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β-Cyclodextrin enhanced desorption of atrazine from soil and its mineralization by oxidative reaction using zer valent iron powder

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ABSTRACT

The combination of atrazine solubility enhancement using saturated aqueous β-cyclodextrin (β-CD) solution and the zero valent iron powder technology was applied to remove the atrazine from contaminated soil. The solubilization of the hydrophobic atrazine by β-cyclodextrin was investigated. Linear and non linear regression methods were used to estimate the formation constants (K). A 1:1 stoichiometric ratio was observed for the binary inclusion complex between atrazine and β-cyclodextrin with a formation constant of 285 ± 15 M^{-1}. Experimental work was conducted to determine the sorption-desorption behavior of atrazine in clayey soil using the batch equilibrium technique and β-cyclodextrin in aqueous solution. The β-cyclodextrin solution facilitated the mass transfer of atrazine molecules from soil to the aqueous phase. The destruction of atrazine by using iron particles under appropriate conditions was achieved 97% More than 97% of atrazine disappeared within 30 minutes of treatment. The decreasing of total organic carbon (TOC), the formation of carbon dioxide and the evolution of atrazine concentrations were respectively analyzed by TOC, HPLC and UV-Vis spectroscopy. The by-products during the reaction were not identified.

KEYWORDS

β-cyclodextrin sorption-desorption;
Atrazine;
Mineralization zero valent iron powder;
In-situ treatment.

INTRODUCTION

Large amounts of pesticides are used in modern agriculture production and the increasing detection of these agrichemicals in underground water[1-3] has prompted the development of different technologies for the remediation of polluted soil. Sparingly-soluble non-ionic pesticides are strongly bound to soil organic matter, due to their rate of desorption and to the mass transfer decreasing from the soil phase to the water phase[4-6]. It is necessary to increase the rate of desorption and to improve the efficiency of technology involving the pumping of polluted water, which extracts pesticides found in the solution. The herbicide atrazine or (6-chloro-N-ethyl-N’-(1-methylethyl)-1, 3, 5-triazine-2, 4-diamine) was used as the model contaminant in this study.

β-cyclodextrins (CD) are excellent extractors of sparingly-soluble organic compounds and could be used to increase the desorption of hydrophobic pollutants from soil to water. The possibility of application of CD for reducing the pollutants in wastewater has long been recognized[7].

On the other hand, the use of 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[8-10]. Iron metal has also high oxidation capacity at appropriate conditions of pH, and oxygen content[12,13].

Our previous work showed that zero valent iron powder (ZVIP) generates free radicals which are able to mineralize organic compounds[13].

This work investigates a new treatment method to remediate soil polluted by atrzine based on the delivery of β-CD into soil in order to facilitate their transfer to the aqueous phase. The atrazine present in the aqueous phase was mineralized by reactions with free radicals generated from zero valent iron powder. This remediation process has been tested on the eluates *in-situ* and outside of the soil.

MATERIALS AND METHODS

Apparatus

Water polluted samples were taken from batch at different time intervals and analyzed by HPLC, UV-visible and TOC-analyzer. All the measurements were carried out at room temperature 20-25°C.

UV–visible spectrophotometry

Atrazine was analyzed by a UV–visible spectrophotometer (UV-1601, Shimadzu), signal wavelength of 223nm with 20nm bandwidth.

High performance liquid chromatography (HPLC) for monitoring of atrazine

The atrazine was monitored by HPLC liquid chromatography using a Hewlett-Packard system (HP1100) equipped with a mono-channel UV-visible detector and an automatic injector. The experiment was performed by UV detector at 223nm by using a reverse phase Merck column (Spherisorb ODS 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% acetic acid (10%) and methanol (90%) at a flow rate of 1.00mL/min.

Atrazine was detected at 223nm, and the retention time was 12.4 min. 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 control. 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 infrared detector was used to determine the formed carbon dioxide.

Reagents

β-cyclodextrin and zero valent iron powder (350 mesh) were purchased from Sigma Aldrich, and used as received. Atrazine was purchased from Rodeldehein. Distilled water was used to prepare aqueous solutions of β-CD and atrazine stock solutions.

Soil preparation and composition

Soil was collected from a non agricultural field in Sanine Mountain (Lebanon) and was transported in coolers to the laboratory and ground to pass through a 2 mm sieve.

Soil sample was analyzed by standard methods according to Klute[14]. The pH was measured in a slurry 1:2.5 soil/aqueous calcium chloride (0.02M). Organic matter content (OM) was determined by the Walkly-black method[18]. The characteristics of the soil are shown in TABLE 1.

Atrazine treatment experiments

An aliquot of 250mL of eluates solution at pH 4 was mixed with 2.5g ZVIP inside a flask of 500mL. The mixture was shaken with air blower pump during the reaction. At different time intervals, adequate volumes of the treated solutions were taken for HPLC, UV-visible and for TOC measurements. The total time of the reaction was about 50 minutes.

In-situ treatment was carried out by shaking the β-cyclodextrin solution directly inside the soil polluted by atrazine for the determined time of desorption. After checking of the total transfer of atrazine from the soil to the aqueous phase, zero valent iron powder was injected inside the solution at pH = 4 and the mixture was bubbled by air blower.

At different time intervals, adequate volumes of the treated solutions were taken for HPLC, UV-visible and for TOC measurements. The total time of the reaction was about 50 minutes.

EXPERIMENTAL

Cyclodextrin-atrazine complex formation

Previous studies were conducted to investigate the inclusion of atrazine inside the hydrophobic cavity of β-CD and to determine the formation constant of the β-CD-Atrazine complex. Linear and non linear regression methods were used to estimate the formation constant K (285 ± 15 mol-1) and a 1:1 stoichiometric ratio was observed for the binary inclusion complex between atrazine and β-CD[16].

Batch studies

Effect of the soil mass on the adsorption of atrazine

In order to study the effect of the soil amount on the adsorption of atrazine, different masses of soil were transferred into 50mL Teflon centrifuge tubes numbered from 1 to 5. Each tube contains 30mL of atrazine aqueous solution with a concentration of 10ppm.

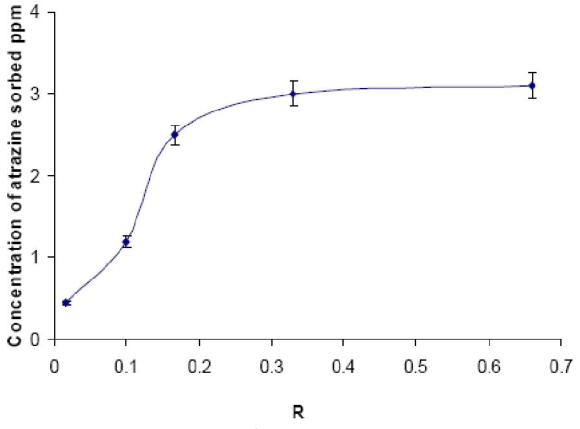

Figure 1 : Concentration of atrazine adsorbed (ppm) plotted against the ratios (R) where R is obtained by dividing respectively the soil masses [0.5g, 2g, 5g ,10g, and 20g] by the volume of atrazine solution which is equal to 30mL at (10ppm)

The masses of the soil transferred respectively into the five tubes: 0.5g, 2g, 5g, 10g, and 20g. The tubes were sealed with a Teflon-lined cap and shaken for 24 h before being centrifuged at 3000rpm for 20 min. After centrifuging, the concentration of atrazine adsorbed by soil was determined by HPLC as the difference between the amount of atrazine before (10ppm) and after the sorption experiment. The concentrations of atrazine adsorbed were measured and plotted against the ratios (R) which was obtained by dividing the mass of the soil by a the volume of atrazine aqueous solution (R is expressed by g/mL).

Adsorption-desorption of atrazine

Adsorption batch experiments were performed in triplicate in 50mL glass centrifuge tubes by mixing 10g of soil with 30mL of atrazine solution at a concentration of 10ppm. The samples were shaken for 24 hours to allow adsorption equilibrium.

Desorption experiments were initiated immediately after 24 hours of the adsorption experiments by replacing the supernatant liquid by the same volume of distilled water or CD solution (0.01M). The tubes were shaken for 3, 6, 10, 18 and 24 hours in order to determine the convenient time for a complete desorption. The concentrations of atrazine in the supernatants were determined by HPLC.

The amount of atrazine adsorbed or desorbed was calculated as the difference between the concentration before and after adsorption or desorption experiments.

TABLE 1 : Physical and chemical properties of tested soil

Nature	Percentage %	Nature	Percentage %
Sand	20	$CaCO_3$	3.8
Silt	35	OM *	1.2
Clay	40	pH	7.6
Texture	Clay loam		

***Organic materials**

TABLE 2 : Sorption of atrazine for different amounts (g) of soil: Each amount was shacked in a tube containing 30mL of atrazine aqueous solution at a concentration of 10ppm. The ratios (R) were obtained by dividing respectively the mass of the soil transferred in each tube by the volume of atrazine aqueous solution which is equal to 30mL (R is expressed as g/mL)

Ratios [R]	0.5/30	3/30	5/30	10/30	20/30
Concentration of atrazine sorbed (ppm)	0.45 ± 0.02	1.2 ± 0.06	2.5 ± 0.1	3.0 ± 0.12	3.1 ± 0.12

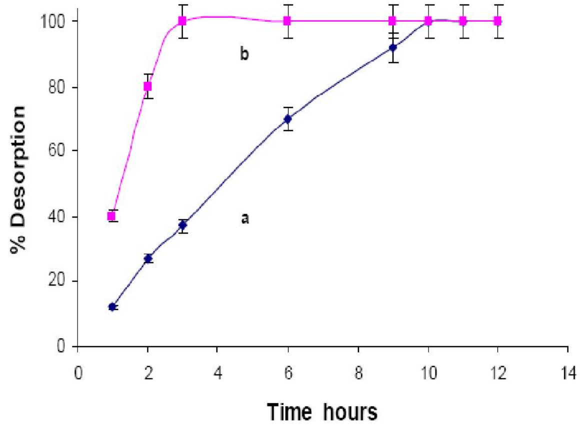

Figure 2 : Percentage of desorption versus time: (a) desorption using distilled water (b) desorption using β-cyclodextrin solution

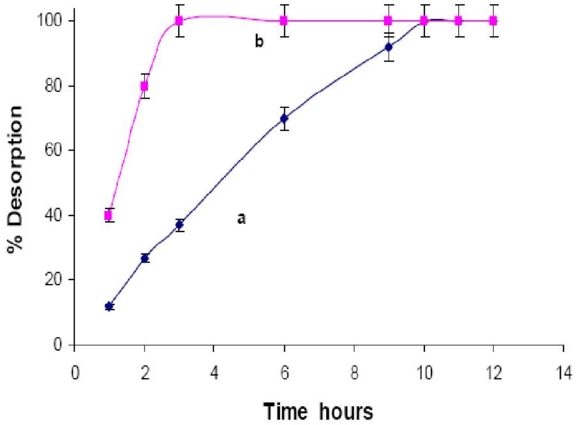

Figure 3 : Evolution of UV-Vis spectra of atrazine at different interval of times of reaction (from up to down: 0, 10, 15 and 20 minutes)

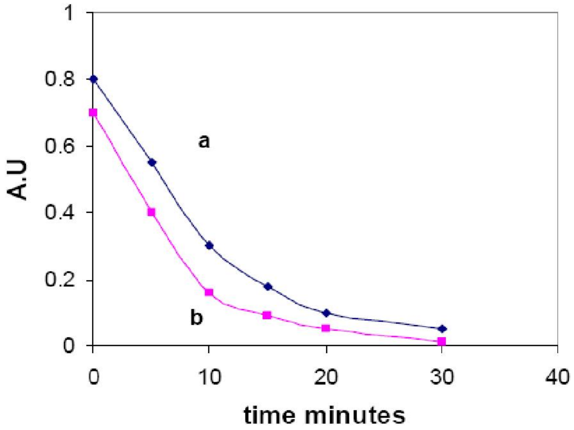

Figure 4 : Degradation of desorbed atrazine: (a) in separate batch and (b) in-situ treatment

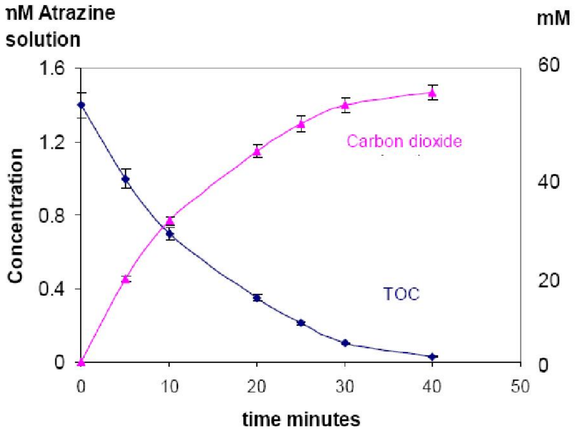

Figure 5 : Evolution of TOC aqueous solution and carbon dioxide formation during the oxidative reaction

RESULTS AND DISCUSSION

Batch studies

Effect of the soil mass on the sorption of atrazine

The HPLC measurements of atrazine adsorbed were plotted against the ratios (R) obtained by dividing the soil masses (g) by the volume of atrazine aqueous solution which is equal to 30mL . The values obtained are summarized in TABLE 2 and plotted in figure 1, which illustrates the atrazine adsorption behavior. The concentration of adsorbed atrazine reached a plateau of 3 ppm at R = 10g/30mL. This value of R will be considered in the subsequent experiments in order to guarantee a maximum atrazine adsorption by the soil particles.

Desorption of atrazine

In this experiment, the optimum desorption time of atrazine from soil was determined using water without β-CD and water with β-CD (0.01 M). Figure 2(a) shows that the soil contaminated by atrazine was completely desorbed after 12 hours of shaking when using distilled water while figure 2(b) shows that after 3 hours of shaking by the aqueous β-CD solution (0.01M), the desorption of atrazine from soil was complete.

Extraction of atrazine and treatment outside and in-situ of the batch

According to the method described above10g of soil were polluted by 30mL of atrazine solution at the concentration of 10ppm.The concentration of the atrazine solution after 24 hours of shaking was 6.8ppm .The quantity of atrazine adsorbed by the soil was 96μg.

Extraction and treatment outside of the batch

The soil polluted by atrazine as described above was shacked with 30mL of β-cyclodextrin aqueous solution (0.01M) for a period of three hours. When the atrazine was totally transferd from the soil to the aqueous phase , the supernatant solution was transferred into a separate flask 0.5g of zero valent iron powder was added into the flask containing the supernatant solution which was adjusted at pH = 4 and air bubbled in the mixture. Samples were withdrawing at different intervals of time for the analysis. The method of treatment is an oxidative reaction process described by Rima et al.[16].

Figure 3 shows the UV spectra of the atrazine evolution with the time of reaction. As shown in this figure the atrazine become undetectable after 30 minutes of treatment.

Extraction and treatment *in-situ* of the batch

In the case of in-situ treatment, iron powder was injected inside the column after three hours of shaking the soil by β-CD solution. Air was bubbling in the mixture in order to favor the oxidative reaction and the samples were analyzed at different intervals of times.

Evolution of the atrazine degradation monitored by spectrophotometer

The effectiveness of fine-grained metallic iron to mineralize organic compounds has been previously demonstrated[16]. Atrazine degradation was monitored by UV-Vis spectroscopy at 0, 10, 15 and 20 minutes (Figure 3). After 30 minutes an undetectable signal was observed.

Differences between in-situ and outside treatment

The treatment of the atrazine solution after extraction from the soil was studied inside the soil and in a separate batch. Figure 4 illustrates a comparison between the separate batch (a) and in-situ (b) degradation of atrazine as monitored by HPLC As shown in this figure a similar results were observed.

In both cases, it was demonstrated that the atrazine degradation has achieved more than 97% after 30 minutes of treatment. However, the possibility for *in-situ* treatment of soil polluted by atrazine or other organic chemicals by applying the "inside soil" procedure, provide highly important applications for the remediation technologies.

Mineralization of atrazine / β-cyclodextrin mixture-TOC measurements

The total organic compounds TOC of atrazine solution was measured before and during the reaction with zero valent iron powder (ZVIP). Carbon dioxide emission was also measured to confirm complete mineralization of atrazine / β-CD by ZVIP under acidic conditions. Figure 5 shows the formation of carbon dioxide regardless of TOC decreasing.

In order to interpret the decreasing of TOC and the formation of carbon dioxide, it has been considered that the mixture of iron, air and acidic aqueous solutions can lead to the free radical formation.

It is hypothesized that the following three reactions are important to the overall Scheme.

$$\mathrm{Fe^{\circ} + O_2\,(aq) + 2\,H^+ \rightarrow Fe^{2+} + H_2O_2} \qquad (1)$$

$$\mathrm{Fe^{2+} + L \rightarrow Fe^{2+}L} \qquad (2)$$

$$\mathrm{Fe^{2+}L + H_2O_2\ Fe^{3+}L + HO^{-} + HO\cdot} \qquad (3)$$

Where L is an organic compound.

Using this system, Nouradoun et al.[20] have demonstrated the complete mineralization of chlorinated phenol, polychlorinated biphenyls (PCB's), nitroaromatics, and organophosphorous compounds. The same hypothesis has been previously proposed to explain the complete destruction of phenol[15,16].

CONCLUSION

It has been demonstrated that the combination of aqueous β-CD solution and the zero valent iron powder technology can be very effective for the removal (97% removed) of atrazine from contaminated soil. A delivery vehicle system for the mineralization of the organic pollutants in soil was developed. Such treatment is not limited to atrazine since β-CD has been also mineralized; but it is general for other organic compounds.

The significant advantage of our technique compared to current techniques is that it completely remediates not only soil but also groundwater contaminated with toxic organic compounds within short time instead of months and years, and leave behind no toxic end-products.

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 different pollutants.

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