OXIDATION OF REACTIVE ORANGE 16 BY COPPER OXIDE SYSTEM

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Faculty: Science

A commercial activated carbon (KI7080) sample was treated by HNO_3 and followed by heat treatment at 500 and 700°C under a flow of N_2. Three types of copper oxide supported-activated carbon catalysts were prepared using impregnation techniques. 5 wt % of Cu was loaded for each catalyst and calcined at 500°C. Samples were characterized by FTIR, XRD and nitrogen adsorption isotherm studies. The adsorption-desorption isotherms of all samples showed a typical Type I with hysteresis loops of H_4.

The decolourisation of reactive orange 16 (RO16) by different advanced oxidation processes was investigated. The rate of colour removal was studied by measuring the absorbance at characteristic wavelengths. The effect of CuO dose, H_2O_2 dose, UV light, added AC and catalyst was studied. These parameters influenced the decolourisation rate. The comparison between powdered and granular CuO was also studied. It was found that the decolourisation rate increased until an optimum H_2O_2 dosage (60 ml of 1 M H_2O_2), beyond which the reagent exerted an inhibitory effect.

For CuO/H_2O_2 system, contribution of the leached Cu^{2+} to the total colour removal by CuO/H_2O_2 can be estimated approximately 40 %. The colour removal by CuO/H_2O_2 system is an adsorption/oxidation process. The effect of UV on the decolourisation of RO16 was in the following order: $CuO/UV/H_2O_2$ > CuO/H_2O_2 > CuO/UV = CuO > UV/H_2O_2 > H_2O_2 > UV.

A simple kinetic model confirmed a pseudo-second order reaction for CuO, CuO/H_2O_2, $CuO/UV/H_2O_2$, CuO/UV, UV/H_2O_2, H_2O_2, $AC/CuO/H_2O_2$, 5%Cu-ACN, 5%Cu-ACN/UV/H_2O_2, 5%Cu-ACN/H_2O_2 and 5%Cu-ACN/UV systems.

The $AC/CuO/H_2O_2$ system exhibited a lower efficiency compared to CuO/H_2O_2 most probably due to decomposition of H_2O_2 and reduction of Cu^{2+}. The decolourisation efficiency of 5% Cu-ACN catalyst under four different conditions was observed in the following order: 5%Cu-ACN/UV/H_2O_2 > 5%Cu-ACN/H_2O_2 > 5%Cu-ACN/UV = 5%Cu-ACN. 5%Cu-ACN/UV/H_2O_2 system was found to be the most efficient method on decolourisation of RO16 in this study.

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PENGOKSIDAAN REAKTIF OREN 16 MENGGUNAKAN SISTEM KUPRUM OKSIDA

Oleh

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Satu karbon teraktif komersil (KI7080) telah dirawat dengan HNO_3 dan diikuti rawatan haba pada 500 dan 700°C di bawah aliran N_2. Tiga mangkin kuprum oksida tersokong pada karbon teraktif telah disediakan dengan menggunakan teknik impregnasi. 5 wt% Cu dimuatkan ke dalam setiap mangkin and dikalsin pada 500°C. Sampel dicirikan dengan FTIR, XRD and isoterma penjerapan nitrogen. Isoterma penjerapan-penyahjerapan bagi semua sampel menunjukkan jenis I dengan lekuk histeresis H_4.

Pelunturan wana bagi reaktif oren 16 dengan proses pengoksidaan yang berbeza telah dikaji. Kadar penyingkiran warna dikaji dengan menyukat serapan pada ciri panjang gelombang. Kesan dos CuO, dos H_2O_2, lampu UV, AC yang ditambah dan mangkin telah dikaji. Parameter ini mempengaruhi kadar pelunturan warna. Perbandingan telah dibuat antara serbuk dan ganul CuO. Takat optimum H_2O_2 yang diperlukan telah dipeperiksa. Didapati kadar pelunturan warna meningkat sampai satu dos H_2O_2 (60 ml

1 M H_2O_2) yang optimum, melebihi dos ini boleh menyebabkan kesan rencatan. Bagi sistem CuO/H_2O_2, sumbangan Cu^{2+} ini kepada pelunturan warna CuO/H_2O_2 boleh dijanggakan sebanyak 40%. Pelunturan warna dengan sistem CuO/H_2O_2 ialah satu process penyerapan/pengoksidaan. Kesan UV ke atas pelunturan warna RO16 adalah dalam order berikut: $CuO/UV/H_2O_2 > CuO/H_2O_2 > CuO/UV = CuO > UV/H_2O_2 > H_2O_2 > UV$.

Satu model kinetik yang mudah telah memastikan tertib tindak balas pseudo-kedua bagi sistem CuO, CuO/H_2O_2, $CuO/UV/H_2O_2$, CuO/UV, UV/H_2O_2, H_2O_2, $AC/CuO/H_2O_2$, 5%Cu-ACN, 5%Cu-ACN/UV/H_2O_2, 5%Cu-ACN/H_2O_2 dan 5%Cu-ACN/UV.

$AC/CuO/H_2O_2$ menunjukkan kecekapan yang lebih rendah berbanding dengan CuO/H_2O_2. Ini disebabkan oleh penguraian H_2O_2 dan pengurangan Cu^{2+}. Kecekapan pelunturan warna bagi mangkin 5%Cu-ACN di bawah 4 keadaan yang berbeza telah dipermerhatikan dalam order 5%Cu-ACN/UV/H_2O_2 > 5%Cu-ACN/H_2O_2 > 5%Cu-ACN/UV = 5%Cu-ACN. Didapati sistem 5%Cu-ACN/UV/H_2O_2 adalah kaedah yang paling efektif untuk pelunturan warna RO16 dalam kajian ini.

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LIST OF ABBREVIATIONS

AC	Activated carbon
AC/HCl	Hydrochloric acid treated activated carbon
ACN	Nitric acid treated activated carbon
AOPs	Advanced Oxidation Processes
BDDT	Brunauer, Denning, Deming, Teller
BET	Brunauer-Emmett-Teller
C_0	Initial concentration of the reactant
C_s	Concentration of the solvent
5%Cu-ACN	5 wt% Cu catalyst supported on nitric acid treated activated carbon
Cu20/AC	20 wt% Cu catalyst supported on activated carbon
Cu20/AC-HF	20 wt% Cu catalyst supported on hydrofluoric acid treated activated carbon
Cu20/AC-HNO_3	20 wt% Cu catalyst supported on nitric acid treated activated carbon
CuO	Copper Oxide
CuO-MAC	Modified activated carbon supported copper oxide catalyst
FT-IR	Fourier Transform Infra Red
H_2O_2	Hydrogen Peroxide
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometer
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee of Powder Diffraction Standard

K	Adsorption coefficient of the reactant
k_2	Pseudo-second order rate constant
k_{app}	Pseudo-first order rate constant
K_r	Reaction rate constant
K_s	Adsorption coefficient of the solvent
MSW	Municipal solid waste
OAC	Non-treated activated carbon
OH•	Hydroxyl radical
OH_2•	Perhydroxyl radical
q_e	Amount of soluted sorbate sorbed at equilibrium concentration of the solvent
q_t	Amount of soluted sorbate on the surface of the sorbent at any time t
R^2	Correlation coefficient
RO16	Reactive Orange 16
TiO_2	Titanium Dioxide
TOC	Total Organic Carbon
TPD	Temperature Programmed Desorption
TPR	Temperature Programmed Reduction
UV	Ultraviolet
V	Oxidation potential
XRD	X-Ray Diffraction
θ	Fraction of the surface covered by the reactant

CHAPTER 1

INTRODUCTION

Currently, it is estimated that industries dump 300 to 500 million tons of heavy metals, solvents, toxic sludge and other wastes into water sources annually. Water usage in the industrial sector is expected to increase from 752 cubic kilometers a year to 1,170 cubic kilometers a year by 2025 (Bender, 2004).

The textile dyeing and printing industries are among the several industries responsible for pollution of aquatic ecosystems. Over 700,000 tons of approximately 10,000 different types of dyes and pigments are produced annually worldwide. Nearly 50 % of these dyes are azo-type dyes. About 20 % of dye of the total world production is assumed to be discharged in industrial effluents during the textile dyeing process (Azbar *et al.*, 2004). Up to 50 % of reactive dyes, 8-20 % of disperse dyes and 1 % of pigments may be lost directly into effluents during the dyeing process (McMullan *et al.*, 2001).

Removal of color in wastewater generated by the textile industries is a current issue of discussion and regulation all over the world. Among the reactive dyes, the textile azo dyes have attracted the most attention with regard to its high environmental impact due to their widespread use, their potential to form toxic aromatic products and their low removal rate during primary and secondary treatment.

A variety of physical and chemical treatment methods are presently available for these dyes. Nevertheless these methods merely transfer the dye to a solid phase which requires further treatment (Carneiro *et al.*, 2004).

Biological processes such as sequenced anaerobic or aerobic digestion, have been proposed in the treatment of textile wastewater, but they are limited due to the fact that many of the dyes are not enobiotic and non-biodegradable (Behnajady *et al.*, 2004)

During the last two decades advanced oxidation processes (AOPs) that are combinations of powerful oxidizing agents (catalytic initiators) with UV or near-UV light have been applied for the removal of refractory organic pollutants and xenobiotics. Destructive oxidation of dyes and textile effluents have recently received considerable attention since coloured aromatic compounds have proven to be degraded effectively by a variety of homogeneous and heterogeneous AOPs . AOPs such as Fenton and photo-Fenton catalytic reactions, H_2O_2/ UV processes and TiO_2 mediated photocatalysis have been studied. A broad range of experimental conditions was established in order to reduce the colour and organic load of dye containing effluent wastewater.

The aim of this work was to evaluate the possibility of treatment alternative for reactive orange 16 (RO16) dye wastewater by copper oxide system. Since copper nitrate is the best catalyst in the catalytic oxidation of dyeing and printing wastewater, copper will be chosen as the active element to be deposited onto the porous support.

1.1 Study Objectives

The objectives of this study are:

1. To study the decolourisation of reactive orange 16 (RO16) by CuO/H_2O_2 system by varying the mass of CuO and concentration of H_2O_2.
2. To prepare and characterize copper oxide-modified activated carbon catalysts (CuO-MAC).
3. To examine the colour removal efficiency of RO16 by modified activated carbon (MAC) and CuO-MAC catalysts via adsorption.
4. To examine the colour removal efficiency of RO16 by a combination of CuO-MAC catalyst and H_2O_2 with and without UV light via oxidation.

CHAPTER 2

LITERATURE REVIEW

2.1 Oxidation

Oxidation is defined as a process of the electron loss from an atom or ion and also the combination of oxygen with other substances. The reactant that gains electrons is called the oxidation agent. The oxidizing agent contains the element that is being reduced (gains electron). If a substance gains electrons easily, it is said to be a strong oxidizing agent.

2.1.1 Advanced oxidation process (AOPs)

AOPs have common principles in terms of the participation of hydroxyl radicals that are assumed to be operative during the reaction. Although it is claimed that there are other species involved, the active species responsible for the destruction of contaminants in most cases seems to be the OH• which is unstable and quite reactive. Due to the instability of the OH• radical, it must be generated continuously "in situ" through chemical or photochemical reactions (Oliver *et al*., 2000).

Hydroxyl radicals may attack organic molecules by abstracting a hydrogen atom from the molecule (Clarke and Knowles, 1982). A common pathway for the degradation of organics by the OH• is described as follows:

$$OH\bullet + RH \rightarrow H_2O + R\bullet \quad (1)$$

$$R\bullet + H_2O_2 \rightarrow ROH + OH\bullet \quad (2)$$

$$R\bullet + O_2 \rightarrow ROO\bullet \quad (3)$$

$$ROO\bullet + RH \rightarrow ROOH + R\bullet \quad (4)$$

A wide variety of advanced oxidation processes are available:

- chemical oxidation processes using H_2O_2, ozone, combined ozone & peroxide, hypochlorite, Fenton's reagent etc.
- ultra-violet enhanced oxidation such as UV/ozone, UV/H_2O_2 , UV/air
- wet air oxidation and catalytic wet air oxidation (where air is used as the oxidant)

AOPs (O_3, O_3/H_2O_2, O_3/UV, H_2O_2/UV, O_3/ H_2O_2/UV, Fe^{2+}/H_2O_2) for the degradation of non-biodegradable organic contaminants in industrial effluents are attractive alternatives to conventional treatment methods. AOPs based on the generation of very reactive and oxidizing free radicals have been used with increasing interest due to their high oxidizing power. Production of these radicals is achieved either using single oxidants or combinations of ozone, H_2O_2 and UV radiation (Glaze and Kang, 1989) and also, with the combination of H_2O_2 with ferrous ions in the so-called Fenton's reagent (Walling, 1975). The oxidation using Fenton's reagent has proven to be a promising and attractive treatment method for the effective decolourisation and degradation of dyes. Complete degradation of organic compounds by Fenton's reagent include phenols, various chlorinated phenols, aromatics like benzene, toluene, xylene,