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Original Research Article

Kinetics of dechlorination of atrazine using tin (SnII) at neutral pH conditions

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ABSTRACT

Atrazine is a broad spectrum herbicide of triazine family. It is a chlorine-containing molecule and it can persist in environment. Chemical and biochemical techniques are the main techniques used to decompose the chemicals. In pre-sent study, the dechlorination of atrazine (Atr) via reaction with Sn(II) ion under aqueous media at neutral pH condi-tions was studied. The observed dechlorinated metabolite was 4-Ethylamino-6-isopropylamino-[1,3,5]triazin-2-ol. Identification of dechlorinated product of Atr was performed by using spectroscopic (FTIR) and mass (ESI-MS) spectrometric analysis. The kinetics of the dechlorination of Atr was measured by using pseudo-first order kinetics. The observed reaction constants was, k_{obs} = 6.11x10^{-2} (at 430 mg/L of Atr), and k_{obs} = 6.14 x10^{-2} (at 215 mg/L of Atr). The calculated half-life ($t_{1/2}$) period was, $t_{1/2}$ = 0.204 d (at 430 mg/L of Atr), and $t_{1/2}$ = 0.205 d (at 215 mg/L of Atr).

Keywords: Atrazine; Dechlorination; Decomposition; IR Analysis; Mass Analysis

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1. Introduction

2-chloro-N^4-N^6-isopropyl-1,3,5-trizine-4,6-diamine or atrazine (Atr) is a broad spectrum herbicide[1–8]. It inhibits photosynthesis and interferes with other enzymatic processes of weeds. It is the member of triazine family, and it is still used in about 90 countries all over the world[5–12]. Annual use of atrazine was estimated to be 80,000 tons worldwide. As a chlorinated molecule, Atr is the big concern for environmental studies. Atr has low volatility, low solubility in water (33 mg/L) and low half life of 244 d through hydrolysis[17]. Transport of pesticides in environment depends upon their electrical potentials, adsorption and complex-formation abilities[13–22]. Atr previously has been the theme of dechlorination by using of zero valent metal ions and theoretical metal complex studies[16–24].

In literature, extensive analysis on dechlorination of chlorinated compounds through zero valent metals has been reported[21-28]. All the studies have demonstrated that dechlorination process enhanced at low pH values from 2 to 5, where, zero-valent metal ions get oxidized[24–29]. In the literature, there are detailed studies about the dechlorination of various organic compounds and atrazine have been reported[5–15]. In recent studies, the reported degradation products of atrazine were 2-ethylamino-4-isopropylamino-1,3,5-triazine, hydroxyatrazine (2-ethylamino-4-isopropylamino-6-hydroxy-s-triazine) and 2,4-bis(ethylamine)-6-methyl-s-triazine[11–28]. None of the above mentioned degradation

product was identified prominently in current study. In current study, dechlorination of Atr was achieved by using least toxic Sn(II) metal ion. As per our best information, no study on current topic is reported in literature. Current study is more important because of its environmental acceptability, as it was performed in aqueous media and at neutral pH conditions.

2. Experimental

All the chemicals used were of analytical reagent grade. The dechlorination/decomposition reactions were performed as per the procedure described below. The FTIR spectrums of dechlorinated product and Atr were taken in potassium bromide (KBr) discs. All spectrums were recorded on a Shimadzu-8400s FTIR spectrophotometer. Mass (ESI-MS) analyses of all the samples (dechlorinated product and Atr) were performed on mass spectrophotometer (Wa-ters, Q-TOF Micromass).

Aqueous solution (100 mL) of metal salts (1 mM; 225 mg/L) was added to ethanolic solution (100 mL) of atrazine (2 mM; 430 mg/L). The pH of reaction mixture was adjusted at 7±0.5 using NaOH solution. Similarly 1:1 reaction was performed by adding the aqueous solution (100 mL) of metal salts (1 mM; 225 mg/L) being added to ethanolic solution (100 mL) of atrazine (1 mM; 215 mg/L). The resulting solution was stirred for 10 h at 150 rpm on a magnetic stirrer at temperature of 25 ± 0.5 °C.

At regular time intervals (0 h, 1 h, 2 h, 3 h, 4 h, 6 h, 8 h and 10 h) 20 mL of reaction mixture was taken off and organic material was extracted by using ethyl-acetate as extracting solvent. Excess ethyl-acetate was evaporated on vacuumed Rotavapor. To analyze the changes w.r.t. parent molecule (Atr), FTIR and mass analyses of well dried extracted organic material were performed.

The rate of dechlorination of atrazine by Sn(II) was analyzed according to pseudo-first order kinetics. Equations (1)–(3) correspond to the equations of the concentration variation with time was plotted on the basis of the linear regression results obtained by plotting Time (in h) Vs Log C_t (in mg/L).

$$d[C]/dt = -k_{obs}[C] \quad (1)$$

$$\log[C]/[C]_0 = k_{obs}t \quad (2)$$

$$t_{1/2} = (1/ k_{obs}) \times \log 2 \quad (3)$$

Where, [C] is the atrazine concentration at time t (mg/L); $[C]_0$ the initial atrazine concentration (mg/ L); k_{obs} is the pseudo-first order constant (h^{-1}).

3. Result and discussion

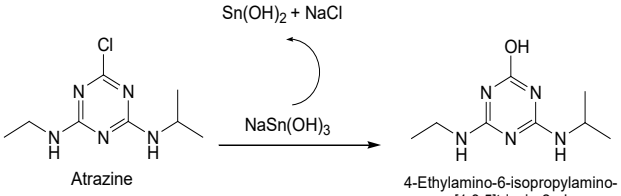
In current study, the mode/mechanism of dechlorinated is explained through following reactions from equations (4)-(6) and under Scheme-1. In equation (6), one mole of each, 4-Ethylamino-6-isopropylamino-[1,3,5]triazin-2-ol, NaCl and $Sn(OH)_2$ was produced via the interactions of one mole of each, Atr and $NaSn(OH)_3$. Equations (4)-(6) have revealed that under neutral to basic pH conditions, dechlorination reaction rate of Atr is independent of concentration of Atr, but linearly dependent of concentration of $SnCl_2$[14,22].

$$SnCl_2(aq) + 2\ NaOH\ (aq) \rightarrow SnO{\cdot}H_2O\ (s) + 2\ NaCl(aq) \quad (4)$$

$$SnO{\cdot}H_2O\ (s) + NaOH\ (aq) \rightarrow NaSn(OH)_3\ (aq) \quad (5)$$

$$NaSn(OH)_3\ (aq) + Atr \rightarrow 4\text{-Ethylamino-6-isopropylamino-[1,3,5]triazin-2-ol} + NaCl\ (aq) + Sn(OH)_2\ (aq) \quad (6)$$

The reaction kinetics of dechlorination of was measured by using pseudo-first order kinetic as mentioned in literature[12–17]. The concentration of $SnCl_2$ was kept constant and concentration of Atr was varied. Mass analysis revealed that at molar ratios 1:2 or 1:1 of Sn(II) to Atr, approximately 70-75% decomposition was achieved after 10 h reaction.



Scheme 1. Schematic representation of dechlorination of atrazine in the presence of Sn under aqueous medium at pH 7.

The observed reaction constants was, $k_{obs} = 6.11 \times 10^{-2}$ with $R^2 = 0.99$ (at 430 mg/ L of Atr), and $k_{obs} = 6.14 \times 10^{-2}$ with $R^2 = 0.99$ (at 215 mg/ L of Atr) (**Figure 1** and **Figure 2**). The calculated half-life ($t_{1/2}$) period was, $t_{1/2} = 0.204$ d (at 430 mg/ L of Atr), and $t_{1/2} = 0.205$ d (at 215 mg/ L of Atr). The observed reaction rates were similar at both ratios (**Figure 2** and **Figure 3**). These values were considerably smaller than the value reported in the litera-

ture[12,17]. Dombek *et al.* have performed dechlorination via using zero valent metallic iron under acidic conditions (pH values of 2.0, 3.0, and 3.8), the observed half-lives of atrazine were 0.06 d at pH value of 2.0, 5.12 d at pH value of 3.0, and 10.36 d at pH value of 3.8[12]. Similarly, Kim *et al.* have performed dechlorination via using zero valent metallic iron under neutral pH conditions, the observed half-lives of atrazine were 8.91 d at 10 mg/L, 9.32 d at 30 mg/L, and 10.00 d at 50 mg/L[17].

Mass (ESI-MS) and FTIR analyses were used to identify the dechlorination of atrazine (**Figure 3**). In current study, the parent ion of degradation product has a mass/charge ratio of 198, corresponding to 4-Ethylamino-6-isopropylamino-[1,3,5]triazin-2-ol (**Figure 3**). It is possible only due to replacement of Cl with OH (215 − 35 + 18 or 215 − 17 = 198) (**Figure 1**). The lack of isotopic ratio as like mass/charge ratio of 216, no isotopic ratio was observed at 198, confirming the absence of chlorine with molecule [28–32].

The comparative IR spectrums of Atr and its dechlorinated products have shown the sharp appearance in the stretching band of the ν(OH) at 3450 cm^{-1}, and sharp disappearance of C-Cl band 660 cm^{-1}[37–39]. FTIR and mass analysis have revealed that the dechlorinated product of atrazine was 4-Ethylamino-6-isopropylamino-[1,3,5]triazin-2-ol having m/z 198 with 100% intensity (Figure

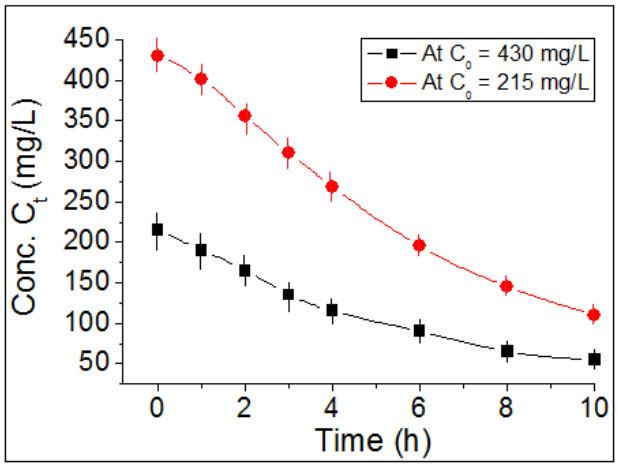


Figure 1. Dechlorination of Atr w.r.t. initial concentrations (C_t at 430 and 215 mg/L) with time.

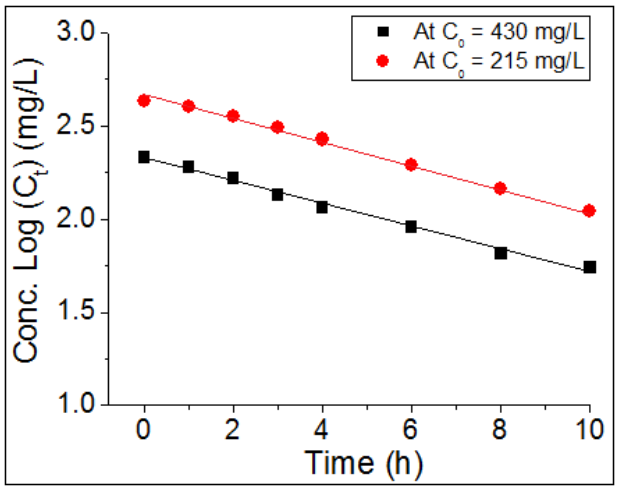


Figure 2. Pseudo-first order kinetics of dechlorination of Atr w.r.t. initial concentrations (Log C_t at 430 and 215 mg/L).

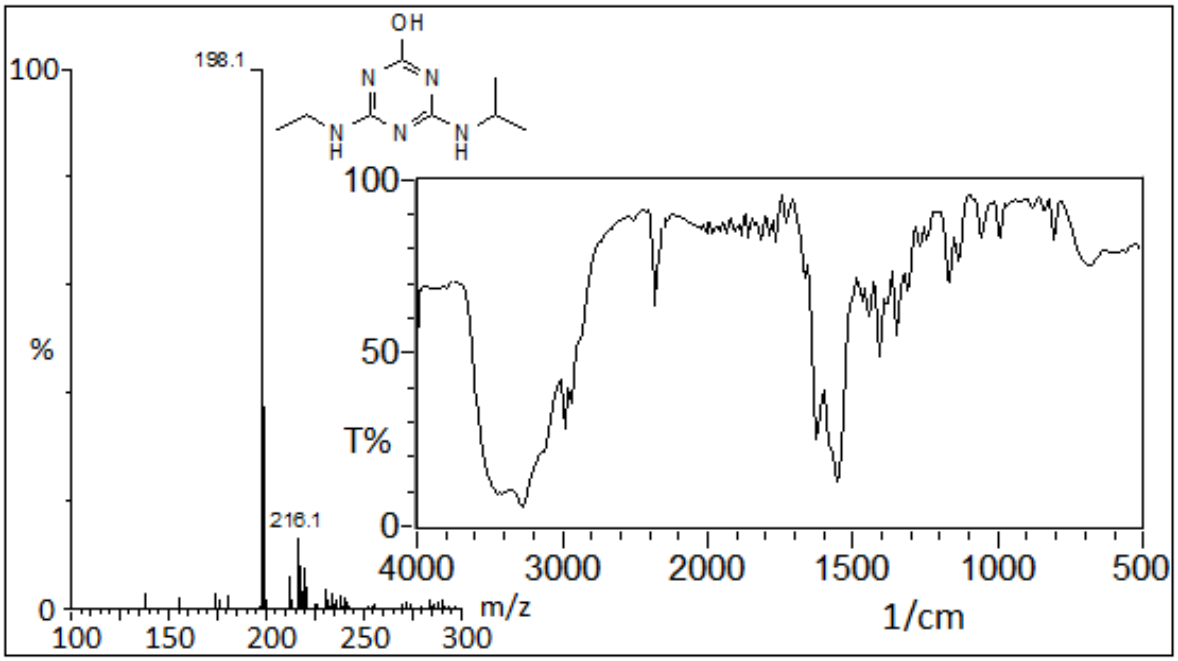


Figure 3. Mass (ESI-MS) and FTIR analysis of dechlorinated product of Atr after 10 h at 430 mg/L of Atr.

3). The observed dechlorinated product of atrazine was quite differ than the reported metabolites[33–42].

4. Conclusion

In summary, large number of aquatic, soil, agricultural and geological material/organisms survive under neutral to basic conditions. In current study the objective of dechlorination of toxic Atr at neutral conditions was achieved successfully. Dechlorination followed pseudo-first order kinetics with reaction constant $k_{obs} = 6.12 \pm 2 \times 10^{-2}$, and half-life period, $t_{1/2} = 0.204 \pm 0.001$ d. In future, we will use agricultural and geological material to check the dechlorination kinetics of Atr at neutral pH with the addition of variable concentrations of $SnCl_2$.

Conflict of interest

The authors declare that they have no conflict of interest.

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