



Tecnología Química

ISSN: 0041-8420

revista.tec.quimica@fiq.uo.edu.cu

Universidad de Oriente

Cuba

GRCIC, Ivana; KOPRIVANAC, Natalija; VUJEVIC, Dinko
REMOVAL OF ATRAZINE HERBICIDE FROM MODEL WASTEWATER
Tecnología Química, vol. XXIX, núm. 1, enero-abril, 2009, pp. 32-42
Universidad de Oriente
Santiago de Cuba, Cuba

Available in: <http://www.redalyc.org/articulo.oa?id=445543758005>

- How to cite
- Complete issue
- More information about this article
- Journal's homepage in redalyc.org

redalyc.org

Scientific Information System

Network of Scientific Journals from Latin America, the Caribbean, Spain and Portugal

Non-profit academic project, developed under the open access initiative

REMOVAL OF ATRAZINE HERBICIDE FROM MODEL WASTEWATER

Ivana GRCIC, Natalija KOPRIVANAC, Dinko VUJEVIC

Faculty of Chemical Engineering and Technology, University of Zagreb, Marulicev Croatia

Application of different types of synthetic zeolites as potential adsorbents for the efficient atrazine removal has been evaluated in this study. Also, atrazine degradation with combination of adsorption and advanced oxidation technologies (AOTs), Fenton and UV/Fenton, has been taken into the consideration. Preliminary results have shown significant efficiency of studied processes. Regarding adsorption experiments, it has been found that residual atrazine concentration was in the range from 40 to 55 % of initial atrazine concentration, depending on type of zeolite. Applied AOTs resulted in complete removal of atrazine from model wastewater and significant decrease in total organic carbon (TOC) value, so they can be used as polishing step after the treatment by adsorption.
Keywords: atrazine, wastewater treatment, adsorption, zeolites, AOTs

Este estudio evalúa la aplicación de tipos diferentes de zeolites sintético como adsorbentes potenciales para la eliminación eficiente de atrazine. También, la degradación de atrazine con la combinación de adsorción y tecnologías avanzadas de oxidación (TAO), Fenton y UV/Fenton, han sido tomados en la consideración. Los resultados del preliminar han mostrado la eficiencia significativa de procesos estudiados. Con respecto a experimentos de adsorción ha sido encontrado que la concentración residual de atrazine estuvo en la gama de 40 a 55 % de la concentración inicial de la atrazine, dependiendo del tipo de zeolite. TAOs aplicado tuvo como resultado la eliminación completa de atrazine del malgaste agua modelo y la disminución significativa en el el valor del carbón orgánico total (TOC), así que ellos pueden ser utilizados como un paso después del tratamiento por adsorción.

Palabras clave: Atrazine, el tratamiento de malgaste agua, adsorción, zeolites, Tecnologías Avanzadas de Oxidación (TAO).

Introduction

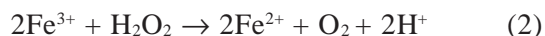
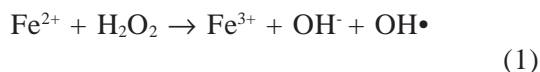
Pesticides, particularly herbicides, have been classified as persistent organic pollutants (POPs) due to resistance to natural degradation processes, and hence ability to remain in the environment for long period of time. Generally, POPs have been identified as an increasing problem in water supplies. Atrazine, 2-chloro-4-ethylamino-6-isopropylamino-s-triazine, is one of the most common herbicide found in groundwater sources and drinking water supplies. Manufacturing and application of atrazine have been already forbidden in the most of countries worldwide while in Croatia it is only listed as a toxic compound, and it is still in use. Atrazine may be released to the environment in wastewater from manufacturing facilities and through its agricultural application.

Although agricultural application results in relatively low soil contamination, much higher concentration is caused by accidental spillage during pesticide mixing, loading and rinsing operations or direct dumping into waste disposal sites (Silva *et al.*, 2004). Point-source contamination due to spillage is considered to be responsible for approximately 45 % cases of groundwater pollution, caused principally by migration, leaching and surface runoff, emphasizing the necessity for quick remediation to prevent the further spread of pollutants. This herbicide presents a serious threat to the local ecosystem because of its easy migration to ground and surface water. Additionally, during spring season there is an excess of atrazine concentration above the maximum contaminant level (MCL) due to leaching of atrazine from agricultural sources. Atrazine,

furthermore, is characterized by a relatively high solubility in water ($1,61 \cdot 10^{-4} \text{ M}$) and like all POPs persists in the environment for long period of time (Hua *et al.*, 2006). Atrazine is rather resistant to conventional wastewater treatment methods such as biological and chemical treatment methods (Camel and Bernard, 1998). Chemical methods such as recently pronounced Advanced Oxidation Processes (AOPs) seem to be more promising. AOPs are a class of processes, where highly oxidizing species, very reactive free radicals, especially hydroxyl radicals ($\bullet\text{OH}$) are primarily produced and have the ability to oxidize and mineralize almost any of the organic molecules in wastewater. Production of free radicals is achieved by the combination of processes; ozone, hydrogen peroxide, Fenton, UV irradiation and other. These species effectively degrade a range of organic pollutants, including chlorinated organic compounds (Bauer, 1994; Ruppert *et al.*, 1994).

Hydroxyl radical is one of the most important oxidants due to its high reactivity and non-selectivity towards organic compounds.

One of typical AOP is based on the property of hydrogen peroxide to generate hydroxyl radicals by reacting with ferrous ions in the well-known Fenton's reaction, Eqs. (1) and (2), (Tarr, 2003):



The influence of the operating conditions on the oxidation performances, in terms of pollutant degradation, were assessed by many authors, namely, the optimal pH value was found to be between 2 and 3 (Ruppert *et al.*, 1994), whereas the optimal ratio between hydrogen peroxide and iron sulfate was observed to depend upon different parameters.

AOPs may also be used for purification of water containing atrazine (Bianchi *et al.*, 2006; Meunier *et al.*, 2006).

In order to maintain quality of river's water

and corresponding recipients, seas and oceans, wastewaters loaded with atrazine are usually treated with activated carbon filters before releasing from industrial outlets. Adsorption behavior of atrazine has been already very well examined by studying of the adsorption on granular activated carbon (GAC) and powdered activated carbon (PAC) (Pelekani and Snoeyink, 1999; Jia *et al.*, 2006). Although PAC and GAC exhibit a high adsorption capacity towards pure solutes, the presence of background organics in natural water was found to decrease the removal of specific micropollutants (Miltner *et al.*, 1989). Concerning that knowledge, there is a great challenge in finding new solids selective enough for depollution. There have been some reports concerning the adsorption of atrazine on soils, mostly inorganic soil components, such as silica gel, γ -alumina and calcite (CaCO_3) that showed preferable adsorption of atrazine onto silica gel than to other adsorbents. The process is considered as reversible (Kovaioš *et al.*, 2006). The limited information about adsorption and retention of atrazine onto solid particles such as zeolites is available in the literature. The enhanced atrazine adsorption on more hydrophobic solids, such as ZMS-5 type zeolite and organoclays, but weak affinity towards hydrophilic solids e.g. zeolites Y was reported (Bottero *et al.*, 1994).

This study presents research attempt of combining AOPs with adsorption for the degradation of atrazine in aqueous systems. Zeolite FeZSM-5 was used as a source of ferric and ferrous ions needed in the Fenton's reactions, as well. In this study efficiency of Fenton process, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, photo assisted Fenton process $\text{UV}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$, Fenton-like and photo assisted Fenton-like processes, $(\text{UV})/\text{Fe}^{3+}/\text{H}_2\text{O}_2$, $(\text{UV})/\text{FeZSM-5}/\text{H}_2\text{O}_2$, was compared. The efficiency of the processes was determined based on two criteria; (i) degradation of atrazine in a model solution, (ii) reduction in total organic carbon. The effect of the dosage of FeZSM-5 zeolite, which was used as the source of iron catalyst and/or adsorbent in

Fenton type processes, on the atrazine removal extent was also studied and optimized.

Experimental

Materials and methods

Chemicals used in this work were supplied by Kemika, Zagreb, Croatia (ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), hydrogen peroxide (30 % w/w) and methanol), Herbos Ltd., Sisak, Croatia (atrazine (figura 1)), Alkaloid, Skopje, Macedonia (ferric sulphate [$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$]), Sigma-

Aldrich (acetonitrile), Zeolyst International, USA (all zeolites used). Zeolite CuZSM-5 was prepared following the procedure described by Tomašić *et al.* (1998). Zeolite FeZSM-5 was prepared by solid phase ionic exchange from ferrous sulphate [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$] and $\text{NH}_4\text{ZSM-5}$ (Rauscher *et al.*, 1999). It need to be point out that the corresponding concentration of ferric ions in 0,5 g L⁻¹ of zeolite is $0,332 \cdot 10^{-3} \text{ mol L}^{-1}$. Atrazine was analyzed by High Performance Liquid Chromatographer HPLC (Shimadzu), C-18 SUPELCO column, length 250 mm, internal diameter 4,6 mm and UV detection at

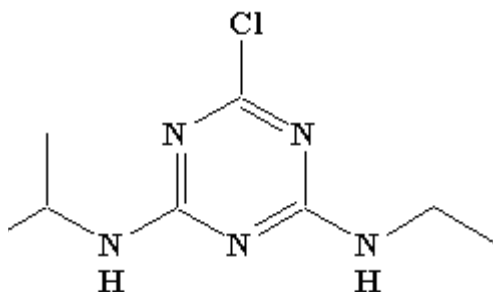


Fig. 1 Structure of atrazine.

Table 1. Results of atrazine adsorption on different zeolites at $23 \pm 1^\circ\text{C}$ after 2 hours treatment

zeolite (0.5 g L ⁻¹)	percentage of atrazine removal (%)
HZSM-5	5.1
$\text{NH}_4\text{ZSM-5}$	39.2
CuZSM-5	54.3
FeZSM-5	45.5
HY	44.9

222 nm. The mobile phase composition was acetonitrile/water (60/40). The flow rate was 0,8 mL/min.

The mineralization extent was determined on the basis of total organic carbon (TOC) content measurements, performed by using TOC analyzer; TOC-VCPN 5 000 A, Shimadzu. The pH values were measured by handy lab pH/LF portable pH/

conductivity meter, Schott Instruments GmbH, Mainz, Germany. The concentration of iron ions in the bulk during the treatment by applied processes were monitored by colorimetric methods using the UV/VIS spectrophotometer, Lambda EZ 201, Perkin Elmer, USA. Ferrous ions were identified by the reaction of Fe^{2+} with 1,10-phenantroline giving orange-red complex ($\epsilon_{\text{max}} =$

510 nm), while ferric ions were determined by the reaction of Fe^{3+} with thiocyanate forming a red-colored complex ($\lambda_{\text{max}} = 480 \text{ nm}$) under acidic conditions (APHA, 1998).

Experiments were performed using two different model wastewaters with initial atrazine concentration of 1 mg L^{-1} . Atrazine stock solution (A) was prepared by dissolving of 10 mg of atrazine in 10 mL of methanol which was followed by dilution with distilled water in 1 L flask. Further, this standard atrazine solution ($= 10 \text{ mg L}^{-1}$) was used for the preparation of 1 mg L^{-1} atrazine solution samples. Another stock solution (B) was prepared by dissolving of 10 mg of atrazine in 1 L of distilled water in 1 L flask by continuous stirring during three days period. This standard atrazine solution ($= 10 \text{ mg L}^{-1}$) was used for the preparation of 1 mg L^{-1} atrazine solution samples, too.

The initial pH of the studied system was adjusted at 3 using sulphuric acid ($c = 4 \text{ mol L}^{-1}$), after addition of zeolite and hydrogen peroxide. The iron ions/hydrogen peroxide ratio was adjusted to 1:50.

Adsorption experiments

Batch experiments of atrazine adsorption on FeZSM-5 zeolite were carried out with continuous magnetic stirring (600 rpm) of 100 mL of model solution with added adsorbent (jar tests). Adsorbent dosage in amount of 0,05g (otherwise indicated) was carefully weighted. Experiments with UV irradiation were performed in batch photo reactor (Subsection 2,3), the volume of reaction mixture was 0,5 L and corresponding added zeolite dosage was five times higher (0,25g).

The adsorption isotherms were determined by performed batch experiments by varying amounts of adsorbent in range 0,02-0,15 g. Batch experiment of atrazine adsorption was performed during 2 hours which was sufficient for achieving the adsorption equilibrium. Other experiments where zeolite was introduced not only as adsorbent but also as the source of iron ions for Fenton's reaction have been carried out for half an hour.

In order to examine adsorption kinetics, samples were taken at chosen time intervals during the batch experiment of atrazine adsorption.

All experiments were conducted at $23 \pm 1 \text{ }^{\circ}\text{C}$, under ambient light. The pH value was adjusted at $3,0 \pm 0,1$. After taking samples, the suspensions were centrifuged at 3 000 rpm for 5 min. After centrifuging, the atrazine concentration of the supernatant was measured using a HPLC and TOC analysis. After the time needed for the attainment of equilibrium, percentage of atrazine removal from model wastewater was calculated.

All experiments were repeated at least once to give reproducibility of the experiments within 5 %, and average results were reported.

Batch photo reactor

Batch photo reactor is consisted of the water-jacketed glass chamber with the total volume of 0,8 L (figura 2). A quartz tube was placed vertically in the middle of the photo reactor with mercury lamp of 125 W (UV-C, 254 nm) located inside of the tube (UVP-Ultra Violet Products, Cambridge, UK). All experiments were performed with constant magnetic stirring, at room temperature.

Results and discussion

Zeolite selection

In this study adsorption properties of the following zeolites were studied: HZSM-5, $\text{NH}_4\text{ZSM-5}$, CuZSM-5, FeZSM-5 and HY. The results for the removal of atrazine (model solution A) by adsorption with different synthetic zeolites are shown in table 1. It can be seen that the highest percentage of atrazine removal was achieved with zeolites FeZSM-5 and HY after 2 hours of contact with solid particles, whereas 45,5 % and 44,9 % of atrazine was adsorbed. Despite of the almost the same result obtained with those two zeolites, FeZSM-5 was chosen for the application in further experiments. It can be explained by the fact that FeZSM-5 zeolite is a potential catalyst in Fenton processes since it has iron in its structure. This approach has an advantage due to the fact that introduced solid particle is an adsorbent and a catalyst at the same time.

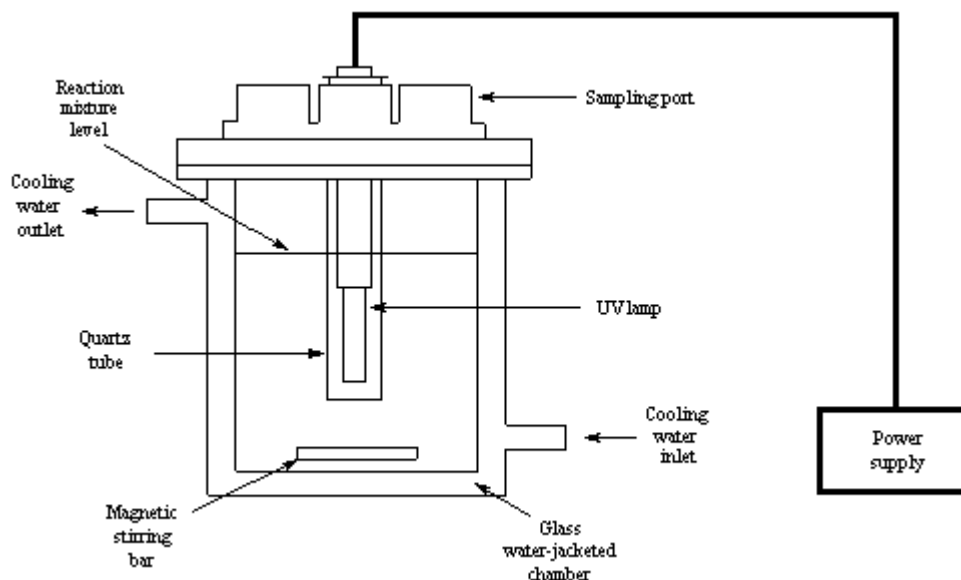


Fig. 2 Batch photo reactor.

Results for atrazine removal extent with copper exchanged zeolite ZSM-5, which was also applied, can be considered as negligible because percentage of removal is directed to copper-atrazine complexation and not adsorption onto zeolite. It has been found in the literature that atrazine and copper form the complexes (Dedock *et al.*, 1985; Grabec *et al.*, 1994).

Adsorption isotherms

The adsorption of atrazine on FeZSM-5 zeolite is shown in figura 3. It can be seen that the presence of methanol enhances atrazine adsorption onto zeolite. Namely, higher percentage of atrazine was adsorbed from model solution A. The adsorption data for model solution A were correlated using the Langmuir and Freundlich isotherms. The Langmuir isotherm is mainly applied to monolayer adsorption while the Freundlich isotherm is widely employed for sorption surfaces with non-uniform energy distribution. In the present investigation, the experimental data were tested with respect to both these isotherms. Langmuir isotherm is expressed as:

$$\frac{1}{q} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (3)$$

where q is the amount of solute (mg) adsorbed per the amount of adsorbent (g) and C_e is the equilibrium concentration of solute in the bulk solution. The constants b ($L \text{ mg}^{-1}$) and Q_0 (mg g^{-1}) are characteristics of the Langmuir equation and they can be evaluated from the linear form represented by previously stated Eq.(3).

A plot of $1/q$ against $1/C_e$ would give a straight line with a slope of $1/Q_0$ and an intercept of $1/bQ_0$.

The Freundlich equation is given as:

$$q = K_f C_e^{1/n} \quad (4)$$

where K_f and n are constants. The linear form of the equation can be expressed as:

$$\log q = \log K_f + n \log C_e \quad (5)$$

Hence, the constants K_f ($\text{mg g}^{-1} (\text{L mg}^{-1})^n$) and n which relate to adsorption capacity and sorption

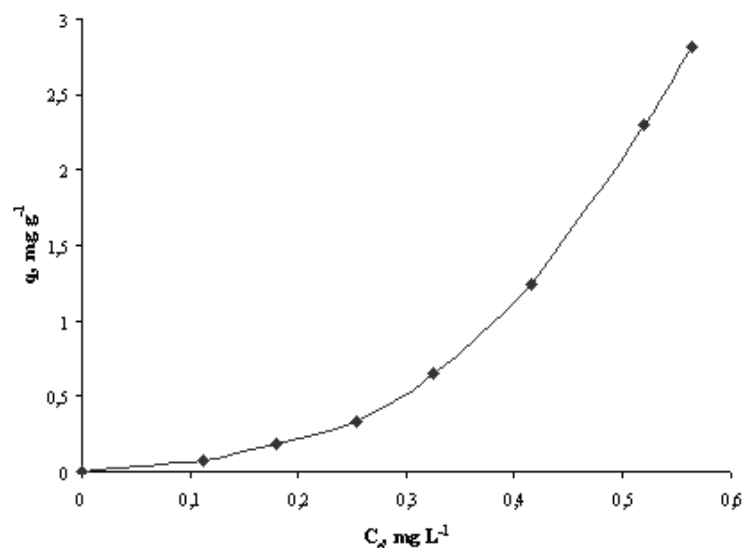


Fig. 3 Adsorption isotherm of atrazine on FeZSM-5 zeolite at 23 ± 1 °C.

intensity of the adsorbent can then be evaluated from the intercept and slope of $\log q$ against $\log C_e$ plot.

The Freundlich and Langmuir isotherms were plotted and shown in figuras 4a,b. Equilibrium data for the two isotherm models are presented in Table 2. However, the linear regression correlation coefficient values show that data were better represented by the Freundlich isotherm model.

Treatment of model wastewaters by Fenton and Fenton-like processes, with and without UV irradiation

The comparison of applied AOPs for atrazine degradation was presented with the Figuras 5a and b. It can be seen that with almost all of the studied AOPs the complete atrazine removal was achieved after 30 minutes with significant 13.

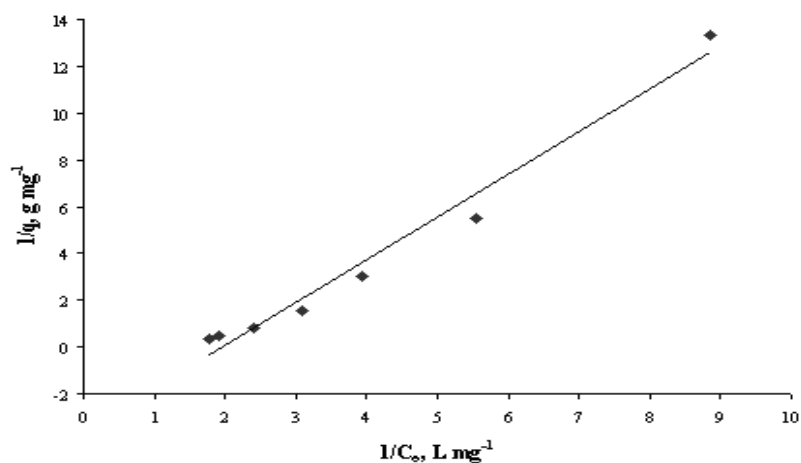


Fig. 4a Langmuir plot for atrazine adsorption on FeZSM-5 zeolite at 23 ± 1 °C.

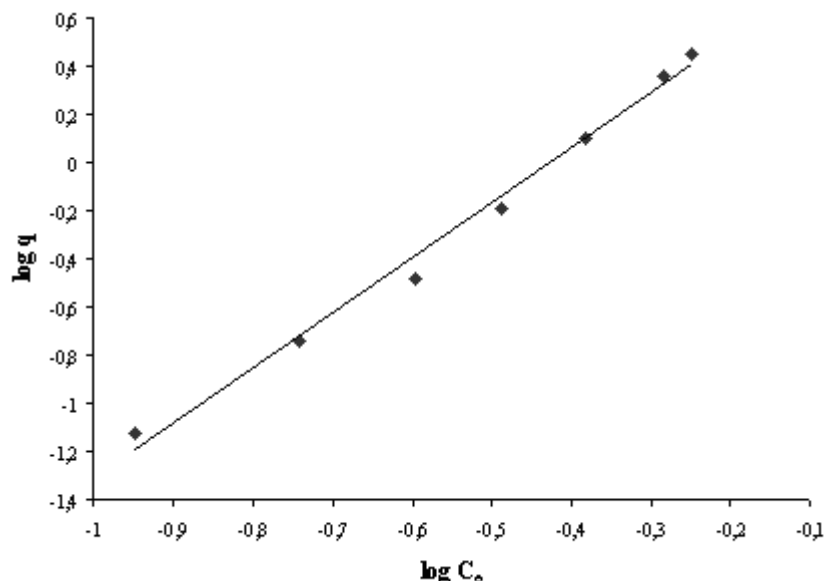


Fig. 4b Freundlich plot for atrazine adsorption on FeZSM-5 zeolite at $23 \pm 1^\circ\text{C}$.

Table 2. Langmuir and Freundlich constants for the adsorption of atrazine on FeZSM-5 zeolite at $23 \pm 1^\circ\text{C}$ under ambient light

equilibrium concentration of atrazine, C_e (mg L^{-1}) for model solution	Langmuir constants		Freundlich constants	
	b (L mg^{-1})	Q_0 (mg g^{-1})	K_F ($\text{mg g}^{-1} (\text{L mg}^{-1})^n$)	n
0.325	1.974	0.277	9.45	2.29



Atrazine is not resistant to self photolysis by UV-C light and it can be seen that the higher percentage of atrazine removal is achieved with photo assisted processes, even after 10 minutes of treatment (figura 5a). Furthermore, higher methanol degradation extent was achieved by introducing UV irradiation into the system (figura 6). This can be ascribed to the formation of additional hydroxyl radicals, Eq. (7).



The high concentration of hydrogen peroxide that was necessary for adjusting the

iron/peroxideratio at 1:50 is available for this photo catalytic degradation of compounds, atrazine and methanol.

Regarding model solution B (figura 5b), only Fenton-like process, where zeolite was used as the source of ferric ions, FeZSM-5/ H_2O_2 resulted in lower degradation extent. There are two reasons for this exception. First, methanol is considered to enhance the atrazine adsorption (Bottero *et al.*, 1994), but in solution B there is no presence of methanol, and whole adsorption process is slower and less efficient than in model solution A. Second, ferrous and ferric sulfate are more effective Fenton reagents than applied Fe-exchanged zeolite.

As in case of solution A, Fenton and Fenton-like processes were enhanced by introducing the UV irradiation. Regardless the fact that FeZSM-5 is

not common used as the source of iron ions in Fenton processes, its application is supported by the data showing very few residual iron in the bulk

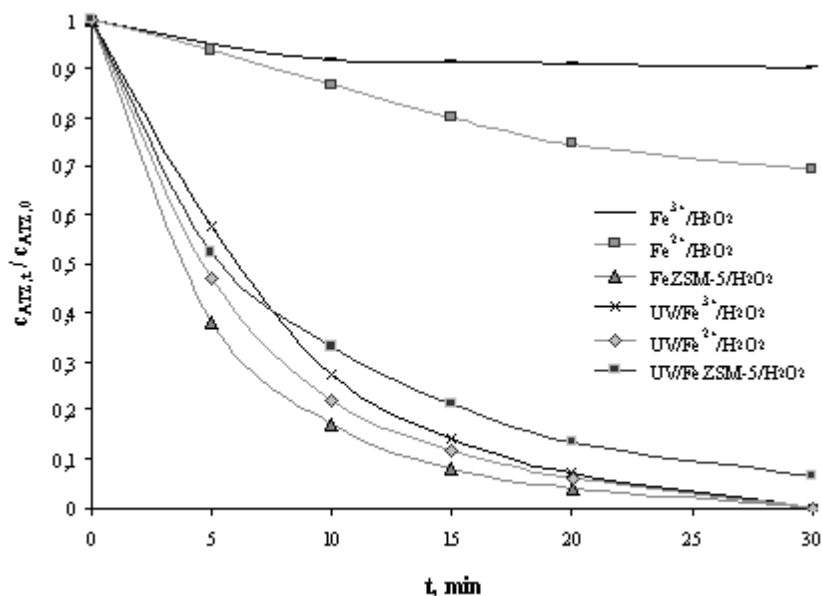


Fig. 5a The efficiency of applied processes for atrazine degradation in model solution A.

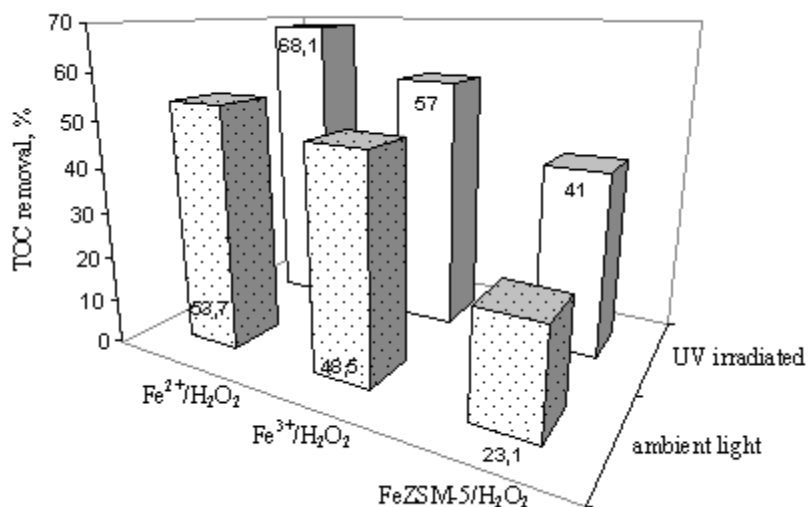


Fig. 6 Comparison of mineralization extents obtained by applied processes.

after treatment. Namely, only a small amount of ferric ions, 3-5 %, is transferred in aqueous solution when zeolite is dispersed in it (figura 7) and remained the same during the treatment. This has been determined by monitoring the concentration of iron ions with adequate colorimetric methods described in Subsection 2,1.

Treatment of atrazine wastewaters by the UV/FeZSM-5/H₂O₂ process can be divided in several 'steps'. It can be seen that iron exchanged zeolite played predominant role during the atrazine removal (Subsections 3,1 and 3,2). One part of atrazine is adsorbed onto the zeolite surface and consequently degraded with hydroxyl radicals

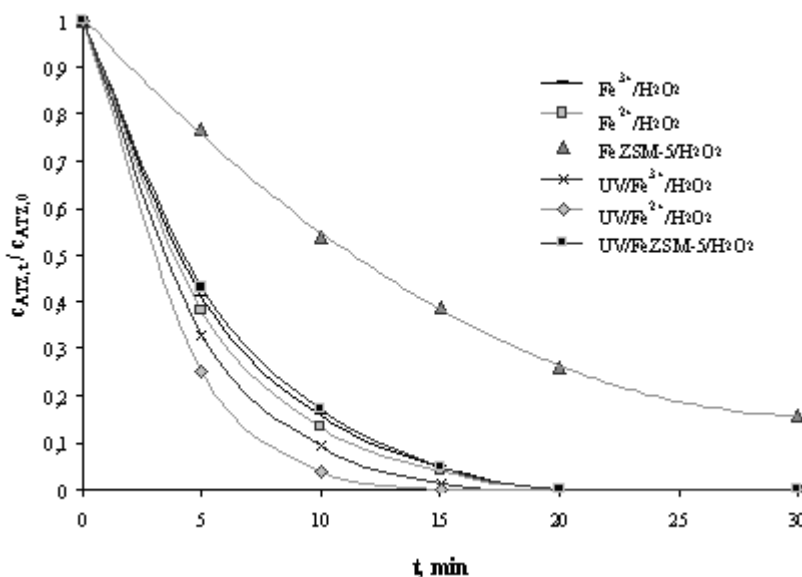
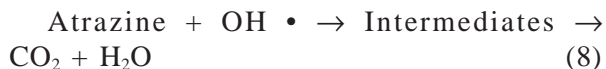


Fig. 5b The efficiency of applied processes for atrazine degradation in model solution B.

and the other part of atrazine will be degraded in the bulk (Chen *et al.*, 2008). Atrazine degradation is presented with Eq. (8).



Hydroxyl radicals are constantly generated due to reactions of Fenton cycle, Eqs. (1) and (2), or due to photolysis of hydrogen peroxide, Eq.(7).Methanol is well-known as a "scavenger" for hydroxyl radicals and if presented in wastewater, a large amount of hydroxyl radicals would also be consumed for methanol degradation (Aguiar and Ferraz, 2007). Despite the fact that methanol presence would 'disturb' the atrazine degradation with hydroxyl radicals, it could be favorable due to enhanced atrazine adsorption

and consequent reaction with radicals on the surface, where impacts of these species are easier to be achieved (Chen *et al.*, 2008).

Conclusions

In the frame of this work, atrazine removal from simple aqueous solution and combined solution with methanol was investigated. Atrazine adsorption from model wastewater onto solid particles, zeolites, HZSM-5, NH₄ZSM-5, CuZSM-5, FeZSM-5 and HY has been studies, as well as Fenton type advanced oxidation processes.

FeZSM-5 zeolite was shown as the most efficient adsorbent. Namely, 45,5 % of atrazine was removed after 2 hours of contact with solid particles from model wastewater using 0,5 g L⁻¹ of

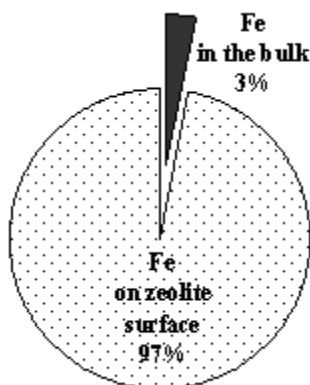


Fig. 7 Approximate percentage of iron ions transferred from zeolite surface to the bulk at initial stage of applied processes

FeZSM-5. Atrazine adsorption was described with Freundlich and Langmuir isotherms therefore implying on physical adsorption mechanism and chemisorption, as well.

Applied AOPs, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, FeZSM-5/ H_2O_2 , UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, UV/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, UV/FeZSM-5/ H_2O_2 , have given egegreous atrazine removal from aqueous solution after half an hour. It was found that the best efficiency of atrazine degradation of 88,3 % was achieved after only 5 minutes using UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ process with addition of $0,5 \text{ g L}^{-1}$ of FeZSM-5 and iron/peroxide ratio adjusted at 1:50.

In combined solution where methanol is in presence, all applied processes resulted in significant mineralization extent, i.e. TOC value was decreased from 23,1 up to 68,1 % which fits methanol degradation. Some of the applied processes; FeZSM-5/ H_2O_2 , UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, UV/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, UV/FeZSM-5/ H_2O_2 , have given sufficient atrazine removal after half an hour. The best efficiency of atrazine degradation of 82,1 % was achieved after only 10 minutes using FeZSM-5/ H_2O_2 process with addition of $0,5 \text{ g L}^{-1}$ of FeZSM-5 and iron/peroxide ratio adjusted at 1:50. This achievement is result not only of oxidative degradation of atrazine in the bulk, but also the result of oxidative degradation on the surface after the adsorption of atrazine.

Acknowledgements

We would like to acknowledge for the financial support from the Ministry of Science, Education and Sport, Project #125-1253092-1981 and HERBOS Ltd., Sisak, Croatia, for supplying atrazine.

Bibliography

- Aguiar A. and Ferraz A. *Fe^{3+} - and Cu^{2+} -reduction by phenol derivatives associated with Azure B degradation in Fenton-like reactions*, Chemosphere, 66:947-954. (2007)
- APHA *Standard methods for the Examination of Water and Wastewater treatment*, 20th edition American Public Health Association, USA. (1998)
- Bauer R. *Applicability of solar irradiation for photochemical wastewater treatment*, Chemosphere, 29:1225-1233. (1994)
- Bianchi C.L.; Pirola C.; Ragaini V. and Selli E. *Mechanism and efficiency of atrazine degradation under combined oxidation processes*, Applied Catalysis B: Environmental, 64:131-138. (2006)
- Bottero J.Y.; Khatib K.; Thomas F.; Jucker K. Bersillon J.L. and Mallevialle J. , *Adsorption of atrazine onto zeolites and organoclays, in the presence of background organics*, Water Research, 28:483-490. (1994)
- Camel V. and Bernard A. , *The use of ozone and associated oxidation processes in drinking water treatment*, Water Research, 32:3208-3222. (1998).

-
- Chen, A.; Ma, X. and Sun, H., *Decolorization of KN-R catalyzed by Fe-containing Y and ZSM-5 zeolites*, Journal of Hazardous Materials, 156:568-575. (2008)
- Dedock P.; Dubois B. and Lerivrey J., *Cu(II) binding by substituted 1,3,5-triazine herbicides*, Inorganica Chimica Acta, 107:63-66. (1985)
- Grabec I.; Ogorevc B. and Hudnik V. *A polarographic investigation on interactions between Cu(II) ions and natural degradation products of herbicide atrazine*, Electroanalysis, 6:908-913. (1994)
- Hua W.; Bennett E.R. and Letcher R.J. *Ozone treatment and depletion of detectable pharmaceuticals and atrazine herbicide in drinking water sourced from the upper Detroit River, Ontario, Canada*, Water Research, 40:2259-2266. (2006)
- Jia Y.; Wang R. and Fane A.G. *Atrazine adsorption from aqueous solution using powdered activated carbon - Improved mass transfer by air bubbling agitation*, Chemical Engineering Journal, 116:53-59. (2006),
- Kovaios I.D.; Paraskeva C.A. and Payatakes A.Ch. *Adsorption of atrazine on soils: Model study*, Journal of Colloid and Interface Science, 299:88-94. (2006)
- Meunier L.; Canonica S. and von Gunter U. *Implications of sequential use of UV and ozone for drinking water quality*, Water Research, 40:1864-1876. (2006)
- Miltner R.J.; Baker D.B.; Speth T.F. and Fronk C.A. *Treatment of seasonal pesticides in surface waters*, Journal - American Water Works Association, 81:43-52. (1989)
- Pelekani C. and Snoeyink V.L. *Competitive adsorption in natural water: Role of activated carbon pore size*, Water Research, 33:1209-1219. (1999)
- Rauscher M.; Kesore K.; Mönning R.; Schwieger W.; Tissler A. and Turek T. *Preparation of a highly reactive Fe-ZSM-5 catalyst through solid-state ion exchange for the catalytic decomposition of N₂O*, Applied Catalysis A: General, 184:249-256. (1999)
- Ruppert G.; Bauer R. and Heisler G. *UV-O₃, UV-H₂O₂, UV-TiO₂ and the photo-fenton reaction-comparison of advanced oxidation processes for wastewater treatment*, Chemosphere, 28:1447-1454. (1994)
- Silva E.; Fialho .M.; Sa-Correja I.; Burns R.G. and Show L.J. *Combined bioaugmentation and biostimulation to cleanup soil contaminated with high concentrations of atrazine*, Environmental Science and Technology, 38:632-637. (2004)
- Tarr, M.A. *Fenton and modified Fenton methods for pollutant degradation*, Chemical Degradation Methods for Wastes and Pollutants, Environmental and Industrial Applications, Marcel Dekker, Inc. New York, USA, p.165-200. (2003)
- Tomašić V.; Gomzi Z. and Zrnčević S. *Catalytic reduction of NO_x over Cu/ZSM-5 catalyst*, Applied Catalysis B: Environmental, 18:233-240. (1998).