ISSN : 0974 - 7451 Volume 6 Issue 5

Trade Science Inc.

Environmental Science
An Indian Journal

Current Research Paper

ESAIJ, 6(5), 2011 [272-278]

Remediation of soil contaminated by atrazine, using delivery vehicle of β-cyclodextrin/SDS (beta-cyclodextrin/sodium dodecyl sulfate) into deep soil, and mineralization of the atrazine present in the eluates by oxidative iron powder technology

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Received: 11th July, 2011 ; Accepted: 11th August, 2011

ABSTRACT

Mixture of β- cyclodextrine and sodium dodecyl sulfate (SDS) was used to enhance the desorption of atrazine from the soil. The effectiveness of atrazine transfer from the soils to the solution reaches 98% with the combination of β-cyclodextrin with SDS. The mineralization of atrazine was carried out by its reaction with hydroxyl free radicals generated from zero valent iron powder by oxidative reaction. The complexation of atrazine with β-cyclodextrin indicates a 1:1 stoichiometric ratio for the binary inclusion complex between atrazine and ß-cyclodextrin with a formation constant K = 285 ± 15 M^{-1}. Batch and columns studies were conducted for the remediation of soil polluted by atrazine. These studies allowed the development of a delivery vehicle for iron particles using aqueous ß-cyclodextrin/SDS solutions. The oxidation reaction of atrazine was carried out by iron particles under appropriate conditions with a nearly 99% removal at pH 6. More than 97 % of atrazine disappeared during 30 minutes of treatment. The evolution of atrazine degradation was monitored by, HPLC, TOC meter and UVVis spectroscopy.

KEYWORDS

Soil pollution;
Zero valent iron powder;
β-cyclodextrin;
Inclusion complex;
Atrazine.

INTRODUCTION

Atrazine [2 - chloro- 4ethylamino - 6 - iso - propylamino - 1, 3, 5 - triazine] is among the most commonly used herbicides in the world. In USA,. Atrazine has been classified as a Restricted Use Pesticide (RUP) due to its potential for groundwater contamination[1]. Atrazine excess and leaching from application sites into rivers, streams, lakes, reservoirs and groundwater is an ecological concern. In some aquatic ecosystems contaminated by atrazine, photosynthesis of algae, a primary producer in food chain, may be inhibited indi-

cates potential toxic effects on animals from atrazine metabolites[2, 3].

Long-term exposure to amounts greater than 300 ppb of atrazine can result in cardiovascular damage, retinal damage, muscle degeneration, and cancer. The treatment of atrazine become an urgent need. Some pesticides that are persistent in aerobic environments are more readily degraded under reducing conditions[4]. Thus generating a reducing (electron-rich) environment in soils, sediments, and aquifers has become a popular treatment option. One application of this technique uses zero valent iron (ZVI) as a chemical reductant. Under aerobic conditions, oxygen is the usual electron acceptor, while in anaerobic environments, electron release from the reaction of ZVI with water can be coupled to the reaction of chlorinated and nitroaromatic compounds[5]. Treatment with ZVI can promote rapid abiotic degradation via reductive dechlorination. When halogonated organic pollutants are treated with ZVI, oxidation of ZVI and Fe(II) provides electrons for dechlorination

$$Fe^0 + R\text{-}Cl + H^+ + \rightarrow Fe^{2+} + R\text{-}H + Cl^- \quad (1)$$

$$2Fe^{2+} + R\text{-}Cl + H_2O \rightarrow 2Fe^{3+} + R\text{-}H + OH^- + Cl^- \quad (2)$$

zero-valent iron as reactive medium for contaminated water treatment, is one of the most promising techniques because the iron metal is of low-cost, easy-to-obtain, and has good effectiveness and ability of degrading organic contaminants[6-12]. Iron metal has also high oxidation capacity at appropriate conditions of pH, and oxygen content[13]. In order to facilitate the atrazine transfer from the soil to the aqueous phase we had to look for an adequate extractors. The possibility of application of

β-cyclodextrin for reducing the pollutants in wastewater has long been recognized[14]

In our previous work we used β-cyclodextrin to extract the atrazine from the soil[15].

The objective of this work was to investigate the decontamination of soil polluted by atrazine using mixture of sodium dodecyl sulfate(SDS) and β-CD to increase the capacity of atrazine extraction from the soil and followed by a treatment using the zero valent iron power technology.

Before performing soil columns studies we have conducted several preliminary batch experiments. The soil columns experiments were as the following:

(1) Delivery of β-cyclodextrin with sodium dodecyl sulfate (SDS) into deep soil and collecting the eluates to be treated a separate batch

(2) Delivery of β-cyclodextrin with sodium dodecyl sulfate (SDS) trapped iron into deep soil and treat the eluates in-situ of the column

METHODS AND MATERIALS

Reagents

β-cyclodextrin, SDS and iron powder (350 mesh) were purchased from Sigma Aldrich, and used as received. Atrazine was purchased from Rodel-dehein. Distilled water was used for preparing aqueous solution of β-cyclodextrin, SDS and atrazine stock solutions.

Apparatus

Atrazine was analyzed by a UV–visible spectrophotometer (UV-1601, Shimadzu), signal wavelength of 222 nm with 20 nm bandwidth. The pH values were measured in open bottles with a WTW pH/mv, and hand-held meter 330/set.

The atrazine was monitored by HPLC liquid chromatography using a Hewlett-Packard system (HP1100) equipped with amono-channel UV-visible detector and an automatic injector. The experiment was performed by UV detector at 222 nm by using a reverse phase Merck column (SpherisorbO DS 25μm; 250.4.6mm). The flow rate was 1mL/mn and the injected volume was 50μL. The conditions for atrazine analysis were ::mobile phase consisting of 1% of acetic acid (10%) and methanol (90%) at a flow rate of 1.00mL/ min. Atrazine was detected at 222 nm, and the retention time was 12.4min. The limit of detection was 10μg/L.

Analysis of total organic carbon (TOC).

Total organic carbon (TOC) contents were measured with a Shimadzu TOC Analyzer model 5050A (Japan). Water was used as blank controls. TOC was measured before and after reaction. TOC contents of the samples were determined with catalytic oxidation at 850°C in presence of O_2 and CeO_2 followed by acidification with 10% H_3PO_4. A non-dispersive infra-

red detector was used to determine the formed carbon dioxide.

Atrazine dilutions

Atrazine was dissolved in deionized water to form a 10 ppm stock solution. All the glass vials containing soils and atrazine solutions (10 mg/L) were shaken until the measurement time was reached.

Soil samples

Clayey soil was collected from an agricultural field, and was transported in coolers to the laboratory where was air-dried and ground to pass through a 2 mm sieve followed by fortification with atrazine solution at 10 mg/L .

Soil column experiment

Experiments were conducted in bench-top soil columns as shown in Figure 1. The external dimensions of the columns were 30 cm x 30 cm x 150 cm. The internal dimensions were 10 cm x10 cm x 150 cm. The column was filled with clayey soil. Extractor mixture (β-cyclodextrin witn SDS) is delivered into deep soil, and it can trap the target pollutant molecules . Sodium dodecyl sulfate (SDS) is used as a detergent at the concentration 5g/L. β-cyclodextrin (β-CD) is used at the concentration of approximately 20 g/L. The eluate is collected and treated with our iron powder oxidative technology for complete mineralization of the pollutants. A small aliquot of the eluate is analyzed for the concentration of the target pollutants and their metabolites, particularly their reduction products. Soil column experiments was performed, based on the experimental design in TABLE 1.

Cyclodextrin-detergent solution was applied on the top of the soil column and allowed to diffuse by gravity. The eluate was treated with our oxidative iron powder technology for complete mineralization of the pollutant.

TABLE 1 : Soil column experimental design

Compound	Description
Soil	Clayey
Detergent	SDS Sodium dodecyl sulfate 5g/L
Cyclodextrin	β-CD 20g/L
Iron	Powder 325 mesh 4g/L of eluate
Target chemicals	Atrazine

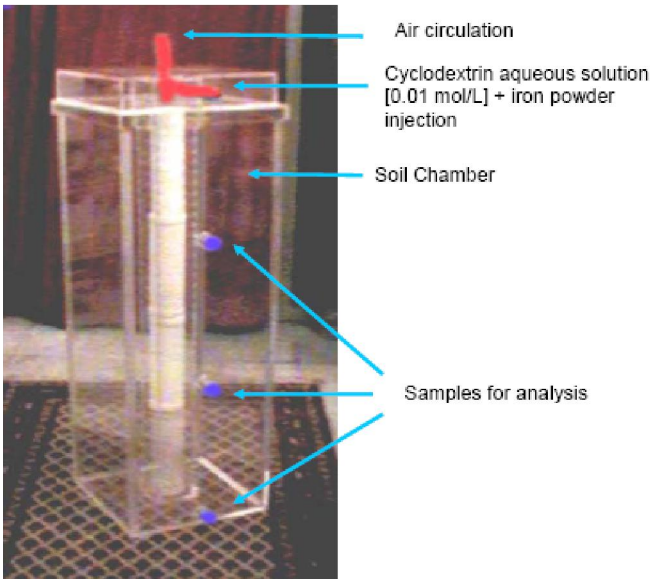

Figure 1 : Prototype soil column treatment using β-cyclodextrin, detergents and zero valent iron. Column external dimensions are 30 cm x 30 cm x 150 cm; and internal dimensions are 10 cm x 10 cm x 150 cm. This compartment is perforated from the bottom to the top. Sampling heights from the top of the column for analysis are: 5 cm, 55 cm, and 110 cm.

PROCEDURES

Sorption and desorption behavior of atrazine

Adsorption

Adsorption isotherms for atrazine was determined using the batch equilibrium technique at 24.2 °C. A 5-mL aliquot of atrazine solution was added to 1 g of soil in a 50-mL glass centrifuge tube resulting in a solution-to soil ratio of 5:1. Each experiment was replicated four times. Slurries were placed on a reciprocal shaker for 24 hours and then centrifuged at 2000 x*g* for 20 min at 24.2 °C. The amount of atrazine adsorbed after each equilibration was calculated as the difference between the supernatant concentration and the amount of chemical initially added.

Desorption

Desorption isotherms were obtained from the adsorption samples in equilibrium with the largest initial concentration in solution. Three milliliters of supernatant solution was removed from the centrifuge tubes and replaced with an equal volume of adequate solutions.[di-ionized water (1), beta-cyclodextrin0.01M aqueous solution(2) and beta-cyclodextrin0.01M aque-

ous solution mixed with SDS 0.001M(3)]. Soil pellets were dispersed using a vortex mixer, and tubes were placed on a reciprocal shaker for 24 h at 24. 2 °C. Tubes were then centrifuged for 20 min at 2000 x *g*. The desorbed concentration was calculated as the difference between the supernatant concentration and the estimated adsorbed atrazine already determined in the adsorption process.

EXPERIMENTAL SECTION

Evidence of atrazine trapped β-cyclodextrin

UV/VIS spectra were obtained for atrazine and β-CD-atrazine complex in water at pH 6.5. Figure 2 shows the absorption spectra of a constant amount of atrazine ($9.26x10^{-6}$ M or 2 ppm) dissolved in varying concentrations solutions ($1x10^{-3}$ – $9x10^{-3}$ M) of β-CD. The absorption intensity of atrazine increased as the concentrations of β-CD increased. The remarkable changes suggest an interaction between β-CD with atrazine, in which atrazine molecules preferentially reside in the non-polar CD cavity.

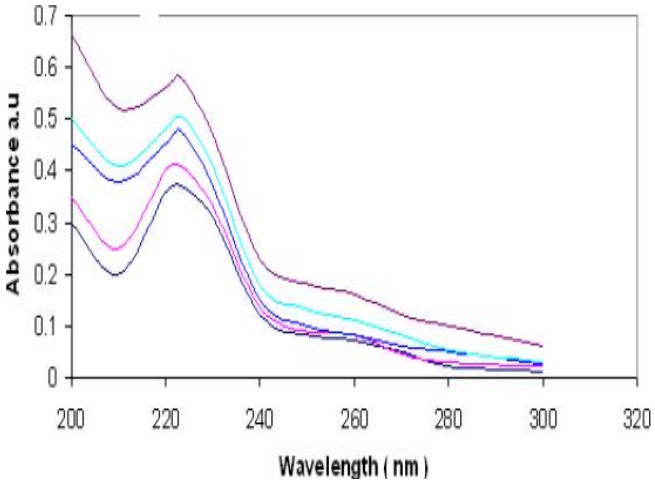

Figure 2 : UV/VIS absorption spectra of atrazine at $9.26x10^{-6}$ M in varying concentrations of β-CD solutions ($1x10^{-3}$ - $9x10^{-3}$ M). The higher concentrations of β-CD, corresponding to the higher absorbance.

Stoichiometry of the inclusion complex

The stoichiometry of β-CD-atrazine complex was analyzed by the Scatchard and Benesi-Hildebrand plots Connors[16, 17].

According to Scatchard's method (equation 1), we assume that β-CD forms an inclusion complex with atrazine by 1:1 ratio. If the β-CD-atrazine complex is formed in a 1:1 ratio, a plot of $(A-A_0)/[\beta\text{-CD}]$ versus $(A-A_0)$ should give a straight line. Figure 3a shows a linear relationship of $(A-A_0)/[\beta\text{-CD}]$ versus $(A-A_0)$.

$$\frac{(A-A_o)}{[\beta-CD]_o} = (A_\infty - A_O)K_1 - (A-A_O)K_1 \qquad (1)$$

Where A_0 denotes the absorbance intensity of atrazine in the absence of β-CD, A_8 denotes the absorbance intensity when all of the guest molecules are essentially complexed with β-CD, A is the observed absorbance at each β-CD concentration tested, K_1 is the association constant and $[\beta\text{-CD}]_0$ is β-CD concentration tested.

When a Benesi-Hildebrand plot of $1/(A-A_0)$ versus $1/[\beta\text{-CD}]$ is constructed according equition-2, a straight line is obtained. Figure 3b shows straight lines. When the plot of $1/(A-A_0)$ versus $1/[\beta\text{-CD}]^2$ is considered, a downward concave curvature is obtained, confirming that the stoichiometry of the [β-CD-atrazine] complex is not 1:2.

$$\frac{1}{(A-A_O)} = \frac{1}{(A_\infty A_o)K_1[CD]_o} = \frac{1}{(A_\infty - A_O)} \qquad (2)$$

Association constant of the inclusion complex

The slope of the Scatchard plot is very close to the value that the intercept is divided by the slope of the Benesi-Hildebrand plot. A non-linear regression provides a more precise method than the double reciprocal plot for the determination of the complex formation constants[17]. The determination is based on equation-3[16].

$$\Delta I = \frac{K_1 H_0 \Delta I_{MAX}}{(1+K_1 H_0)} \qquad (3)$$

Where $\Delta I = (A-A_0)$ is the guest-induced absorbance intensity, and is equal to $\Delta I_{max} = (A_8-A_0)$ when every host exists as the inclusion complex. I_{max} is obtained from the double reciprocal plot equation 1. H_0 is the initial concentration of the host. The formation constant (K_1) is estimated by fitting Eq-3 to the data obtained.

Figure 4 : Shows the curve fitting for atrazine. According to this curve the value of K_1 is 285 ± 15 mol^{-1}.

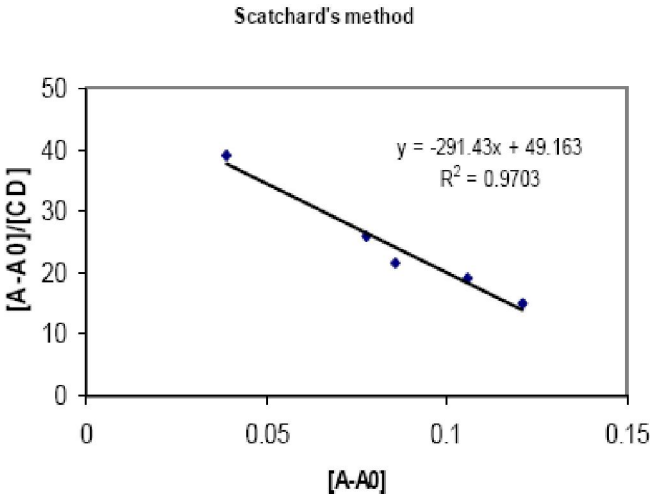

Figure 3a : The Scatchard plot is (A-A_0)/[β-CD] *vs.* (A-A_0);

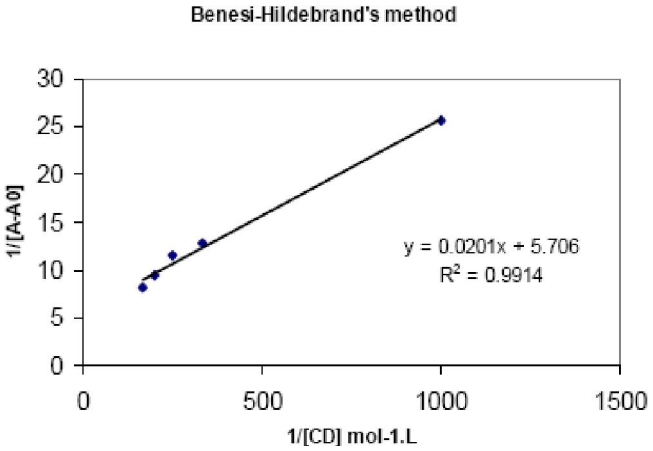

Figure 3b : Benesi-Hildebrand plot 1/ (A-A_0) *vs.* 1/[β-CD].

Figure 3 : Scatchard plot (a) and Benesi-Hildebrand plot (b) of β-CD-atrazine complex formation. The Scatchard plot is (A-A_0)/[β-CD] *vs.* (A-A_0); and the Benesi-Hildebrand plot 1/ (A-A_0) *vs.* 1/[β-CD].

Effect of β-cycodextrin and sodium dodecyl sulfate [SDS] on the effectiveness of the atrazine extraction from the soil

Adsorption batch experiments were performed in triplicate in 50 ml glass centrifuge tubes by mixing 6 g of soil with 30 ml of atrazine solution 10 ppm . The samples were shaken at 22 ± 2 °C for 24 hours to allow adsorption equilibrium.

Desorption or extraction experiments were initiated immediately after ascertaining sorption by replacing the supernatant by the same volume of de-ionized water [1] β-CD solution (10mM) [2] and β-CD (10mM) mixed with SDS (0.1mM)respectively. The tubes were shaken again, allowing desorption equilibration for 12

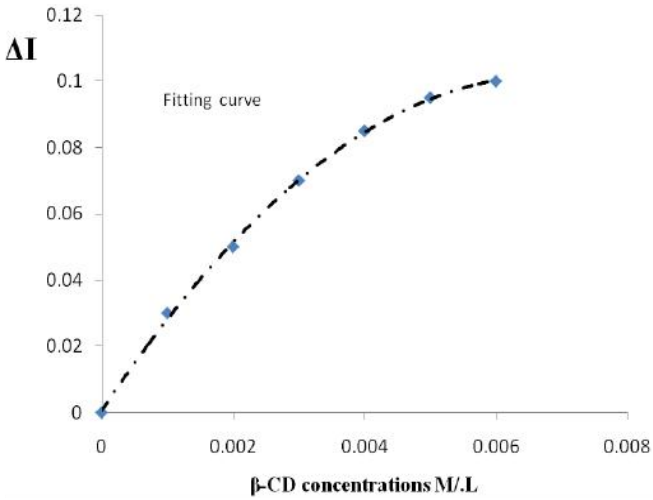

Figure 4 : Fitting curve of the guest-induced absorbance intensity (ΔI) vs. the initial concentration of the host β-CD (H_0). Where ΔI = (A-A_0), and is equal to I_{max} = (A_8-A_0) when every host exists as the inclusion complex

hours . samples were withdrawn each two hours. The concentrations of atrazine in the supernatants were determined by HPLC.

The amount of atrazine desorbed was calculated from the difference between the concentration of the supernatant and the estimated adsorbed atrazine. Extraction experiments were performed in triplicates. The reproducibility of these measurements was around 5%.

Three types of solvent to extract the atrazine from the soil;

1- Di-ionized water
2- Betat-cyclodextrin solution 10mM
3- Beta-cyclodextrin10mM mixed with SDS 0.1mM

The three tubes containing the samples of soil were shaken for 12 hours . Samples were withdrawn each two hours for analysis were withdrawn.

Figure 5 presents the evolution of effectiveness of the solvents on the desorption operation.. As shown in this Figure the desorption of atrazine from the soil by water need 10 hours of shaking while the β- CD solution need 2 hours to reach95%. The mixture CD with SDS need less than two hours to reach 99.7 % desorption of atrazine from the soil.

TABLE 2 summarizes the final results of the extraction of atrazine using the solvents mentioned above.

Analysis of atrazine

The chromatogram of atrazine in the conditions mentioned above shows that the retention time of atrazine is

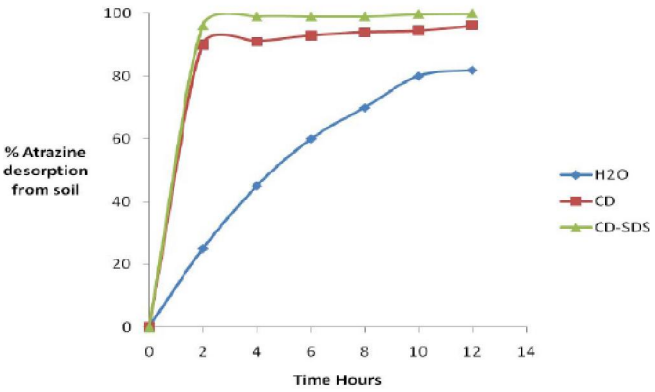

Figure 5 : Effect of β-cycodextrin and SDS on the effectiveness of the atrazine extraction from the soil : The solvents used are respectively:H2O, β-CD [10mM], and [mixture of β-CD 10mM with SDS 0.1mM]

TABLE 2 : The experimental results of atrazine extraction using water, *β*-cycoldextrin solution (10 mM) and β-cycoldextrin (10 mM) and SDS (0.1 mM) solution

Eluting solution	Percent of atrazine extracted
Water	78 ± 0.2
β-cycoldextrin solution (10 mM)	95 ± 0.2
SDS (0.1 mM) solution	90± 0.2
β-cycoldextrin (10 mM) and SDS (0.1 mM) solution	99.7 ± 0.15

12.4 minutes.

Degradation of atrazine by metallic iron powder

The evolution of UV/Vis spectra Figure shows a degradation of the atrazine with the time of treatment. At 20 minutes 80% of atrazine disappeared

The HPLC analysis of the samples as shown in Figure 7 demonstrate an exponential decreasing of the atrazine. After 30 minutes the atrazine cbecome undetectable.

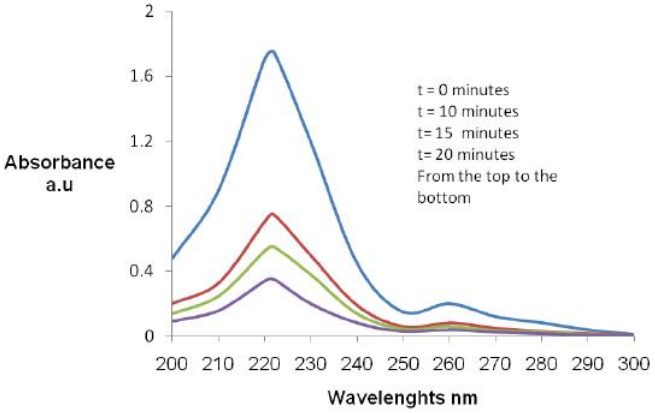

Figure 6 : UV/Vis spectra of the atrazine degradation at 0, 10, 15 and 20 minutes

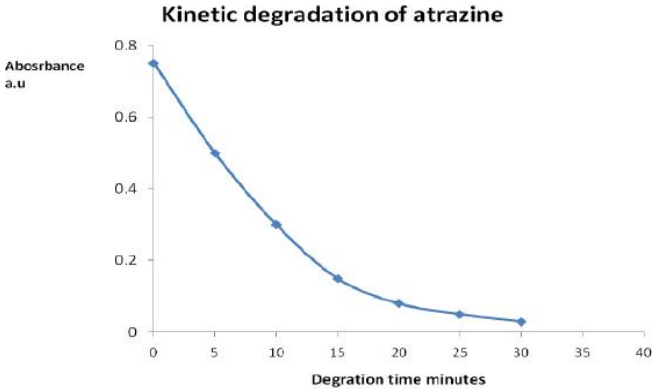

Figure 7 : Kinetic of atrazine degradation with the time of reaction- (minutes)

Total Organic Compounds (TOC) measurement. Figure 8 shows plots of atrazine dissipation and carbon dioxide emitted over the course of reaction. The results show the production of carbon dioxide as decreasing TOC and the rate of the atrazine degradation, which indicates that after 30 minutes s, more than 98 % of atrazine disappeared.

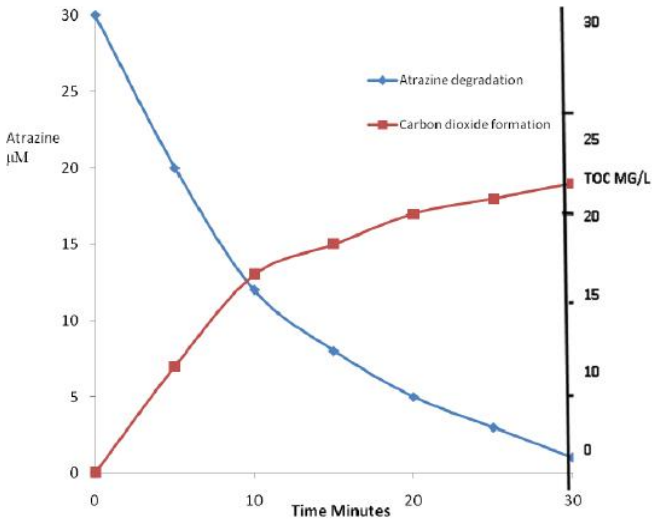

Figure 8 : Mineralization of atrazine and conversion into carbon dioxide as shown in the Figure . Blue is the degradation of atrazine. Read is the formation of carbon dioxide

Degradation of atrazine *in-situ* after its extraction by using the mixture of β-cyclodextrin/SDS

The soil in the column experiment was shaking during three hours until a complete extraction of the atrazine from the soil. Then we injected 4g of iron per kg of soil and air circulation was carried out inside the column. Figure (9) shows, the atrazine became undetectable after 30 minutes of treatment.

In this Figure we presented the evolution of the atra-

zine degradation when we treated the contaminated solution in a separate batch (Blue line) and in-situ treatment (red Line).

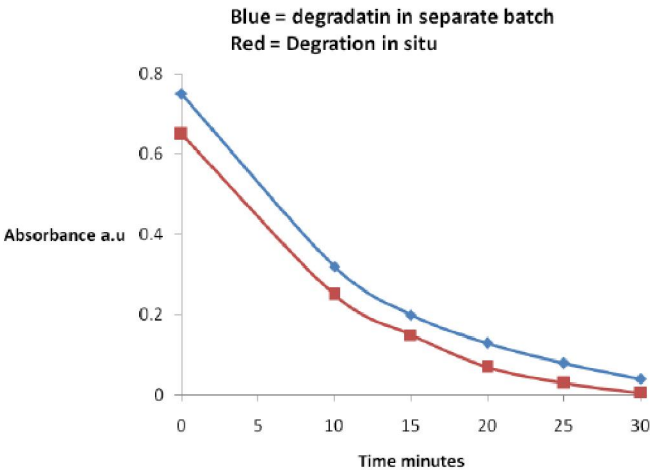

Figure 9 : Degradation of atrazine extracted from soil column by iron powder: (Blue) in separate batch; (Red) *in-situ* treatment

CONCLUSION

The combination aqueous ß-cyclodextrin solution/ SDS and the zero valent iron powder technology, was investigated to study the removal of atrazine from contaminated soil.

The atrazine was destroyed completely in about 30 minutes by zero valent iron powder oxidative reaction.. The mechanism of the degradation was published in the reference[13]

A double significant advantages were offered to the remediation of the soil polluted byatrazine :

The first one appears in the combination of beta-cyclodextri and sodium dodecyl sulfate due to the efficiency of the transfer of atrazine from soil to the aqueous solution

The second one was because the zero valent iron powder was in the conditions to generate hydroxyl free radicals which are responsible tto destroy the atrazine.

We plan to demonstrate our technology for other toxic organic compounds, particularly PCBs and PAHs and we will test the system in situ soils contaminated with several pollutants.

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