

Declaration

I declare that the work embodied in this thesis has not previously been submitted, and is not currently being submitted, for any other degree than that of the degree of Doctor of philosophy of the Sudan University of science and Technology. All work reported herein is my own, except where acknowledged in the text.

_____ **(CANDIDATE)**

_____ **(SUPERVISORS)**

Dedication

I dedicate this work to the soul of My Father, To My Mother, To My Wife (Abeer), To My Children (Eiman, Abdalla, Raya, Deema, and Duha), To My Sisters (Yusra, Yusr, Myasar, and Muneera). To Mousab, Assem, Ahmed, Qutaeba, Jenan, Hannan, and Mahasen.

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ملخص

تم دراسة سرعة أكسدة الفينولات في المياه العادمة بواسطة مفاعلتها مع مركبات المعادن عديدة الأكاسيد لتنشيط بيروكسيد الهيدروجين. الفينولات التي تمت دراستها هي: فينول، بارا-كريسول، ميتا-كريسول، بارا-كلوروفينول، وبارا-نيتروفينول.

مركبات المعادن عديدة الأكاسيد التي تمت دراستها هي: HWP

Ph-HWP, HMoP و HMoV.

تم حساب السرعة وثابت السرعة لجميع هذه التفاعلات بتغيير تركيز كل من الفينول، بيروكسيد الهيدروجين ومركب المعدن، وتبين بأن ميتا-كريسول له أكثر ثابت سرعة وبارا-نيتروفينول له أقل ثابت سرعة. وقد تبين أيضاً بأن سرعة هذه التفاعلات تزداد بزيادة تركيز المتفاعلات وزيادة درجة الحرارة وتزداد قليلاً بزيادة القوة الأيونية.

تم استخدام معادلة هامت من أجل دراسة تأثير وجود مجموعات مانحة للإلكترونات (مجموعة ميثيل) ومجموعات كاسبة للإلكترونات (مجموعة كلورو، ومجموعة نايترو) على الفينول على سرعة هذه التفاعلات وتبين بأن المجموعات المانحة للإلكترونات تزيد من سرعة التفاعلات ولكن المجموعات الكاسبة للإلكترونات تقلل من سرعة هذه التفاعلات، وكذلك تم حساب ثابت التفاعل (ρ) لجميع التفاعلات باستخدام معادلة هامت.

تم استخدام معادلة إيرنج من أجل حساب حرارة التنشيط لهذه التفاعلات وتبين بان ال HWPA له اقل طاقة تنشيط (38.7 KJ/ mole) وأن HMoVPA له أكثر طاقة تنشيط (110.8 KJ/mole).

تم دراسة تأثير الأوكسجين (الهواء) على سرعة التفاعلات وتبين بأنه ليس له تأثير على سرعة هذه التفاعلات. تقل سرعة هذه التفاعلات بزيادة الحامضية وزيادة نسبة الاستيتونايترايل وكذلك بإضافة الإמידازول إلى هذه التفاعلات. الماء هو أفضل مذيب يستخدم لهذه التفاعلات. ال HWPA هو أفضل مركب معدن عديد الأكاسيد (عامل مساعد) لتحطيم الفينولات كاملاً في المياه العادمة.

تم استخدام جهاز غاز الكروماتوغرافيا وجهاز الأشعة تحت الحمراء من اجل تشخيص نواتج هذه التفاعلات والتي من الممكن أن تكون: غاز ثاني أوكسيد الكربون، ماء، وبعض الحوامض العضوية.

Abstract

The rate of oxidation of substituted phenols in wastewater was studied by reaction of phenols with polyoxometalate catalysts to activate H_2O_2 . The substituted phenols used in this study are, phenol, para-Cresol, meta-Cresol, para-Chlorophenol, and para-nitrophenol. The polyoxometalates used are, $H_3PW_{12}O_{40}$ (HWPAs), *ph*- $H_3PW_{12}O_{40}$ (ph-HWPA), $H_3PMo_{12}O_{40}$ (HMoPA), and $Na_5Mo_{10}V_2PO_{40}$ (HMoVPA).

The catalyzed rate and catalyzed rate constants were calculated for these catalytic reactions. meta-Cresol has the highest value of rate constant, while para-nitrophenol has the lowest value. The rate of these reactions increases with increasing the concentration of H_2O_2 , catalyst, and substituted phenol. Also, increase in temperature increases the rate of these reactions while increase in ionic strength increases them only slightly.

Hammett equation was used to study the effect of the presence of electron donating and withdrawing groups on phenol on the rate of these reactions. Electron donating groups (eg. $-CH_3$ group) on phenol increase the rate of these reactions, but electron withdrawing groups (NO_2 , and Cl groups) on phenol decrease the rate. Also, the reaction constant (ρ) was calculated for these reactions by using Hammett equation and it was observed to be negative value, which indicates that, the reaction follows free-radical mechanism.

Eyring equation was used to calculate the enthalpy of activation for these reactions. HWPAs has the lowest value of enthalpy of activation ($\Delta H^\ddagger=38.7$ kJ/mole), but HMoVPA has the highest value ($\Delta H^\ddagger=110.8$ kJ/mole). It means that, HWPAs is the most reactive catalyst, while HMoVPA is the lowest reactive among the catalysts studied.

The effect of oxygen (air) was studied. It was found that it has no effect on the rate of these reactions. The rate of these reactions decreases with increase in acidity, and also with increase in volume percentage of Acetonitrile. Imidazole decreases the rate of these reactions.

Water was found to be the best solvent for these reactions. H₂O₂ was the most effective catalyst among the group of catalysts studied, for complete degradation of substituted phenols in wastewater. GC-Mass spectroscopy and IR - spectroscopy were used to identify the products of these reactions, which were CO₂, H₂O, and some organic acids. Methacrylic acid test was used to prove that, the reaction follows free-radical mechanism.