig. 3**. Cadmium retention by DE from soil filtrate.*

The experiment has been carried out without any pH adjustment. An interesting study of the DE capacity retention depending on the soil pH and redox conditions should be done. It is well known that Cd solubility and consequently, bio-availability is highly dependent on the pH and redox conditions.[5]

Pesticides stability studies

As it has been stated in the experimental procedure, atrazina and chlorpirifos stability in DE has been studied. This stability has been evaluated by comparing the results obtained at different temperatures and times versus those obtained for samples recently prepared. Calculations have been made on the basis of R factor:

$$R = x/x_{(t = 0)}$$

and the combined uncertainty:

$$[U = CV^2 + CV^2_{(t = 0)}]^{1/2} \cdot R/100$$

of the measurements, where x is the mean value of the measurements made at different times within the three months period, and CV are the coefficient of variation of x.

The results obtained in these assays showed a high stability for both pesticides for the three months tested at –20 and 4 °C . However, at room temperature some losses have been observed from the second storage month, meaning possible changes of the initial compounds. Further experiments can be undertaken with this substrate.

Atrazina removal from irrigation waters by DE retention

As it has been stated, field scale information about mobility of pesticides in soils is very scarce.[10] This experience has been performed by testing five soils (Table 2), being soil E selected for remediation purposes as it presented the highest leaching effect, corresponding to the highest sand amount. Then, the procedure exposed (Fig. 2) has been applied. Different leaching fractions (taken 24 h after the corresponding irrigation) were analysed after filtration trough diatomite earth and without filtration (Fig. 4). The first two leaching (collected 24 and 48 h , respectively) presented a half reduction on the atrazina amount present in water when treated with DE. However, the third one shows less atrazina concentration but no retention by DE. This disability to retain the pesticide can be assigned to a competition between atrazina and other organic compounds present in the matrix (fulvic, humic acids, for instance): DE is not a specific adsorbent as the main mechanism for retention is supposed to be adsorption.[11] Then, to prevent or minimise this interference, the DE thickness could be increased.

These preliminary results point out the interest of this material to prevent possible contamination of greenhouses accidentally irrigated with pesticides and evaluate, acorn with the preliminary results, the possibility to be applicable for cleaning natural and underground waters polluted with these compounds.

CONCLUSIONS

Preliminary results presented here emphasises the potential of diatomaceous earth for remediation and cleaning purposes for persistent contaminants, such as heavy metals and pesticides. This new approach offers new perspectives in two fields: remediation field with direct application to soils (by placing a DE layer under the surface) or as a filter for polluted waters.

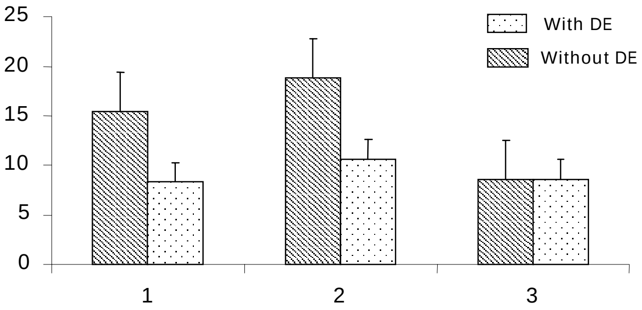

Fig. 4. *Atrazina retention by DE from irrigation water.*

The retention of these analytes offers the possibility of field sampling and storage due to the good stabilisation of the pesticides in the substrate; secondly, DE can be used as a direct system of pesticides retention and pre-concentration.

These promising results have to be completed by studying more deeply factors that at field scale can affect the retention, such as pH, redox conditions, humidity, etc.

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