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THEME

**Photodegradation of organic contaminants by photolysis
and H₂O₂/UV processes: QSPR and kinetic modeling**

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Abstract

Organic contaminants are an emerging concern in environmental sciences. The use of ultraviolet-initiated advanced oxidation processes (AOPs) is becoming an attractive alternative for the degradation of harmful organic contaminants that are not easily removed using conventional water treatment processes. Although several UV-initiated AOPs are available, the focus of the research undertaken in this thesis is the hydrogen peroxide-ultraviolet irradiation ($\text{H}_2\text{O}_2/\text{UV}$) process, in addition to direct photolysis.

The main goal of this thesis is to develop kinetic models for the prediction of organic contaminants degradation and to elucidate the relevance of the computational predictive models that can be used to fill the lack of knowledge on photochemical properties for environmental issues.

Quantitative structure property relationship (QSPR) models were used to predict the photochemical properties of organic compounds from their structures. These modeling techniques make use of existing experimental data to predict unknown chemical properties. The conceptual basis of QSPR models is that similar structures are expected to exhibit similar chemical properties.

In this thesis computer simulations of combined QSPR and kinetic models were carried out to investigate the various photochemical parameters and the removal potential of organic contaminants.

First a kinetic model, which predicts organic contaminants degradation by low-pressure UV irradiation in aqueous media, was developed and verified based on experimental results obtained from the literature. Pollutants with different chemical natures and belonging to various organic contaminant classes, including pharmaceuticals, pesticides and disinfection by-products were selected as model compounds. The specific objective was to assess the predictive ability of the kinetic model with different organic contaminants and under various process and experimental conditions. The combined approach QSPR / kinetic modeling was then used to predict the photodegradation of commercially unavailable halogenated disinfection by-products.

Second a dynamic chemical kinetic model was developed to predict DBCP and Alachlor photodegradation by $\text{H}_2\text{O}_2/\text{UV}$ process in aqueous media in a completely mixed batch reactor under various process and experimental conditions. The validated kinetic model was then combined with QSPR model to predict the photodegradation of p-Cresol by $\text{H}_2\text{O}_2/\text{UV}$ process in aqueous media considering the formation and fate of its intermediate compounds. The validation of the combined approach was conducted by testing the prediction of the p-Cresol degradation under different initial concentrations of p-Cresol and H_2O_2 .

In this thesis, the stiff differential equations that describe the organic contaminants photodegradation were implemented and solved within the Matlab environment. QSPR models were constructed with QSARINS software by multiple linear regression and genetic algorithm analysis with the use of Dragon generated molecular descriptors and quantum descriptors performed with Gaussian software on the basis of density functional theory method.

Keywords: organic contaminants, direct photolysis process, $\text{H}_2\text{O}_2/\text{UV}$ process, kinetic modeling, QSPR modeling.

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ملخص

تعتبر الملوثات العضوية مصدر قلق متزايد في العلوم البيئية. أصبح استخدام عمليات الأكسدة المتقدمة التي تبدأ بالأشعة فوق البنفسجية و المتعارف عليها اختصاراً بـ (AOPs) بديلاً مستقطباً للقضاء على الملوثات العضوية الضارة التي لا يمكن إزالتها بسهولة باستخدام عمليات معالجة المياه بالطرق التقليدية. على الرغم من توفر العديد من عمليات الأكسدة المتقدمة و التي تبدأ بالأشعة فوق البنفسجية ، إلا أن تركيز البحث الذي تم إجراؤه في هذه الأطروحة هو عملية التشيع فوق البنفسجي بيروكسيد الهيدروجين (H2O2 / UV) ، بالإضافة إلى التحلل الضوئي المباشر.

الهدف الرئيسي من هذه الأطروحة هو تطوير نماذج حركية للتنبؤ لازالة الملوثات العضوية وتوضيح أهمية النماذج التنبؤية الحسابية التي يمكن استخدامها. لإثراء البحوث حول الخصائص الكيميائية الضوئية للقضايا البيئية.

تم استخدام نماذج علاقة خصائص البنية الكمية (QSPR) للتنبؤ بالخصائص الكيميائية الضوئية للمركبات العضوية من هياكلها. تستفيد تقنيات النمذجة هذه من البيانات التجريبية الحالية للتنبؤ بخصائص كيميائية غير معروفة. الأساس المفاهيمي لنماذج QSPR هو أنه من المتوقع أن تظهر الهياكل المماثلة خصائص كيميائية مماثلة.

في هذا البحث، تم إجراء محاكاة حاسوبية لنماذج QSPR مجتمعة ونماذج حركية للتحقيق في المتغيرات الكيميائية الضوئية المختلفة وإمكانية إزالة الملوثات العضوية.

أولاً ، تم تطوير النموذج الحركي ، الذي يتنبأ بالقضاء على الملوثات العضوية عن طريق الإشعاع المنخفض الضغط فوق البنفسجي، في الوسط المائي ، والتحقق منه بناءً على النتائج التجريبية التي تم الحصول عليها من الأدبيات المختلفة. تم اختيار الملوثات ذات الخصائص الكيميائية المختلفة والتي تنتمي إلى فئات مختلفة من الملوثات العضوية، بما في ذلك المستحضرات الصيدلانية والمبيدات والمنتجات الثانوية للتطهير، كمركبات نموذجية. كان الهدف المحدد هو تقييم القدرة التنبؤية للنموذج الحركي مع ملوثات عضوية مختلفة وتحت ظروف عملية وتجريبية مختلفة. ثم تم استخدام النهج المشترك / QSPR النمذجة الحركية للتنبؤ بالتحلل الضوئي للمنتجات الثانوية للتطهير المهلجنة غير المتوفرة تجارياً.

ثانياً ، تم تطوير نموذج حركي كيميائي ديناميكي للتنبؤ بالتحلل الضوئي DBCP و Alachlor بواسطة عملية H2O2 / UV في وسط مائي في مفاعل دفعي مختلط تماماً في ظل ظروف عملية وتجريبية مختلفة. تم بعد ذلك دمج النموذج الحركي المعتمد مع نموذج QSPR للتنبؤ بالتحلل الضوئي لـ p-Cresol بواسطة عملية H2O2 / UV في الوسط المائي مع الأخذ في الاعتبار تكوين ومصير مركباته الوسيطة. تم إجراء التحقق من صحة النهج المشترك عن طريق اختبار التنبؤ بتدهور p-Cresol تحت تركيزات أولية مختلفة من p-Cresol و H2O2 .

في هذا البحث، تم تنفيذ المعادلات التفاضلية القاسية التي تصف التحلل الضوئي للملوثات العضوية وحلها في بيئة MATLAB. تم إنشاء نماذج QSPR باستخدام برنامج QSARINS من خلال الانحدار الخطي المتعدد وتحليل الخوارزمية الجينية باستخدام واصفات جزئية من Dragon ووصفات كمومية يتم إجراؤها باستخدام برنامج Gaussian على أساس طريقة نظرية الكثافة الوظيفية.

الكلمات المفتاحية: الملوثات العضوية ، عملية التحلل الضوئي المباشر ، عملية H2O2 / UV ، النمذجة الحركية ،

نمذجة QSPR.

Résumé

Le devenir des contaminants organiques émergents est une préoccupation en sciences de l'environnement. L'utilisation de procédés d'oxydation avancés (POA) initiés par les radiations ultraviolettes est devenue une alternative intéressante pour la dégradation des contaminants organiques nocifs qui ne sont pas facilement éliminés à l'aide des procédés conventionnels de traitement de l'eau. Bien que plusieurs POA initiés par UV existent, dans cette thèse, le procédé utilisé est l'association du peroxyde d'hydrogène et la lumière ultraviolette (H_2O_2 / UV), en plus de la photolyse directe.

L'objectif principal de cette thèse est de développer des modèles cinétiques pour la prédiction de la dégradation des contaminants organiques et d'élucider la pertinence des modèles de calcul prédictifs pouvant être utilisés pour combler le manque de connaissances sur les propriétés photochimiques au profit des solutions environnementales.

Des modèles de relations quantitatives de structures et de propriétés (QSPR) ont été utilisés pour prédire les propriétés photochimiques des composés organiques à partir de leurs structures. Ces techniques de modélisation utilisent des données expérimentales existantes pour prédire des propriétés chimiques inconnues. Le concept de base des modèles QSPR est que des structures similaires devraient présenter des propriétés chimiques similaires.

Dans cette thèse, des simulations numériques par des modèles QSPR et cinétiques combinés ont été réalisées pour étudier les divers paramètres photochimiques et le potentiel d'élimination des contaminants organiques.

Tout d'abord, un modèle cinétique, qui prédit la dégradation des contaminants organiques par irradiation UV à basse pression en milieu aqueux, a été développé et validé par des résultats expérimentaux issus de la littérature. Des polluants appartenant à diverses classes de contaminants organiques, à savoir les produits pharmaceutiques, les pesticides et les sous-produits de désinfection, ont été sélectionnés comme composés modèles. L'objectif spécifique était d'évaluer la pertinence du modèle cinétique à prédire la dégradation de contaminants organiques pour différents processus et conditions expérimentales. L'approche combinée QSPR / modélisation cinétique a ensuite été utilisée pour prédire la photodégradation de sous-produits de désinfection halogénés non disponibles dans le commerce.

Deuxièmement, un modèle dynamique de la cinétique chimique a été développé pour prédire la photodégradation du DBCP et de l'Alachlore par le procédé H_2O_2 / UV en milieu aqueux, dans un réacteur batch parfaitement agité pour divers processus et conditions expérimentales. Le modèle cinétique validé a ensuite été combiné avec le modèle QSPR pour prédire la photodégradation du p-crésol par le procédé H_2O_2 / UV en milieu aqueux compte tenu de la formation et du devenir de composés intermédiaires issus de la photodégradation du p-crésol. La validation de l'approche combinée a été menée en testant la prédiction de la dégradation du p-crésol sous différentes concentrations initiales du p-crésol et de H_2O_2 .

Dans cette thèse, les équations différentielles aux dérivées partielles qui décrivent la photodégradation des contaminants organiques ont été résolues en utilisant le logiciel Matlab. Les modèles QSPR ont été construits avec le logiciel QSARINS par régression linéaire multiple et analyse d'algorithmes génétiques avec l'utilisation de descripteurs moléculaires générés par Dragon et de descripteurs quantiques obtenus par le logiciel Gaussien basé sur la méthode de la théorie de la densité fonctionnelle.

Mots clés: contaminants organiques, procédé de photolyse directe, procédé H_2O_2 /UV, modélisation cinétique, modélisation QSPR.

Abstract

Organic contaminants are an emerging concern in environmental sciences. The use of ultraviolet-initiated advanced oxidation processes (AOPs) is becoming an attractive alternative for the degradation of harmful organic contaminants that are not easily removed using conventional water treatment processes. Although several UV-initiated AOPs are available, the focus of the research undertaken in this thesis is the hydrogen peroxide-ultraviolet irradiation ($\text{H}_2\text{O}_2/\text{UV}$) process, in addition to direct photolysis.

The main goal of this thesis is to develop kinetic models for the prediction of organic contaminants degradation and to elucidate the relevance of the computational predictive models that can be used to fill the lack of knowledge on photochemical properties for environmental issues.

Quantitative structure property relationship (QSPR) models were used to predict the photochemical properties of organic compounds from their structures. These modeling techniques make use of existing experimental data to predict unknown chemical properties. The conceptual basis of QSPR models is that similar structures are expected to exhibit similar chemical properties.

In this thesis computer simulations of combined QSPR and kinetic models were carried out to investigate the various photochemical parameters and the removal potential of organic contaminants.

First a kinetic model, which predicts organic contaminants degradation by low-pressure UV irradiation in aqueous media, was developed and verified based on experimental results obtained from the literature. Pollutants with different chemical natures and belonging to various organic contaminant classes, including pharmaceuticals, pesticides and disinfection by-products were selected as model compounds. The specific objective was to assess the predictive ability of the kinetic model with different organic contaminants and under various process and experimental conditions. The combined approach QSPR / kinetic modeling was then used to predict the photodegradation of commercially unavailable halogenated disinfection by-products.

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In this thesis, the stiff differential equations that describe the organic contaminants photodegradation were implemented and solved within the Matlab environment. QSPR models were constructed with QSARINS software by multiple linear regression and genetic algorithm analysis with the use of Dragon generated molecular descriptors and quantum descriptors performed with Gaussian software on the basis of density functional theory method.

Keywords: organic contaminants, direct photolysis process, $\text{H}_2\text{O}_2/\text{UV}$ process, kinetic modeling, QSPR modeling.