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Photolytic and photocatalytic degradation of atrazine in the presence of activated carbon

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ABSTRACT

The removal of atrazine (2-chloro-4-ethylamino-6-isopropylamino 1,3,5-triazine) by photolysis, photocatalysis and adsorption on jack fruit peel carbon (JPC) was investigated as separate and combined processes. Under the experimental conditions used, JPC was not capable of completely removing atrazine in reasonable time. On the other hand, degradation with UV-light (254) nm and TiO_2, the intermediates and by-products were found to be toxic. The combination of JPC with 254 nm UV light and TiO_2 enhanced the removal of atrazine and especially the mineralization of the organic matter. The mineralization process was followed by measuring the total organic carbon (TOC). JPC acts both as an adsorbent and a catalyst in the degradation process. The total mineralization of atrazine, through the combination of adsorption and degradation was achieved in a reasonable time, and can therefore be suggested as an efficient, cost-effective and environment friendly water treatment methodology.

1. Introduction

Contamination of water is a worldwide problem due to agricultural, non-agricultural, and industrial pollution. The extent of the problem is highlighted by the US Geological Survey National Water Quality Assessment program where it is reported that over 95% of surface water and 50% of groundwater samples (sample size 8200) are contaminated with at least one pesticide [1]. These pesticides are amongst the most refractory organic chemicals and they have been long suspected of causing severe health hazards including leukemia [2].

Amongst the different pollutants, herbicides such as *s*-triazines are priority pollutants as they are widely used all over the world. Atrazine, the most common amongst triazines is used as pre- and post-emergence herbicide for the control of annual and perennial grass and annual broad-weeds [3]. Atrazine is not readily biodegradable and persists in soil and even reaches the groundwater. Despite the existence of a wide range of wastewater treatment techniques, there is no single process capable of adequate treatment for atrazine contaminated water at affordable costs.

Atrazine degradation has been studied by various biological [4–6] and advanced oxidation processes (AOP) that include UV and H_2O_2 [7], Fenton reagent [8], photoassisted Fenton reagent [9], ozonation [10] and photocatalysis [11]. All such processes were shown to involve the de-alkylation of the atrazine amino group and/or atrazine hydroxylation via de-amination and/or de-chlorination, but not *s*-triazine ring opening, with cyanuric acid (2,4,6-trihydroxy-*s*-triazine) have been detected as the most oxidized product. Cyanuric acid LD_{50} is 7700 mg/kg and hence it is also harmful. *s*-Triazine ring opening can be achieved only under hydrothermal conditions [12] and in supercritical water [13], which can hardly be employed in routine water treatment. The intermediate and by-products generated during the phase of atrazine photocatalytic oxidation were also found to be toxic [14].

On the other hand, adsorption of these pollutants on activated carbon can lead to better results than degradation in term of total organic carbon (TOC) removal. The draw back of commercial activated carbon is high cost, easy surface saturation and need for frequent regeneration.

In this paper, the removal of atrazine was studied in a laboratory scale reactor by different processes: adsorption on jack fruit peel carbon (JPC), photolysis at 254 nm and photocatalysis in the presence of TiO_2 employed either separately or in combination. The mineralization of the solutions was followed by measurement of TOC. The identification of degradation products was done with the help of LC–MS technique and the possible degradation pathways are also predicted and proposed.

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2. Experimental

2.1. Materials

Activated carbon was prepared from jack fruit peel, which was treated with concentrated sulphuric acid [15]. Titanium *n*-butoxide [Ti $(OC_4H_9)_2$] and butyl alcohol, obtained from Merck (India), were used as the precursors for TiO_2. Atrazine (2-chloro-4-ethylamino-6-isopropylamino 1,3,5-triazine), HIET (2-hydroxy-4-ethylamino-6-isopropyl-amino-*s*-triazine), CEAT (2-chloro-4-ethylamino-6-amino-triazine), CDT (2-chloro-4,6-diamino-triazine), HDT (2-hydroxy-4,6-diamino-triazine) and cyanuric acid were obtained from Fluka. All solutions were prepared in double distilled water, and all other organic solvents used were analytical grade.

2.2. Preparation of the TiO_2

TiO_2 was prepared by sol–gel method as follows; the mixture of butyl alcohol and titanium *n*-butoxide in the ratio of 30:10 (v/v) was placed in a rotary evaporating flask and rotated for few minutes. 100 ml of distilled water was then added and after the rotation of the solution for 1 h, the solvent (mixture of butyl alcohol and water) was evaporated out. The prepared sample was heat treated at 650 °C for 3 h.

2.3. Adsorption studies

In batch method, a fixed amount of the adsorbent (0.1 g) was added to 100 ml of atrazine solution of varying concentrations taken in 250 ml stoppered conical flasks, which were placed in a thermostated agitation (32 °C) assembly. The solution was agitated continuously (140 rpm) at constant temperature for 5 h to achieve equilibration. At the end of the adsorption period, the solution was centrifuged for 10 min at 3000 rpm. After centrifugation the atrazine concentration in the supernatant solution was determined spectrophotometrically at λ_{max} 222.80 nm.

The adsorbate uptake q_e (mg/g), can be calculated as

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 is the initial adsorbate concentration (mg/L); C_e is the equilibrium adsorbate concentration in solution (mg/L); V is the volume of the solution; W is the mass of the adsorbent (g) and q_e is the amount adsorbed.

2.4. Degradation studies

Monochromatic irradiation at 254 nm was carried out in a 1000 ml magnetically stirred reactor, equipped with a quartz jacketed 15 W immersion low pressure mercury arc lamp (Philips, model TUV) as irradiation source emitting with a radiation flow of 2.8×10^{-6} einstein s^{-1}, according to ferrioxalate actinometry. The reactor was thermostated at 32 °C during the runs, by continuous water recirculation through an external glass jacket. Samples were taken from the irradiated suspension at predetermined intervals and subjected to analysis.

2.5. Analytical determinations

Analysis was done on HPLC using a C8 column. Acetonitrile:water (60:40) mixture was employed as the mobile phase, at a constant flow rate of 1 ml min^{-1}. The major intermediates were identified by comparing the retention times and the adsorption spectra obtained by injecting aqueous solutions containing the single compounds. Their concentration during the runs was evaluated by comparing the area count of the HPLC peaks at 220 nm with those recorded in calibration analyses of aqueous solutions of the individual component, in concentrations up to 30 ppm.

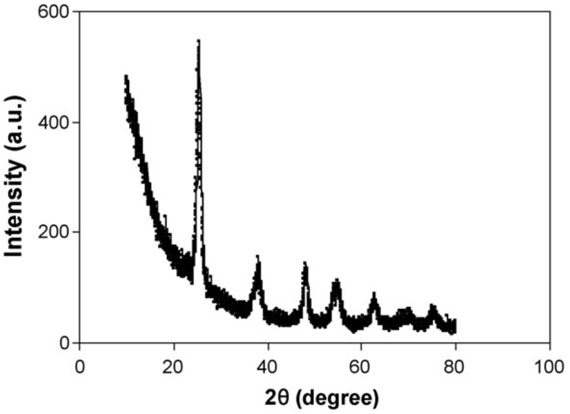


Fig. 1. XRD pattern of TiO_2.

Identification of atrazine degradation products was achieved with the aid of LC–MS (ThermoQuest LCQ Duo, USA) with a C8 HPLC column. The concentration of atrazine in the solution was determined spectrophotometrically on a Shimadzu 1650PC UV–vis spectrophotometer. TOC was measured in a Shimadzu TOC-5000A analyzer. XRD measurements were done on a Phillips X-ray diffractometer using Ni-filtered Cu Kα radiation.

3. Results and discussion

3.1. Characterization of JPC

Physical and surface characterization of JPC were carefully performed using instrumental techniques such as scanning electron microscopy, X-ray diffraction, infrared spectroscopy and surface area analyzer and the results were discussed in our earlier publication [15]. BET surface area of TiO_2 is 45 m^2 g^{-1}. XRD patterns of the TiO_2 sample are shown in Fig. 1. After calcinations at 650 °C, the sample become crystalline with predominantly anatase structure because $2\theta^\circ$ value from the diffraction pattern are 25.2, 37.8 and 48.0° and crystalline plane are (1 0 1), (0 0 4) and (2 0 0).

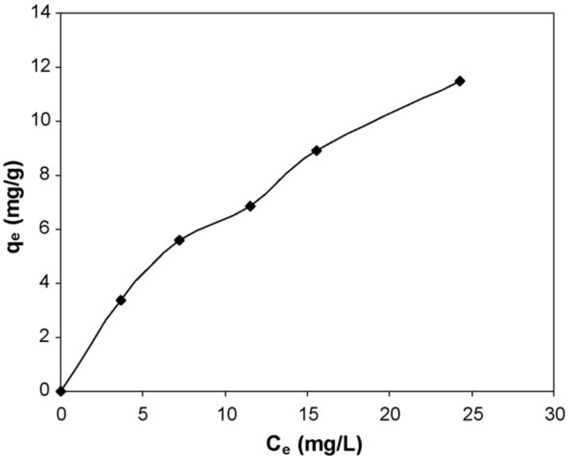


Fig. 2. Adsorption isotherms (305 K) from aqueous atrazine solution.

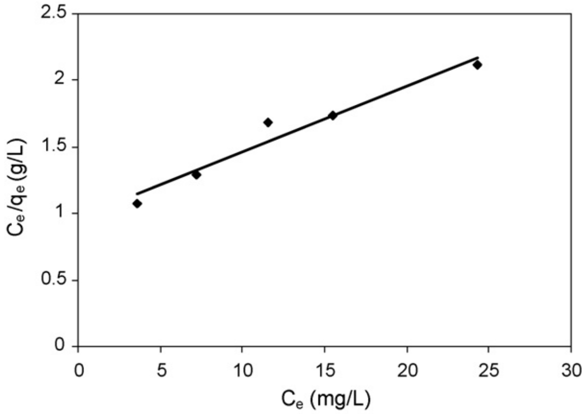


Fig. 3. Langmuir plots for the adsorption of atrazine on JPC. JPC dose; 1 g/L, temperature; 305 K.

3.2. Adsorption studies

The isotherm in Fig. 2 is of type L-shape according to the classification of Giles et al. [16]. The L-shape isotherm indicates that there is no strong competition between the solvent and the atrazine for the JPC surface sites [17]. Several models have been proposed to describe experimental data of adsorption isotherms. For the sake of convenience, explicit and simple models are preferred and commonly used. The Langmuir and Freundlich models are the most frequently employed models.

Langmuir isotherm [18] is represented by the following equation:

$$q_e = \frac{Q_0 bC}{1 + bC} \quad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

where C_e is the concentration of the adsorbate (mg/L) at equilibrium, q_e is the amount of adsorbate per unit mass of adsorbent at equilibrium in mg/g, Q_0 is the maximum adsorption at monolayer coverage in mg/g, b is the adsorption equilibrium constant related to the energy of adsorption in L/mg. The plots of C_e/q_e vs C_e are linear and presented in Fig. 3. $Q_0 = 20.12$ mg/g and $b = 0.05$ L/mg, as found from the intercept and slope of the plots.

The logarithmic form of the Freundlich model is given by the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), K_f (L/g) and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. $K_f = 1.50$ and $n = 1.56$, as calculated from the intercept and slope of the plot in Fig. 4. The correlation coefficient values show (Table 1) that the data can be better represented by the Freundlich isotherm model. Atrazine is expected to be adsorbed on JPC through van der Waals force and hydrogen bonding. The ability of atrazine to form hydrogen bonds has been reported by Welhouse and Bleam [19] and Saha and coworkers [20].

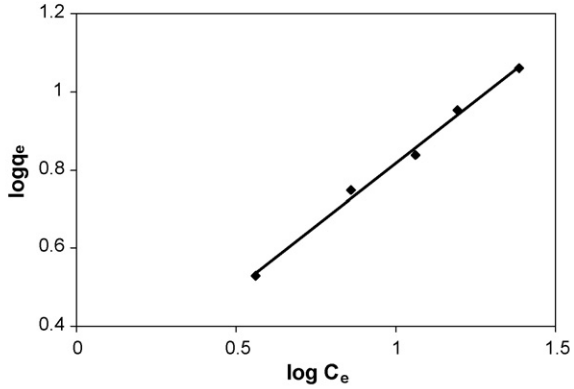


Fig. 4. Freundlich plots for the adsorption of atrazine on JPC. JPC dose; 1 g/L, temperature; 305 K.

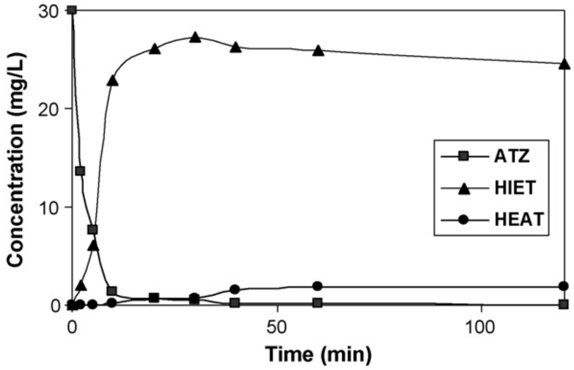


Fig. 5. Direct photolysis of Atrazine and formation of intermediate species.

3.3. Direct photolysis of atrazine with irradiation at 254 nm (ATZ/UV-254 nm)

Photolysis of ATZ by UV radiation at 254 nm was investigated as shown in Fig. 5. A single major peak was observed by LC–MS analysis. ATZ was completely removed after 120 min and HIET was formed. This suggests that the photolysis of ATZ via the dechlorination process is the dominant mechanism for the decay of ATZ. Formation of HIET could result either from a homolytic cleavage of the C–Cl bond, followed by an electron transfer from the carbon to the chlorine radical processed by the carbonation reaction with water; or from the heterolytic cleavage of the excited ATZ molecule, which is favored by polar solvents such as water [21].

Table 1
Langmuir and Freundlich constants for the adsorption of atrazine on JPC.

Langmuir constants			Freundlich constants		
Q_0 (mg/g)	b (L/mg)	R^2	K_f (L/g)	n	R^2
20.12	0.05	0.9547	1.50	1.56	0.9938

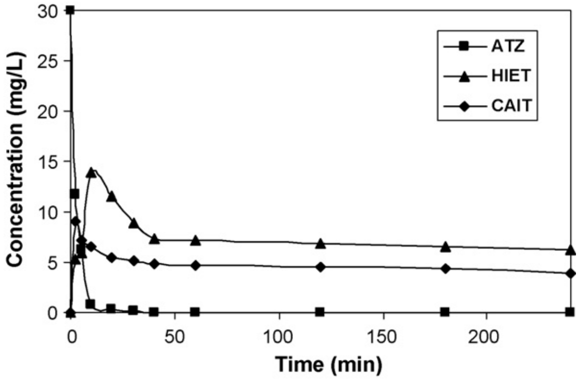


Fig. 6. Photolysis of atrazine and formation of intermediate species in the presence of 1 g/L of JPC.

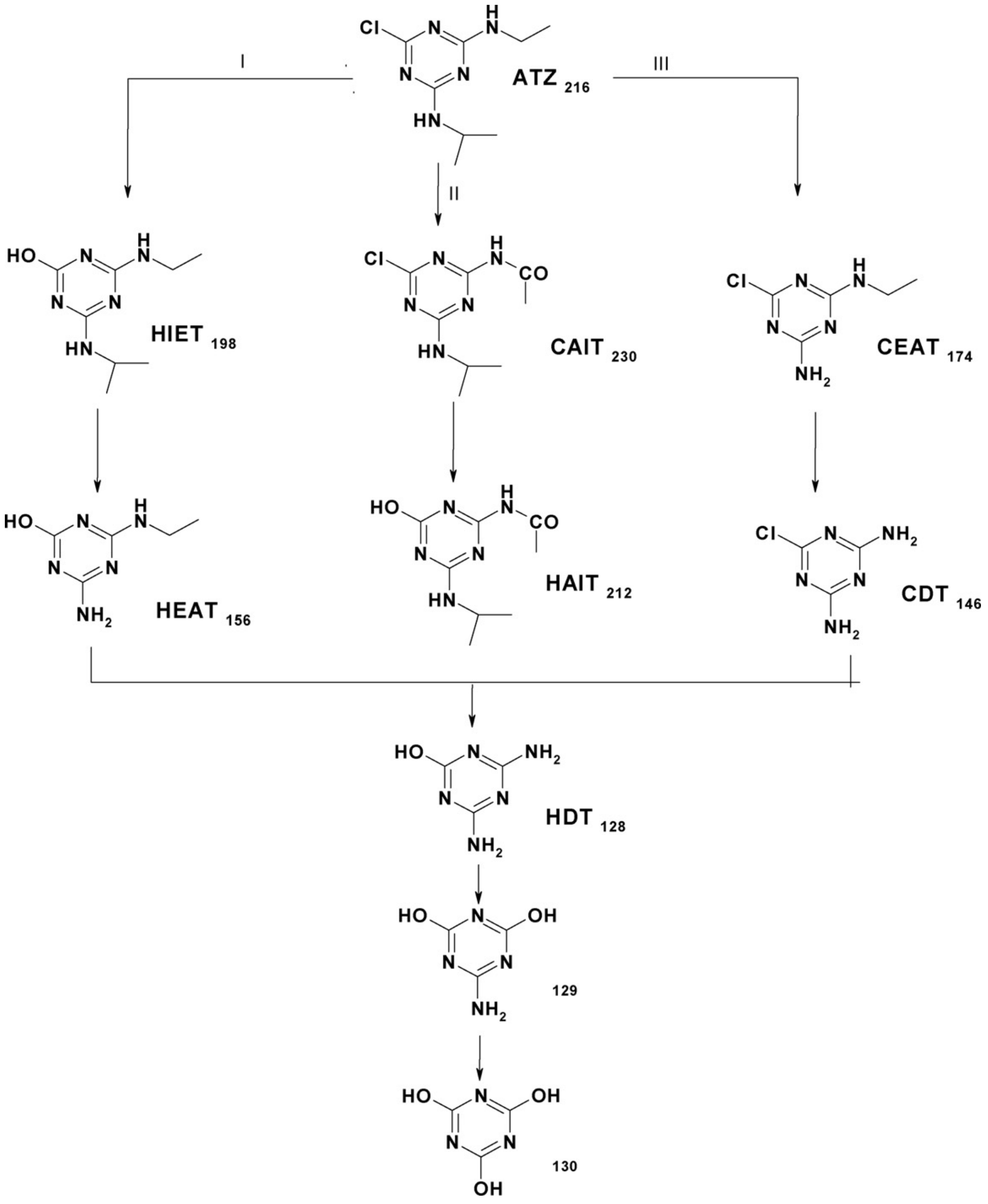


Fig. 7. Degradation pathways of atrazine under photolysis at 254 nm (I), degradation with carbon (II) and photocatalysis (III).

HIET appeared to be quite stable to direct photolysis and undergoes de-alkylation at a very low rate, as demonstrated by the very low concentrations of the de-alkylated product HEAT appearing at the end of the run [22].

3.4. *JPC photolysis hybrid system (ATZ/UV-254/JPC)*

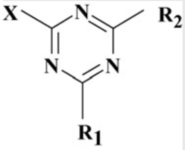
The effect of the combined use of photolysis and adsorption is shown in Fig. 6. Photolysis at 254 nm was found to be most effective for atrazine de-chlorination and with JPC, most effective in overall detoxification. When JPC was added into the atrazine water solution irradiated at 254 nm, HIET and CAIT were detected by LC–MS analysis. HIET was formed in photolysis and the concentration was very low in solution due to adsorption on JPC. CAIT has also appeared because the reaction of the polar groups present on the JPC surface with the free radicals formed in atrazine (see the path II in Fig. 5). The results show that JPC not only function as an adsorbent, but also as a catalyst in the photolysis.

Fig. 7 Degradation pathways of atrazine under photolysis at 254 nm (I), degradation with carbon (II) and photocatalysis (III).

3.5. *Photocatalytic degradation of atrazine with irradiation at 254 nm (ATZ/UV-254 nm/TiO_2)*

With TiO_2 as a catalyst, almost complete degradation of atrazine was achieved after 240 min. As shown in Fig. 8, almost complete de-

Table 2
Degradation products determined by LC–MS.



m/z	Retention time (min)	Abbreviation	Chemical name	X	R_1	R_2
230	8.41	CAIT	2-Chloro-4-acetamindo-6-(isopropylamino)-*s*-triazine	Cl	$NHCOCH_3$	$NHCH(CH_3)_2$
216	5.67	ATZ	2-Chloro-4-ethylamino-6-isopropylamino 1,3,5-*s*-triazine	Cl	NHC_2H_5	$NHCH(CH_3)_2$
198	4.38	HIET	2-Hydroxy-4-ethylamino-6-isopropyl-amino-*s*-triazine	OH	NHC_2H_5	$NHCH(CH_3)_2$
156	3.89	HEAT	2-Hydroxy-4-ethylamino-6-amino-*s*-triazine	OH	NHC_2H_5	NH_2
174	2.88	CEAT	2-Chloro-4-ethylamino-6-amino-*s*-triazine	Cl	NHC_2H_5	NH_2
146	2.27	CDT	2-Chloro-4,6-diamino-*s*-triazine	Cl	NH_2	NH_2
128	2.01	HDT	2-Hydroxy-4,6-diamino-*s*-triazine	OH	NH_2	NH_2

alkylation was testified by the formation and early disappearance of the de-alkylated by product CEAT and CDT followed by continuous increase of the HDT by product. TiO_2 being a stable photoactive semiconductor material causes the formation of radical species in situ, like $OH^{\bullet}$ which is predicted as a strong oxidizing agent.

3.6. *JPC photocatalysis hybrid system (ATZ/UV-254 nm/TiO_2/JPC)*

Under both photocatalysis and adsorption, the rate of atrazine degradation increased when adsorption was simultaneously carried out during the runs. The intermediate, which formed in photocatalysis, was almost completely adsorbed by JPC after 120 min and the solution was detoxified as shown in Fig. 9.

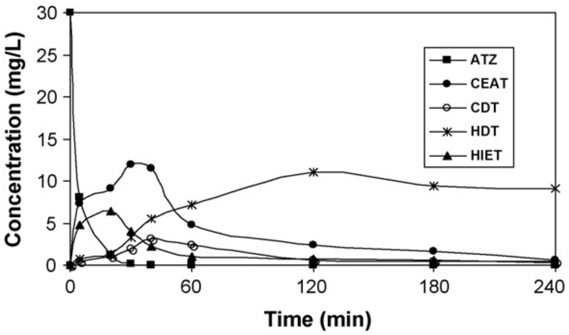


Fig. 8. Photocatalysis of atrazine and formation of intermediate species in the presence of 1 g/L of TiO_2.

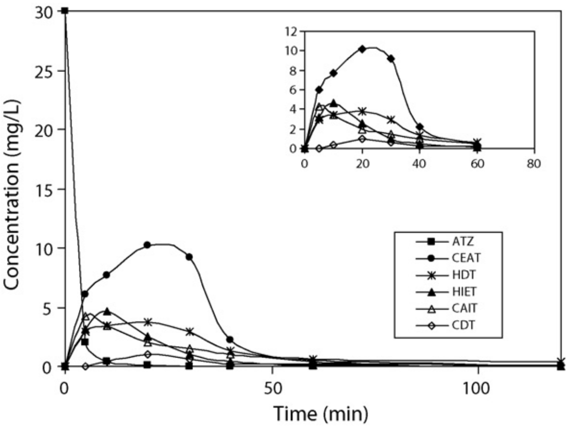


Fig. 9. Removal of atrazine and formation of intermediate species under photocatalysis (TiO_2 +254 nm) combined with adsorption (JPC).

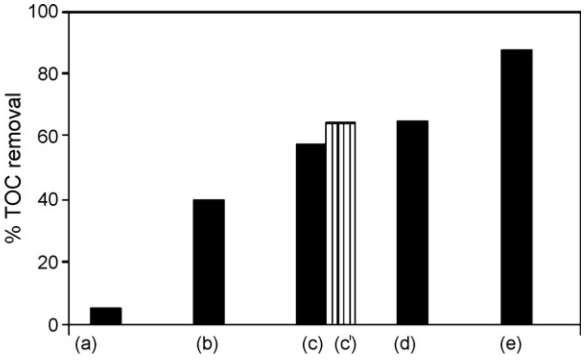


Fig. 10. TOC removal in atrazine solution obtained by photolysis (a), adsorption (b), photolysis followed by adsorption on JPC (c), photolysis in the presence of JPC (c′), photocatalysis (d) and photocatalysis in the presence of JPC (e) [C_0 = 30 ppm, JPC dose 1 g/L, TiO_2 dose 1 g/L and temperature 305 K].

Degradation products determined by LC–MS Table 2.

3.7. *Extent of overall mineralization*

As shown in Fig. 10, direct photolysis at 254 nm induced an almost negligible decrease of total organic carbon content. TOC removal by photolysis in the presence of JPC is higher (c′) than that obtained by the sum of the contribution of photolysis and subsequent adsorption (c) indicating, a synergistic effect appears. JPC itself is supposed to contribute in two different ways; acting as a catalyst promoting the degradation of atrazine and also acting as an adsorbent, removing the intermediate and by-products originated by the degradation of atrazine. Most efficient mineralization was attained during photocatalysis in the presence of JPC. In photocatalysis, photolysis (254 nm) combined with ozonation [22], degradation by microwave-assisted electrodeless discharge mercury lamp [23], sonochemical and photocatalytic in the presence of $SiW_{12}O_{40}^{4-}$ [24], the removal of TOC did not proceed beyond 65% corresponding to the removal of five out of the eight carbon atoms originally present in the molecule, resulting in atrazine oxidative degradation to cyanuric acid.

4. Conclusions

The adsorption of atrazine from aqueous solution onto JPC has been studied in detail. Freundlich adsorption isotherm fits well for the systems. With the experimental conditions employed, JPC alone is not efficient enough for the removal of atrazine. The results obtained show that photolysis and photocatalysis in the presence of JPC is a promising technique for the removal of atrazine. Sequential experiments of photolysis and adsorption revealed that there is a synergistic effect when the photolysis is carried out in presence of JPC.

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References

[1] R.J. Gilliom, J.E. Barbash, Y.M. Gobert, D.W. Kolpin, S.J. Larson, N. Nakagaki, W.G. Wilber, Pesticides in streams and ground after of the United State, 1993–1995, in: Ninth International Congress of Pesticide Chemistry, 1998.

[2] P. Hurst, A. Hay, N. Dudley, The Pesticide Handbook, Journeyman Pree, London, 1991.

[3] I.K. Konstantinou, T.A. Albanis, D.E. Petrakis, P.J. Pomonis, Removal of herbicides from aqueous solutions by adsorption on Al-pillared clays, Fe–Al-pillared clays and mesoporrous alumina aluminum phosphates, Water Res. 34 (2000) 3123–3136.

[4] C.Y. Kontchou, N. Gschwind, Mineralization of the herbicide atrazine in soil inoculated with a *Pseudomonas* strain, J. Agric. Food Chem. 43 (8) (1995) 2291–2294.

[5] C.J. Hapeman, J.S. Karns, D.R. Shelton, Total mineralization of aqueous atrazine in the presence of ammonium nitrate using ozone and *Klebsiella terragena* (strain DRS-I): mechanistic considerations for pilot scale disposal, J. Agric. Food Chem. 43 (5) (1995) 1383–1391.

[6] R.M. Behki, S.U. Khan, Degradation of atrazine, propazine, and simazine by *Rhodococcus* strain B-30, J. Agric. Food Chem. 42 (1994) 1237–1241.

[7] J. Arantegui, J. Prado, E. Chamarro, S. Esplugas, Kinetics of the UV degradation of atrazine in aqueous solution in the presence of hydrogen peroxide, J. Photochem. Photobiol. A: Chem. 88 (1995) 65–74.

[8] S.M. Arnold, W.J. Hickey, R.F. Harris, Degradation of atrazine by Fenton's reagent: condition optimization and product quantification, Environ. Sci. Technol. 29 (1995) 2083–2089.

[9] P.L. Huston, J.J. Pignatello, Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction, Water Res. 33 (1999) 1238–1246.

[10] C.J. Hapeman-Somich, Z. Gui-Ming, W.R. Lusby, M.T. Muldoon, R. Waters, Aqueous ozonation of atrazine. Product identification and description of the degradation pathway, J. Agric. Food Chem. 40 (1992) 2294–2298.

[11] E. Pelizzetti, V. Maurino, C. Minero, V. Carlin, E. Pramauro, O. Zerbinati, M.L. Tosato, Photocatalytic degradation of atrazine and other s-triazine herbicides, Environ. Sci. Technol. 24 (1990) 1559–1565.

[12] S. Horikoshi, H. Hidaka, Non-degradable triazine substrates of atrazine and cyanuric acid hydrothermally and in supercritical water under the UV-illuminated photocatalytic cooperation, Chemosphere 51 (2003) 139–142.

[13] S. Horikoshi, Y. Wada, N. Watanabe, H. Hidaka, N. Serpone, Near-quantitative mineralization of two refractory triazines under hydrothermal-supercritical aqueous conditions assisted by ozone and UV/ozone, New J. Chem. 27 (2003) 1216–1223.

[14] C.Y. Chan, S. Tao, R. Dawson, P.K. Wong, Treatment of atrazine by integrating photocatalytic and biological processes, Environ. Pollut. 131 (2004) 44–45.

[15] S. Jain, R.V. Jayaram, Adsorption of phenol and substituted chlorophenols from aqueous solution by activated carbon prepared from Jack fruit (*Artocarpus heterophyllus*) peel—kinetics and equilibrium studies, Sep. Sci. Technol. 42 (2007) 2019–2032.

[16] C.H. Giles, A.P.D. Silva, I.A. Easton, A general treatment and classification of the solute adsorption isotherm part. II. Experimental interpretation, J. Colloid Interface Sci. 47 (1974) 766–778.

[17] M. Muruganaadham, M. Swaminathan, Solar photocatalytic degradation of a reactive azo dye in TiO_2-suspension, Solar Energy Mater. Solar Cells 81 (2004) 439–457.

[18] G. Mckay, Adsorption of dyestuff from aqueous solution with activated carbon. I. Equilibrium and batch contact time studies, J. Chem. Technol. Biotechnol. 32 (1982) 759–772.

[19] G.J. Welhouse, W.F. Bleam, Atrazine hydrogen-bonding potentials, Environ. Sci. Technol. 27 (1993) 494–500.

[20] P. Chingombe, B. Saha, R.J. Wakeman, Sorption of atrazine on conventional and surface modified activated carbons, J. Colloid Interface Sci. 302 (2006) 408–416.

[21] V. Hequet, C. Gonzalez, P. Le Cloirec, Photochemical processes for atrazine degradation: methodological approach, Water Res. 35 (2001) 4253–4260.

[22] C.L. Bianchi, C. Pirola, V. Ragaini, E. Selli, Mechanism and efficiency of atrazine degradation under combined oxidation processes, Appl. Catal. B: Environ. 64 (2006) 131–138.

[23] N. Ta, J. Hong, T. Liu, C. Sun, Degradation of atrazine by microwave- assisted electrodeless discharge mercury lamp in aqueous solution, J. Hazard. Mater. B 138 (2006) 187–194.

[24] A. Hiskia, M. Ecke, A. Troupis, A. Kokorakis, H. Hennig, E. Papaconstantinou, Sonolytic, photolytic, and photolytic decomposition of atrazine in the presence of polyoxometalates, Environ. Sci. Technol. 35 (2001) 2358–2364.