Carbon and nitrogen Isotope fractionation of the photo-degradation of herbicides in aqueous solution by nitrates under ultraviolet radiation

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Research

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Carbon and nitrogen Isotope fractionation of the photo-degradation of herbicides in aqueous solution by nitrates under ultraviolet radiation

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Abstract

Background: Phenylurea herbicides are one of the most important and widely used pesticides in the world. Due to its potential persistence and toxicity in the aquatic environment, it poses certain risks to the ecological environment and human health. Studying the photochemical degradation behavior of herbicides is important for understanding the degradation and transformation fate in the environment.

Results: This study evaluated the effectiveness of direct and indirect photo-degradation of the herbicides isopropiron (IUP) and methylamine (MN), investigating the influence of operational variables (initial herbicide concentration and light sources) and initial of induced nitrate concentration on these processes in aqueous solution. We also introduced a new technology of compound-specific isotope analysis (CSIA) to provide deeper information of the photochemical degradation mechanism. Results showed that the light source and the initial concentration have an important effect on the degradation of herbicides IUP and MN. The photolysis rate under the Hg lamp is higher than photolysis rate under Xe lamp. It is found that photolysis kinetics of herbicides were consistent with the quasi-first order model, and the photolysis rate decreases with the increasing of the initial concentration. In indirect photodegradation, the degradation rate increases with increasing NO_3^- concentration at low concentrations of pesticides (8 mg/L); while the degradation rate decreases with increasing NO_3^- concentration at high concentrations of pesticides (30 mg/L). According to the isotope fractionation, photolysis of IUP exhibits normal carbon isotope fractionation with the degradation rate increases, and the stable isotope enrichment factors under different photolysis pathways

are different. In the indirect photo-degradation process, no significant fractionation of nitrogen isotopes occurred, and stable nitrogen isotopes fractionation could not be fitted well in either of the two photodegradation pathways.

Conclusion: Therefore, the structure and chemical characteristics of the molecules of herbicides play a determinant role in their photodegradation. The CSIA is useful both for a mechanism-based evaluation of experimental results and as a valuable tool to explore transformation pathways for organic pollutants in different environmental systems.

Keywords: Herbicides; Photodegradation; CSIA; Isotope fractionation

Background

Environmental contamination by pesticides is an issue of general concern since these compounds can adversely affect human and ecosystem health, due to the highly toxic, carcinogenic, and biological pollutants with a long-term residual nature [1-4]. In response to the rapid development of agriculture in recent years, herbicides are widely used to achieve maximum crop yields [4, 5]. Since the 1990s, the application amount of pesticide in China has been on a rapid rise, increasing to 1.8 million tons in 2013, with an average annual growth rate of 7.4% [6]. Most pesticides can be discharged from agricultural activities, industrial wastewater, dispersed through evaporation into the air, attached to plants, or leached into groundwater, leading to greater serious chemical pollution in the water and soil environment [1, 5, 7]. The pesticide residue concern has

increased significantly, the government and scientists have made tremendous efforts in detecting, monitoring, and degradation of the various pesticides residue in the environment over the past several years [2, 8, 9]. Pesticide degradation includes both microbial or plant-mediated biotransformation processes, as well as non-biological processes such as chemical and photochemical reactions [10-12].The transformation process of a pesticide depends on its structural affinity for a particular type of transformation and the environmental conditions to which its distribution and transportation behavior is exposed [5, 13]. The resistance of some compounds to conventional treatments has led to the application of other methods, such as photo-oxidation which apply the radiant energy to the system, which generates electronically excited molecules in different states. These molecules can be split, split, or photoionized. In addition, the absorption of light in the visible or ultraviolet radiation range can change the internal energy of the molecules, creating electronic transitions between the molecules [5, 14].

Light-induced organic pollutants degradation (direct or indirect photolysis), is an important degradation pathway for removing pesticides such as pesticides and herbicides on surface water, soil and plant surfaces [15-18]. It has been reported that ultraviolet (UV) radiation is considered as an alternative technology for removing organic pollutants, owing to its high efficiency in removing certain pesticides and drugs from water [19-23]. Most herbicides are photosensitive because their structures include aromatic rings, heteroatoms, and other functional groups that make them susceptible to UV radiation absorption (direct photolysis), or with photo-degradation that can induce

herbicides in water of light-sensitive species (indirect photolysis) [5, 23]. There have been various studies on the use of direct and indirect UV photolysis to remove herbicides from water [12, 21, 22, 24, 25]. Significant advances have recently been made in our understanding of the photochemical processes undergone by organic contaminants and pharmaceuticals in aqueous medium [26-30]. Some of these studies have reported the indirect photodegradation by heterogeneous TiO_2 photocatalysis [31, 32], determined by the photo-induced by Fe(III) in aqueous solutions [33] and the generation of situ hydroxyl radicals (˙OH) [34]. It have been reported that nitrates (NO_3^-) is inorganic ions present in natural waters and can also induce the photodegradation of phenylureas [35, 36]. The photochemistry of NO_3^- ions in aerated aqueous solutions contains two main processes: the first yields $^{\cdot}NO_2$ and ˙OH, and the second yields NO_2^- and $O(^3P)$ [37-39]. The assessment of the fate of these chemicals in the environment requires knowledge and information on their degradation pathways [40]. However, there has been little information on the use of these methods to treat other pesticides widely used in agriculture, e.g., substituted phenylureas as a group of herbicides widely used for general weed control of non-crop area and as pre-emergence treatment on cereals and vegetable crops [41], despite their frequent detection in ground, surface, and even tap waters [5, 42]. Furthermore, the conventional approach based on concentration measurements of parent compounds and transformation products are not conclusive, since a decrease of concentration might also be caused by dilution, sorption and further transformation of metabolites [43-46]. Physical processes such as dilution, diffusion, and volatilization almost do not change the isotope compositions to the same

extent as chemical or biochemical processes such as degradation [43, 44, 47, 48]. Compound-specific isotope analysis (CSIA) is a helpful analytical method for characterizing the (bio)chemical transformation of organic contaminants based on kinetic isotope effects during unidirectional reaction processes [40, 49-51]. Over recent years, the method has become an increasingly valuable tool to assess the origin and fate of organic contaminants in the environment [52-55]. CSIA may identify and quantify transformation reactions of organic contaminants [56-58]. To date, there is little information on the photolysis of organic pollutants associated with CSIA.

Based on these backgrounds, the purpose of the present study are (1) investigate the effectiveness and importance of UV radiation on the direct photo-degradation and the nitrate-induced photo-degradation process on isopropiron (IUP) and methylamine (MN) in aquatic mesocosms; (2) explore the influence of different operational variables (initial herbicide concentration and nitrate concentration) during photodegradation of the herbicides; (3) apply the CSIA to further investigate the reactivity and photodegradation of IUP, providing a theoretical basis for comprehensive understanding of the photolysis and degradation characteristics of herbicides and evaluating their behavior and safety in water environment.

Materials and methods

Chemicals

IUP (purity ≥ 99%) and MN (purity ≥98.5%) were analytical reagent grade and supplied by Zhongshan Chemical Co., Ltd. HPLC grade organic solvents such as methyl alcohol, acetonitrile, acetone and other chemical reagents were purchased from

ANPEL Scientific Instrument (Shanghai) Co., Ltd.

Photodegradation experiments

All herbicide degradation experiments were conducted in Rotary photodegradation reactor. The light source is placed in a cold trap inside the double-layer quartz, and the external cooling circulating water is used to reduce the temperature of the lamp tube and filter out most of the infrared heat. The reaction temperature of the dark box is maintained at 25 ℃. Before each photodegradation experiment, the light source is preheated. After 20 minutes of stabilization, a photodegradation experiment was performed. In each experiment, after stabilizing the lamp and controlling the temperature (25 ℃), the photoreactor was turned on, and aliquots were drawn from the reactor at different time intervals in order to assess the herbicide concentration. In the direct photodegradation experiments, there are two different light sources in the cold trap: high-pressure mercury lamp (main wavelength 365 nm, 500 W) and simulated natural light long arc xenon lamp (300 ~ 800 nm, 500 W). While in the nitrate induced degradation experiments, all reserve fluids were prepared with ultra-pure water to exclude the quenching effect of organic solvents such as methanol on the instantaneous photoactive product-OH. Further experiments focused on investigating: (1) the influence of different light sources (Hg lamp and Xe lamp) on the concentrations of IUP and MN (20 mg/L) photodegradation; (2) the influence of IUP and MN initial concentrations (6, 12, and 25 mg/L) under the irradiation of Hg lamp; (3) the effect of NO_3^- concentration (0, 0.5, 1, and 5 mM) under herbicides concentration of 8 and 30 mg/L; (4) the influence of herbicides concentrations (8, 15, and 20 mg/L) under a fixed

154 NO_3^- concentration of 5 mM. Control tests in the absence of nitrate induced under
155 different conditions were conducted in parallel.

156 **Chemical analysis**

157 Aqueous herbicide samples were filtered and then measured using a HPLC-DAD
158 system (LC-A10 series system, Shimadzu, Japan) and separation was conducted by an
159 ACE Excle 5 C_{18}-AR column (5 μm, 250×4.6mm, Advanced Chromatography
160 Technologies Ltd.). The mobile phase was acetonitrile/water for IUP (70 : 30, v/v) and
161 MN (60 : 40, v/v), at a flow rate of 1 mL/min and the herbicides were detected and
162 quantified at a wavelength of 245 nm.

163 **Compound-specific stable isotope analysis for carbon by GC-IRMS**

164 Sample preparation and isotope analysis were adapted from methods reported by
165 Meyer et al. [59]. The GC-IRMS system consists of TRACE GC Ultra gas
166 chromatograph (Thermo Fisher Scientific) equipped with a Trace Gold analytical
167 column (30 m×0.25 mm×0.25 um), which was coupled to a Finnigan MAT 253 isotope
168 ratio mass spectrometer (IRMS) via a Finnigan GC Combustion III interface (Thermo
169 Fisher Scientific). Liquid samples were injected with a GC Pal auto sampler. The GC
170 oven temperature started at 40 ℃ (hold 5min) and consequently increased to 100℃
171 (hold 5 min) at rate of 50 ℃/min. Then at a ramp of 15 ℃/min consequently increased
172 to 300 ℃ (hold 5 min). During isotope analysis by GC-IRMS, analytes were measured
173 against a laboratory standard gas, which was introduced into at the beginning and the
174 end of each run. Both standard gases were calibrated to Vienna Pee Dee Belemnite (V-
175 PDB) and Air, respectively. Isotope values of carbon and nitrogen was reported as $\delta^{13}C$

and $\delta^{15}N$ values in ‰ relative to Vienna Pee Dee Belemnite (VPDB) according to eq. (1) [60]:

$$\delta^{13}E = \frac{R_{sample} - R_{reference}}{R_{reference}} \times 1000 \quad (1)$$

where R_{sample} and $R_{reference}$ are isotope ratios of the elements of concern in the target compound and the international reference standard (e.g., VPDB for the carbon isotope), respectively.

The changes in bulk isotope ratios of target compounds can be directly related to the degradation progress by the enrichment factor (ε) following the Rayleigh equation (eq. (2)) [61]:

$$\ln\left(\frac{R_t}{R_0}\right) = \varepsilon \times \ln\left(\frac{c_t}{c_0}\right) = \varepsilon \times \ln(f) \quad (2)$$

where R_t and R_0 are the stable isotope ratios of the elements of concern in the molecules of the target compounds at reaction time t and the beginning of degradation. f is the remaining fraction of target compounds in the reaction pool.

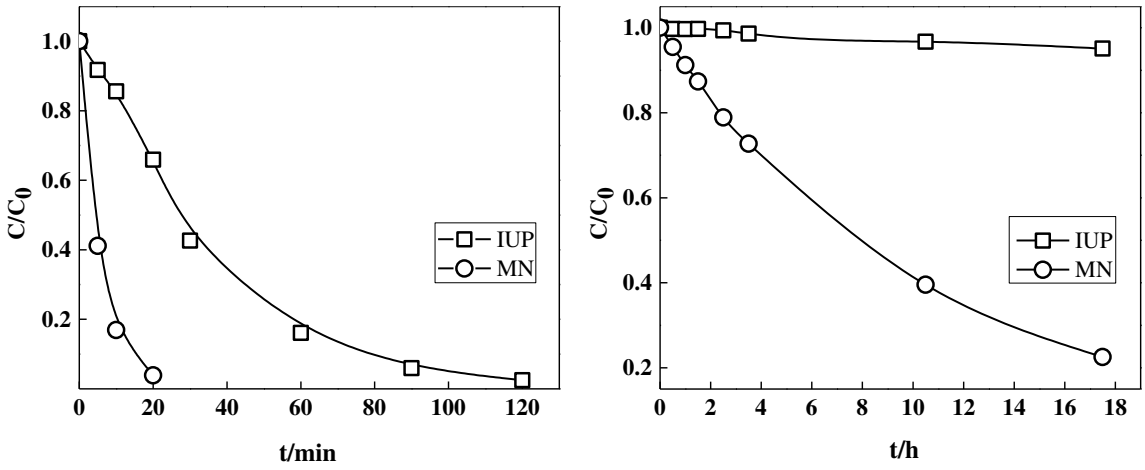
Results and discussion

The factors affecting photodegradation of herbicides

Effects of light sources kinetics of herbicides photochemical reaction

The photodegradation of IUP and MN with concentrations at 20 mg/L under high pressure Hg lamp and Xe lamp were investigated, and the results are shown in Fig. 1. As shown in Fig. 1, no obvious degradation of IUP and MN was observed in dark controls. The degradation rate of MN reached 99% within 60 min and IPU reached 99% within 120 min under the condition of Hg lamp. Meanwhile, the degradation rate of each organic pesticide significantly decreased, when the irradiation time reached 18 h,

198 the MN degradation rate was 78%, while the degradation rate of IPU was only 5% under
199 the condition of Xe lamp. The extremely low light absorption of IUP and MN at
200 wavelengths >290 nm is the reason for its persistence to photo-degradation [62]. In the
201 natural environment, the emission wavelength of sunlight reaching the ground is mainly
202 above 290 nm, while those less than 290 nm are absorbed by the ozone layer. Therefore,
203 ultraviolet light at 290 nm ~ 450 nm is an important factor for the photodegradation of
204 organic pesticides in the natural environment. Experiment of high pressure mercury
205 lamp within 290 ~ 450 nm wavelength distribution (emission wavelength are centered
206 around 360 nm), and maximum absorption spectrum of organic pesticide height weight
207 stack with isopropyl lung and destroy the grass long because both belong to the benzene
208 urea herbicide (functional groups -$CH(CH_3)_2$, its absorption spectrums are similar, there
209 are two strong suction wave period, points don't in the left right around 240 nm and 210
210 nm.
211



212

213 **Fig. 1.** Removal kinetics of herbicides by ultraviolet photodegradation. Notes: “a” presents Hg
214 lamp, “b” presents Xe lamp.

The linearized pseudo-first order kinetic model of IUP and MN under different light conditions and the assessed parameters are presented in Table S1. According to the fitting correlation coefficient (r^2), the pseudo-first order kinetic model exhibited good consistency with experimental data and could describe the dynamic processes of photodegradation. Under the two light sources, the photodegradation rate of the two organic pesticides presented the same rule, and the degradation rate was MN > IPU. Among them, MN degrades the fastest, and the half-life of Hg lamp and Xe lamp were about 4 min and 8 h, respectively. IPU descending solution is the slowest, with half-life of 22 min and 239 h, respectively.

It's well known that the photodegradation rate of organic pesticides is related to environmental factors (pH, temperature, and light source, etc.) [63], as well as its structure [64]. The photolysis rate varies with the absorbance of different molecular structures. According to the photolysis reactions of IPU and MN, the biggest difference is that the IPU is demethylated, while the first reaction for MN is the dehalogen reaction. In terms of the electron effect, MN as the chlorinated heterocyclic organic compounds, since chlorine atom Cl (halogen atom) belongs to a strong electron-withdrawing group, the electron cloud density on the heterocyclic ring decreases, and the C-Cl bond is very easy to break through the isomerism mechanism. The $-CH(CH_3)_2$ at the end of the aromatic ring of IPU belongs to the electron-donating group, and the electron cloud density on the aromatic ring increases. Therefore, under the same light source, the degradation of IPU requires more radiation energy and slower degradation rate. Furthermore, from the absorption scanning spectrum of organic pesticides themselves,

MN has two strong absorption bands in the ultraviolet region, so it is highly active and easy to absorb light radiation energy, leading to faster degradation. In addition, the photo-degradation rate of organic pesticides is also related to the spatial structure of parent molecules. Direct photolysis of MN is mainly through aromatic/heterocyclic dechlorination of Cl and hydroxylation, which will undergo a series of free radical reactions after being photoexcited. It has been reported that the shorter the chain length, the more compact the molecular space structure, and the lower the degradation rate [5].

Effect of initial concentration of IPU and MN

The effect of initial concentration of IPU and MN were examined with different concentrations at 6, 12, and 25 mg/L under the irradiation of Hg lamp (Fig. 2 and Table S2). As shown in Fig. 2, with the increasing of initial concentration of herbicides, the degradations were decreased. It indicates that initial concentration greatly affects the degradation of IPU and MN. When initial concentration was 6 mg/L, the degradation rate constant was 0.654 min^{-1}, and IPU was degraded completely within 60 min. However, when the initial concentration was increased to 25 mg/L, degradation rate constant was decreased to 0.0199 min^{-1}, complete degradation of which needed more than 120 min. It might be the reason that degradation amount of atrazine is affected by light intensity [65]. Therefore, under invariable light intensity, the degradation rate of atrazine decreases when the concentration of IPU and MN in the aqueous solution is increased. The degradation followed a first order rate equation, which is confirmed by the evidence of a straight line relationship of logarithmic IPU and MN concentration versus irradiation time ($r^2 > 0.9$), which is similar to other researches [65, 66].

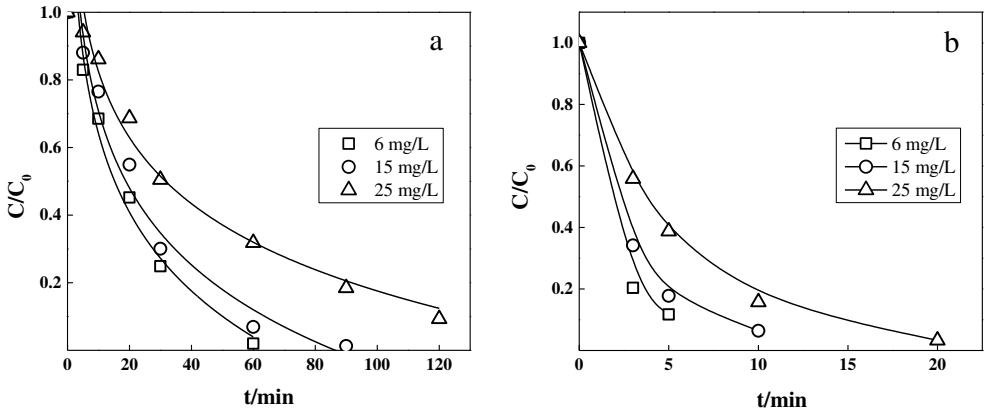


Fig. 2. Influence of the initial concentration of herbicides on the photodegradation. Notes: "a" presents IUP, "b" presents MN.

Photo-degradation induced by nitrate ions

Effect of nitrate concentration

In order to explore the effect of NO_3^- concentration, degradation of IPU and MN (8 mg/L and 30 mg/L) in the presence of different NO_3^- concentration was carried out. The results of these experiments are shown in Fig. 3 and Fig. 4. The linearized pseudo-first order kinetic model of IPU and MN degradation and the assessed parameters are presented in Table S3. The transformation of IPU and MN followed pseudo-first order kinetics in the NO_3^- degradation system ($r^2 > 0.9$), and the presence of NO_3^- has a photosensitizing effect on IPU and MN. Fig. 3 and Fig. 4 shows the experimental result when the same concentration of IPU and MN (8 mg/L) was conducted with different concentration at 0, 0.5, 1 and 5 mM. It was obvious that nitrate induction can significantly affect the degradation rate of organic pollutants, which is consistent with the research results of Shankar et al. [35]. The experiment with low

concentration of the IUP (8 mg/L), the degradation rate increased with the increase of NO_3^- concentration. The result was directly linked to the production rates of the ·OH radical reactive species and constituted the main active species generated after irradiation [39]. However, at a higher concentration level (30 mg/L), the degradation rate decreased with the increase of NO_3^- concentration. It might be the reason that when the concentration of NO_3^- increases, NO_2^- as a quencher of -OH starts to limit the reaction of -OH with organic substrates, resulting in an increase in NO_3^- with a linear relationship with the generated -OH; meanwhile, since the light intensity irradiated into the solution is a certain value, when the NO_3^- concentration increases, the unit of light energy received by NO_3^- decreases, and the excited NO_3^- by irradiation decreases, so the -OH produced decrease [65, 67], resulting in the degradation rate of the organic matrix decreases with increasing NO_3^- concentration. It's worth noting that there is no obvious degradation was found in the control group in the light solution without NO_3^- for IUP, indicating that the presence of NO_3^- was the main cause of herbicide degradation under light conditions.

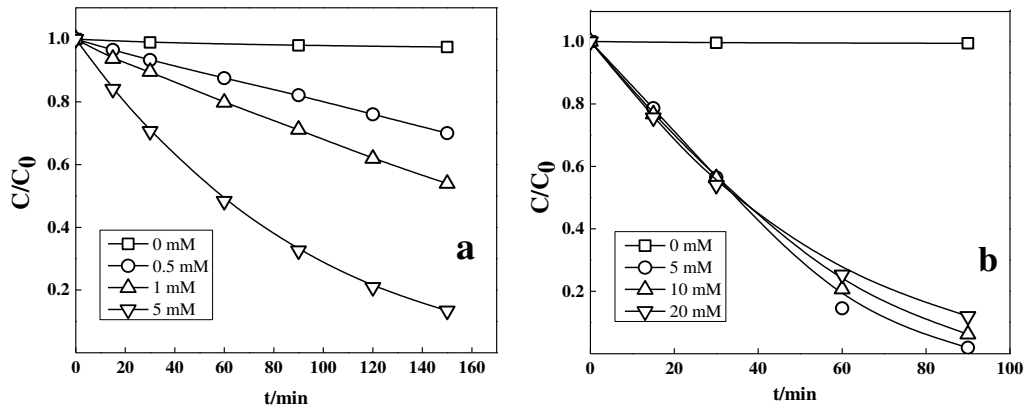


Fig. 3. Influence of the nitrate concentration on the photodegradation of IUP by UV radiation. Notes:

"a" presents substrate concentration is 8 mg/L, "b" presents substrate concentration is 30 mg/L.

It's worth noting that the photodegradation rate of MN was higher than that of IUP. However, with the increase of NO_3^- concentration, the degradation rate ratio of IUP was significantly greater than that of MN with the same NO_3^- concentration. When the NO_3^- concentration was increased to 5 mM, the ratio of photo-degradation rate of IUP to its single light exposure was 12.3 times, while the ratio of photodegradation rate of MN to its single light exposure was 4 times, suggesting that IUP was more easily degraded under the induction of NO_3^- due to the activity of alkyl on -OH and the deactivation of electron-absorbing group halogen (-Cl) by electrophilic attack [35, 68]. In addition, we found that although both IUP and MN belong to the phenylurea herbicides, their photo-degradation promotion under NO_3^- induced is completely different, indicating that the structure and chemical characteristics of herbicide molecules played a decisive role in photo-degradation [5]. Hence, after initiation of the degradation process (a stage that is closely related to the herbicide quantum yield), the degradation rate depends on the lability of molecules faced by the attack of the radicals that are formed [5].

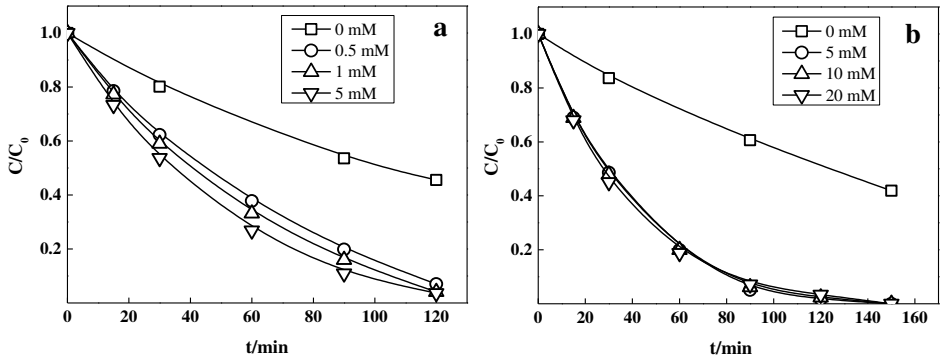


Fig. 4. Influence of the nitrate concentration on the photodegradation of MN by UV radiation. Notes:

"a" presents the substrate concentration is 8 mg/L, "b" presents the substrate concentration is 30 mg/L.

Effect of substrate concentration

To explore the influence of substrate concentration on the photodegradation rate was studied at different concentrations (8, 15, 20 mg/L) with a certain concentration of NO_3^- as the photoinducer (5 mM), and the results are shown in Fig. 5 and Table S4. The photodegradation reactions followed pseudo-first order kinetics and the k_{obs} values that were obtained clearly depended on the substrate concentration. The substrate concentration increased from 8 mg/L to 20 mg/L, the degradation rate of IUP decreased from 0.0222 min^{-1} to 0.019 min^{-1}, and the degradation rate of MN decreased from 0.0272 min^{-1} to 0.0228 min^{-1}. It was found that the photodegradation rate decreased with the increase of organic substrate concentration with a certain concentration of NO_3^-, which could be explained by competitive absorption between nitrate and herbicides [39]. Therefore, an indirect reduction in ˙OH radicals (screen effect) or the production of ˙OH was not in excess compared to the organic pollutants molecules [41]. With the concentration of the organic substrate increasing, the number of organic substrate molecules per unit volume is increased, and the amount of ·OH produced by NO_3^- is constant, resulting in a decrease in the degradation rate of the matrix. Another important reason is that with the organic substrate concentration increasing, it absorbs light energy in a competitive relationship with the nitrate, resulting in ·OH becoming the rate control step [41]. These results were the same as that of Nelieu et al. and Hadjira

Boucheloukh et al. [39, 41], the increase in substrate concentration leads to an indirect decrease in OH, and the amount of OH produced is not sufficient to react with organic substrates.

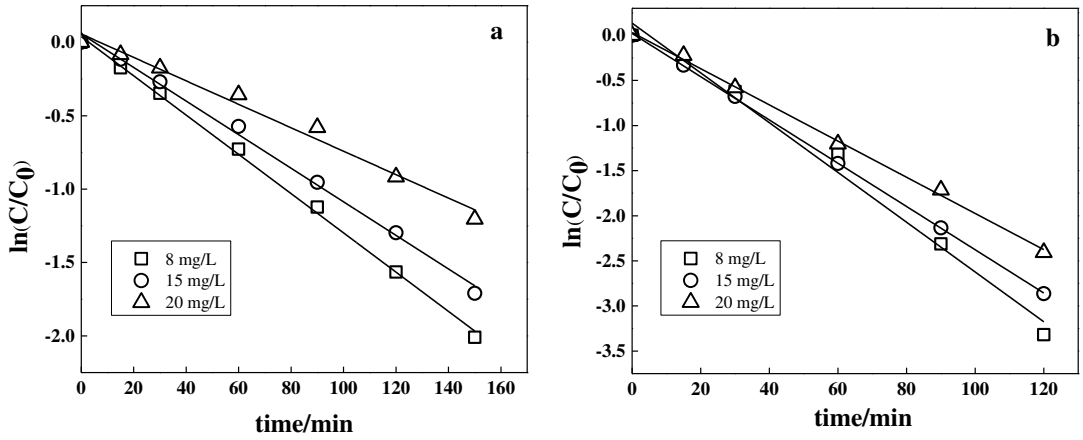


Fig. 5. Influence of the substrate concentration on the photodegradation in the presence of NO_3^-(5 mM). Notes: "a" presents IUP, "b" presents MN.

Carbon and nitrogen isotope fractionation during photo-degradation of IUP

Compound specific isotope analysis is a valuable tool to identify such degradation pathways in different environmental systems [69]. The isotope fractionation for $\delta^{13}C$ $\delta^{15}N$ were observed in photodegradation of IUP by direct and indirect photo-degradation. The ratio of carbon isotopes ($^{13}C/^{12}C$) increased in the reactant while the light isotopes (^{12}C) tended to go into reaction products, presenting a normal isotope effect. In contrast, the ratio of nitrogen isotopes ($^{15}N/^{14}N$) decreased in the substrate, showing an inverse isotope effect (Fig.6). The $\delta^{13}C$ values of IUP at the beginning of the experiment was −30.361 ± 0.08‰ and 32.3965 ± 0.04‰ in direct photolysis and

nitrate induced photo-degradation conditions, respectively. The different initial carbon isotope values may be related to the initial concentration. In blank controls, the value of $\delta^{13}C$ remained constant during the whole experiment (data not shown) confirming that besides photodegradation no other processes lead to changes in carbon isotope ratios of IUP. It worth noting that when the degradation rate was 57%, the value of $\delta^{15}N$ is 15.148 ± 0.76‰, showing obvious inverse fractionation (Δ=12.6615 ± 1.2‰); However, no significant fractionation of N isotopes occurred during indirect photo-degradation (Fig. 6b)

As shown in Fig.6, IUP photolysis resulted in a normal isotope fractionation of ^{13}C, that is the substrate was enriched with the light isotopologues during the reaction. The value of $\delta^{13}C$ shifts confirms that the observed fractionation was associated with the direct photolysis and nitrate induced photo-degradation of IUP. Note that the degradation was 15% and 57% in direct photolysis condition, the value of $\delta^{13}C$ was 33.9285 ± 0.4‰ (Δ= 3.5675 ± 0.49‰) and -17.8695 ± 0.3‰ (Δ=12.50 ± 0.5‰); While the degradation was 25% and 88% with indirect photolysis, the value of $\delta^{13}C$ was 37.65 ± 0.9‰ (Δ=5.2535 ± 0.68‰) and -29.896 ± 0.2‰ (Δ=2.5 ± 0.28‰), respectively. The phenomenon of inverse isotope fractionation has also appeared in the study of photodegradation of other organic pollutant, which may be related to the nuclear magnetic moment/nuclear spin of the isotope, rather than the isotope mass [70]. Hartenbac et al. [71] in the study of photolysis of atrazine, points out that the hydrolysis of atrazine in normal fractional steps before other process of molecules led to such an isotope effect should be (such as molecular excitation singlet and triplet can through a

variety of light physical process returns to the electronic ground state). Therefore, under the sunlight radiation can cause molecules in the isotope carry nuclear spin and the interaction of unpaired electrons, can produce magnetic isotope effect at this time. The result is not a light-isotope priority reaction, depending on their nuclear spin quantum number [72]. However, isotope effects associated with photophysical excitation and relaxation processes could have caused the observed isotope fractionation, but little is known that would allow one to confirm such hypotheses and requires further study [14].

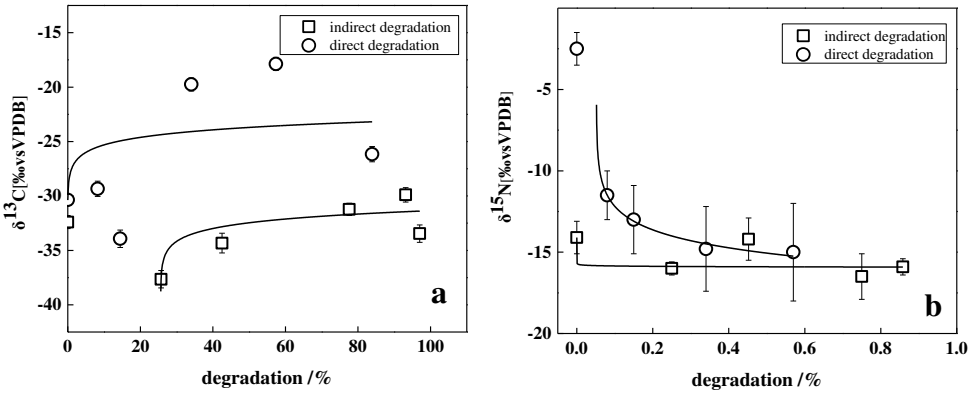


Fig. 6. Carbon (a) and nitrogen (b) isotope fractionation of IUP under different conditions.

The isotope enrichment factors for carbon was calculated according to the Rayleigh equation (eq. (2)) by a linear regression as displayed in Fig. 7a. On the contrary, nitrogen stable isotope fractionation can not be fitted well by Rayleigh equation under both photodegradation pathways, and its r^2 is less than 0.5 (Fig. 7b). It was obvious that the isotope enrichment factor for IUP is significantly different between the direct photodegradation (ε_c= -0.018 ± 0.006‰) and nitrate induced photodegradation (ε_c= -0.002 ± 0.001‰). The difference in the degree of stable

isotope fractionation between different degradation pathways is not only related to specific degradation conditions (for example, the higher energy of light can break the corresponding chemical bonds more quickly in the process of photodegradation), but also related to the reaction mechanism of different degradation pathways [57]. It has been reported that the cleavage of the bond between the carbonyl carbon and the alkyl nitrogen of IPU results in primary carbon isotope effects [40]. Moreover, secondary isotope effects occur at the alkyl nitrogen and the two methyl carbons, indicating that the reaction of isopropyl chain does not cause carbon stable isotope fractionation, which is consistent with the other reports [73].

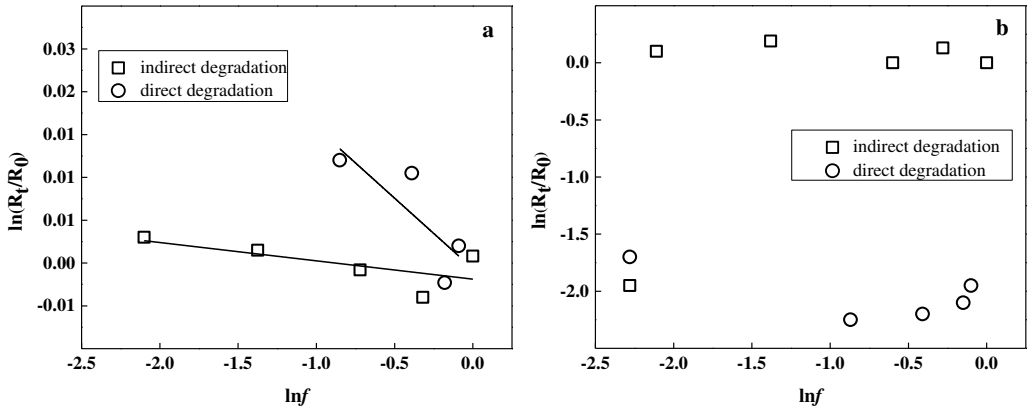


Fig. 7. Carbon (a) and nitrogen (b) isotope enrichment factors were determined by a linear regression according to the Rayleigh equation.

Conclusions

The direct photolysis of two organic pesticides under different light sources follows first-order degradation kinetics, and the herbicides photodegradation rate follows the order MN > IUP, reaching 99% degradation at 60 min of Hg lamp treatment

for MN and at 120 min for IUP. The irradiation time reached 18h, the MN degradation rate was 78%, while the degradation rate was only 5% for IPU under the condition of Xe lamp. Structural and molecular characteristics play a decisive role in these photo-degradation rates. The presence of NO_3^- has a photosensitizing effect on IPU and MN, and the nitrate induction can significantly affect the degradation rate of organic pollutants. In indirect photodegradation, the degradation rate decreased with the increase of organic substrate concentration with a certain concentration of NO_3^-. The degradation rate of ·OH on organic pesticides was independent of its functional groups (IPU and MN), but related to substituents on aromatic rings. Therefore, it was suggested to classify different substituents on aromatic rings of organic pesticides, so as to further obtain the photodegradation law of different organic pesticides. According to the isotope fractionation, photolysis of IUP exhibits normal carbon isotope fractionation with the degradation rate increases, and the stable isotope enrichment factors under different photolysis pathways are different. In the indirect photodegradation process, no significant fractionation of nitrogen isotopes occurred, and stable nitrogen isotopes fractionation could not be fitted well in either of the two photodegradation pathways. These results are useful for evaluating the environmental fate of phenylurea herbicides as well as other organic pollutants.

Abbreviations

IUP: isopropiron; MN: methylamine; CSIA: compound-specific isotope analysis; UV: ultraviolet; $\delta^{13}C$: carbon stable isotope; $\delta^{15}N$: nitrogen stable isotope; C: carbon; N:

nitrogen; VPDB: Vienna Pee Dee Belemnite; $^{13}C/^{12}C$: carbon isotopes ratio; $^{15}N/^{14}N$: nitrogen isotopes ratio.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

The data sets supporting the conclusions of this article are included within the article.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

Haiyan Yu, Jinling Liu, Changxu Han, Han Fang, Xingquan Shu, and Yongfeng Liu performed the experiments. Haiyan Yu wrote the manuscript. Limin Ma and Yuwei Pan contributed to the manuscript correction. All authors read and approved the final manuscript.

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Figures

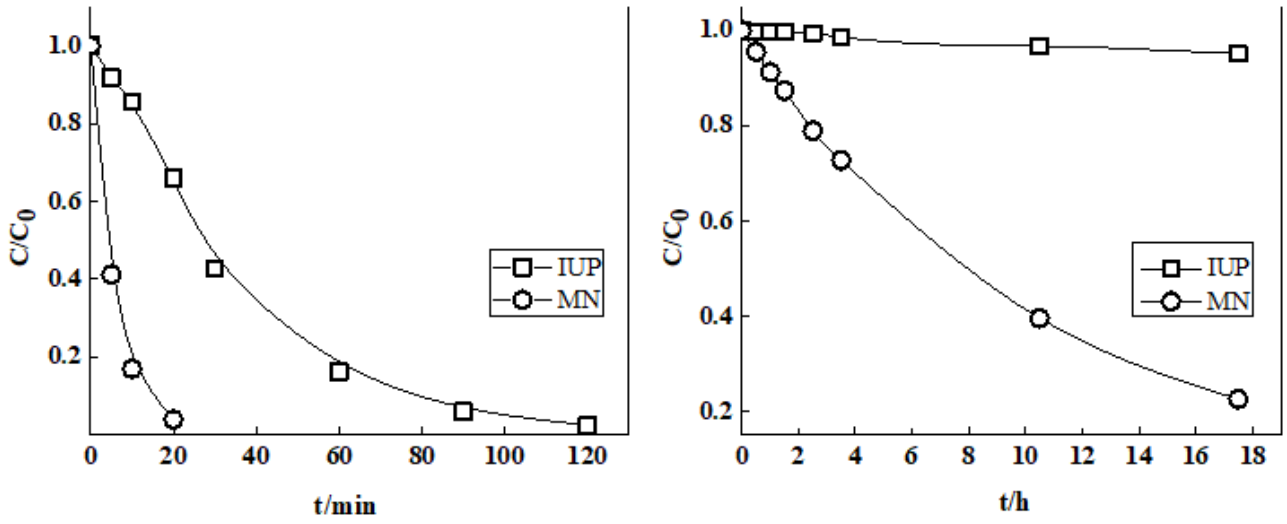

Figure 1

Removal kinetics of herbicides by ultraviolet photodegradation. Notes: “a” presents Hg lamp, “b” presents Xe lamp.

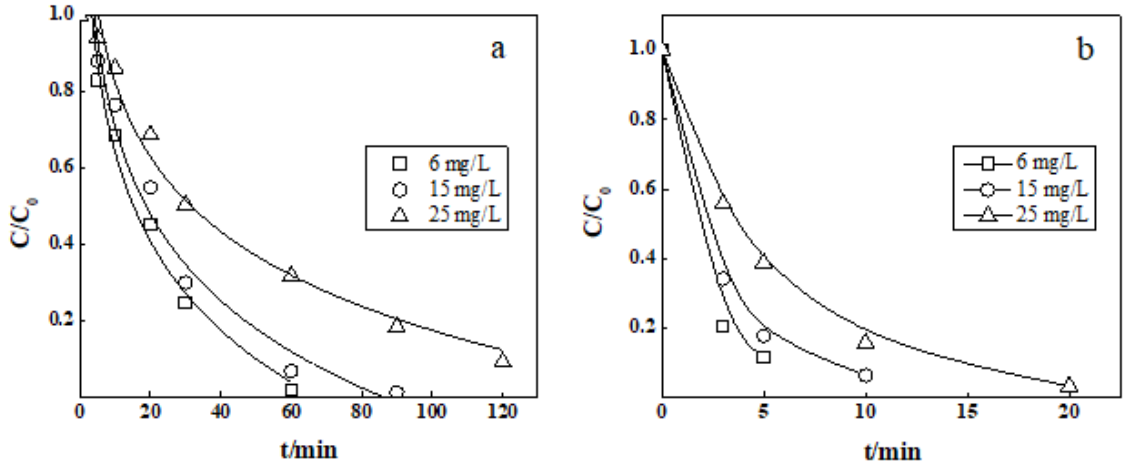

Figure 2

Influence of the initial concentration of herbicides on the photodegradation. Notes: “a” presents IUP, “b” presents MN.

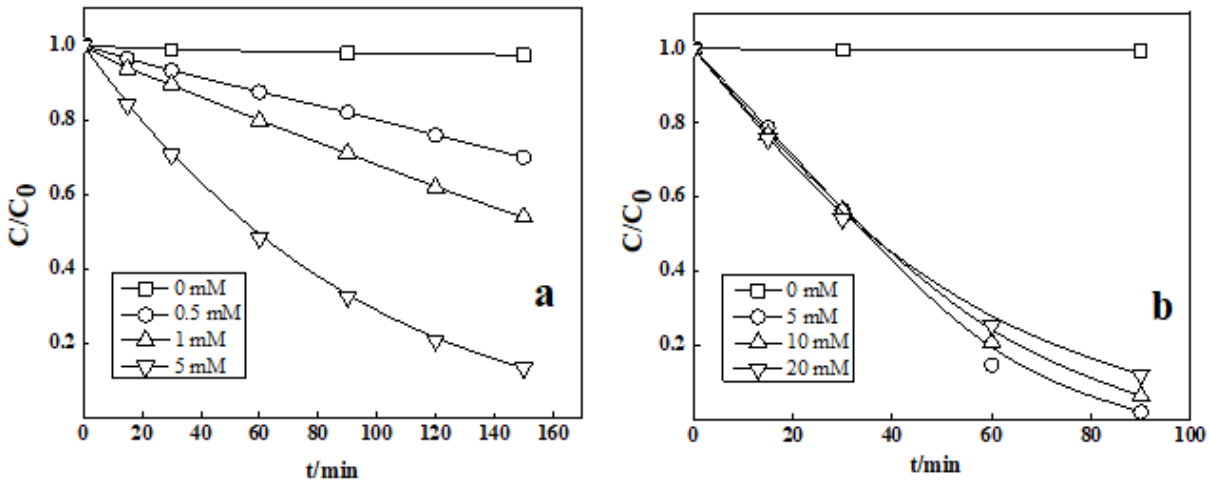

Figure 3

Influence of the nitrate concentration on the photodegradation of IUP by UV radiation. Notes: “a” presents substrate concentration is 8 mg/L, “b” presents substrate concentration is 30 mg/L.

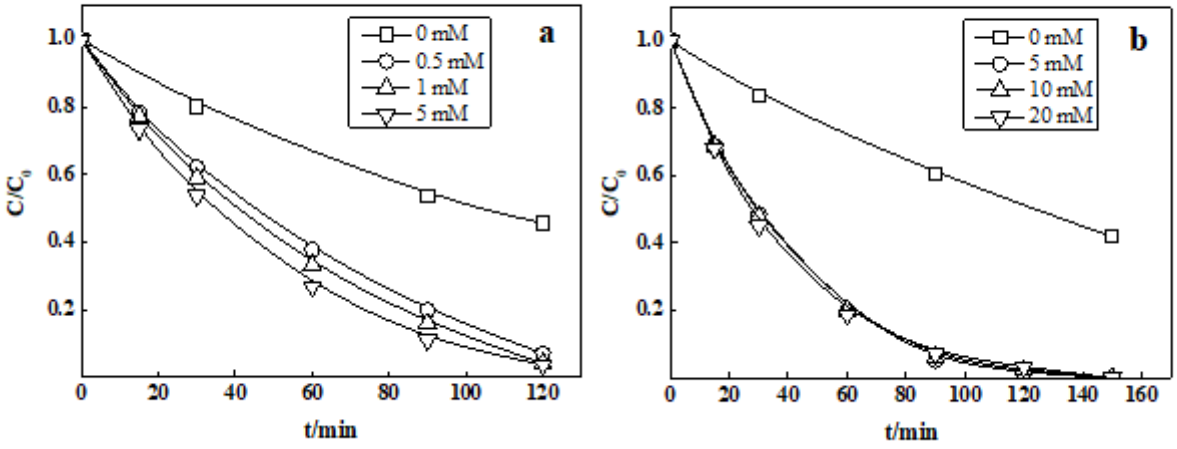

Figure 4

Influence of the nitrate concentration on the photodegradation of MN by UV radiation. Notes: “a” presents the substrate concentration is 8 mg/L, “b” presents the substrate concentration is 30 mg/L.

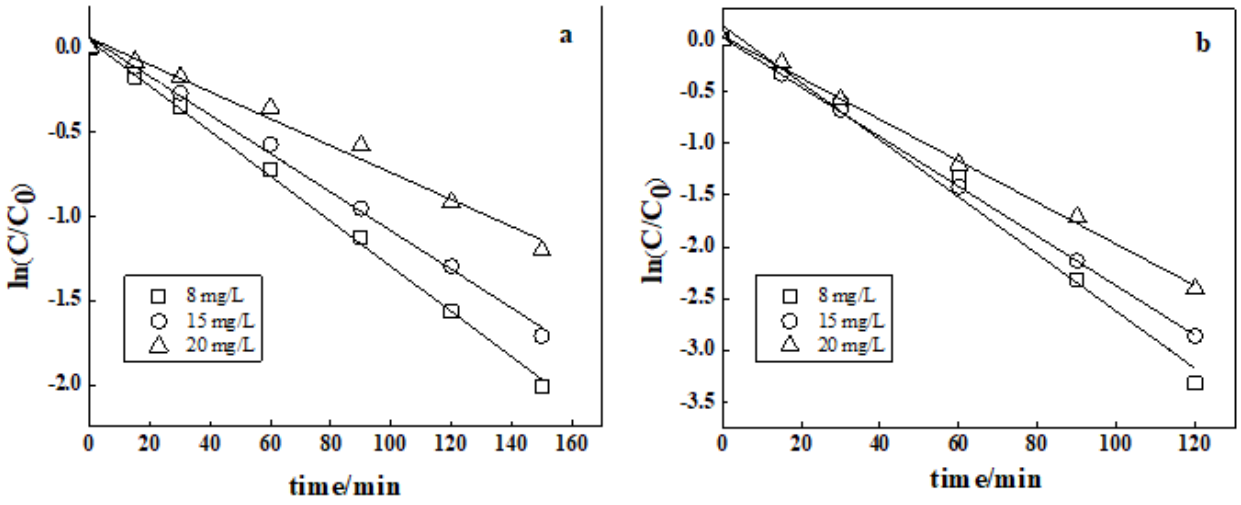

Figure 5

Influence of the substrate concentration on the photodegradation in the presence of NO3−(5 mM). Notes: “a” presents IUP, “b” presents MN.

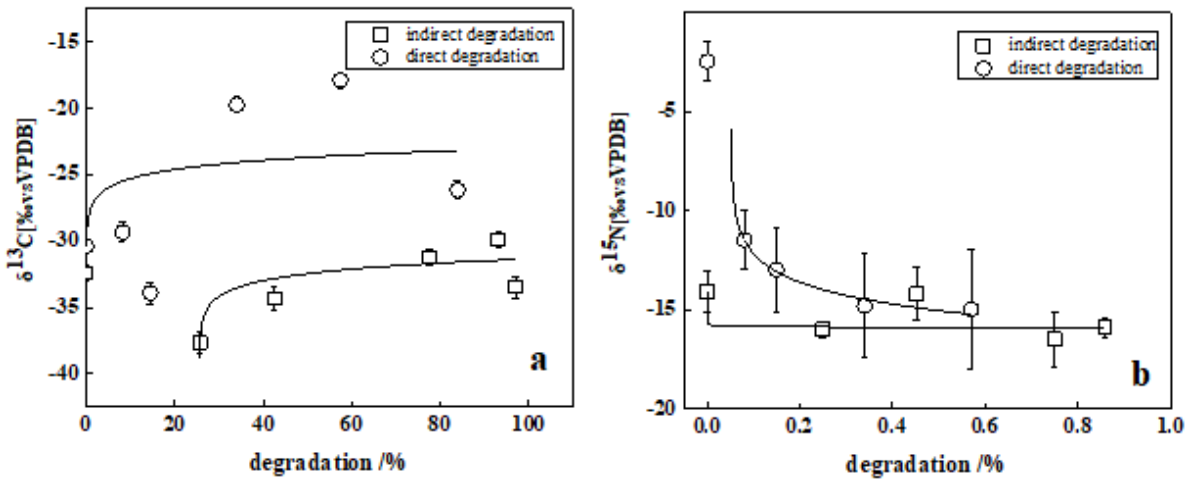

Figure 6

Carbon (a) and nitrogen (b) isotope fractionation of IUP under different conditions.

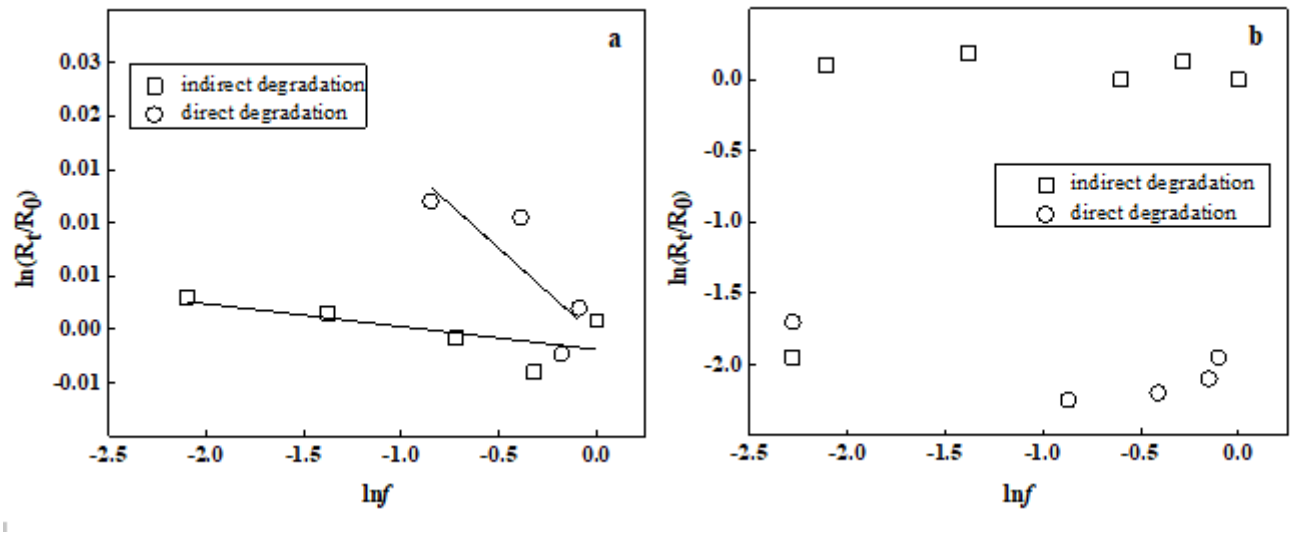

Figure 7

Carbon (a) and nitrogen (b) isotope enrichment factors were determined by a linear regression according to the Rayleigh equation.

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