

**REMOVAL OF COLOR, SUSPENDED SOLIDS AND COD FROM TEXTILE
WASTEWATER USING CLINOPTILOLITE AND PERSULFATE,
IN BATCH SYSTEM**

by

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
AOP	Advanced oxidation process
AP	Adequate precision
BAF	Biological aerated filter
BET	Brunauer-Emmet-Teller
BOD	Biochemical oxygen demand
CCD	Central composite design
CEC	Cation exchange capacity
CPL	Clinoptilolite
COD	Chemical oxygen demand
CV	Coefficient of variance
De	Desirability
DF	Degree of freedom
DOE	Design of experiment
FTIR	Fourier transform infrared
GAC	Granular activated carbon
MBBR	Moving-bed biofilm reactor
MBR	Membrane bioreactor
MF	Microfiltration
NF	Nanofiltration
OH·	Hydroxyl radical
PAC	Powdered activated carbon
PS	Persulphate
pH	Hydrogen ions
PRESS	Predicted residual sum of squares
R ²	Coefficient of determination

$R^2_{\text{adj.}}$	Adjusted coefficient of determination
R^2_{pre}	Predicted coefficient of determination
RSM	Response surface methodology
SBR	Sequencing batch reactor
SEM	Scanning electron microscope
SG	specific gravity
SS	Suspended solids
TSS	Total suspended solids

**PENYINGKIRAN WARNA, PEPEJAL TERAMPAI DAN COD DARI AIR SISA
TEKSTIL MENGGUNAKAN *CLINOPTILOLIT* DAN PERSULFAT,
DALAM SISTEM KELOMPOK**

ABSTRAK

Bekalan air bersih semakin terhad disebabkan oleh berbagai bentuk pencemaran seperti disebabkan oleh industri pencelup dan tekstil. Kajian terdahulu menunjukkan bahawa air sisa tekstil adalah toksik, karsinogen dan mutagen. Cirinya yang ketara adalah warna yang pekat, serta mengandungi nilai Keperluan Oksigen Kimia (COD) dan pepejal terampai yang tinggi disebabkan oleh pencelup berlebihan yang hadir dalam air-sisa selepas produksi. Salah satu industri tekstil di kawasan utara Malaysia sedang menghadapi masalah untuk mematuhi piawai pelepasan efluen terhadap tiga parameter di atas. Sehubungan itu, parameter tersebut dipilih sebagai fokus kajian ini. Disebabkan air sisa tekstil adalah *recalcitrant* terhadap teknik olahan konvensional, proses pra-olahan berasas kimia telah dicadangkan untuk membolehkan penguraian biologi dilakukan di mana sesuai. Lanjutan itu, potensi olahan oleh *clinoptilolite* (CPL), persulfat (PS) dan gabungan keduanya diselidiki dalam kajian ini melalui proses-proses penjerapan, pengoksidaan dan penjerapan-pengoksidaan. Beberapa siri pra-eksperimen kelompok dilakukan untuk menentukan julat pembolehubah proses tidak bersandar yang cenderung terhadap ketiga-tiga proses (olahan oleh; CPL, PS, and CPL/PS). Setelah julat setiap pembolehubah bekerja (operasi) ditentukan, mereka dioptimumkan dalam siri eksperimen berikutnya menggunakan kaedah klasik. Kaedah Tindakbalas Permukaan (RSM) diaplikasikan bagi membuktikan saling tindak balas antara pembolehubah bersandar dan tidak bersandar. Berikutnya, pembolehubah-pembolehubah proses, seperti dos media, pH

awal dan masa tindakbalas juga dioptimumkan seiring dengan parameter tindakbalas (warna, SS, dan COD). Kesan pengaktifan haba PS pada suhu 40°C, 50°C dan 60°C dikaji dalam proses pengoksidaan PS. Dalam analisis akhir, keupayaan setiap sistem yang telah dioptimumkan dibandingkan untuk menentukan sistem yang paling berkesan. Keputusan menunjukkan bahawa pada keadaan optimum yang telah ditentukan (saiz zarah: <75µm-250µm, kelajuan adukan: 150rpm, pH: 2, dos: 8g dan masa tindakbalas: 100minit) olahan oleh CPL, penyingkiran *optimum* warna, SS dan COD adalah masing-masing 90%, 90% dan 79%. Manakala, untuk pengoksidaan PS (pada suhu bilik), 90%, 78% dan 50% warna, SS dan COD berjaya disingkirkan pada keadaan optimum (kelajuan adukan: 150rpm, dos: 1/4 (i.e. nisbah pencemar/pengoksida), pH: 3 dan masa tindakbalas dalam minit: 360 (warna), 420 (SS) dan 60 (COD). Kombinasi olahan CPL/PS menghasilkan masing-masing 98%, 99% dan 74% penyingkiran untuk warna, SS dan COD pada keadaan optimum (CPL dos: 8g, dos PS: 1/4, pH: 4 dan masa tindakbalas dalam minit: 300 (warna), 210 (SS) dan 30 (COD). Perbandingan ketiga-tiga proses menunjukkan pencapaian yang lebih baik untuk proses kombinasi CPL/PS yang hampir menyahkan keseluruhannya warna dan pepejal terampai. Walaubagaimanapun, ia kurang berkesan untuk penyingkiran COD, berbanding penggunaan CPL. Penyingkiran oleh PS teraktif haba didapati lebih baik berbanding pengoksidaan PS pada suhu bilik. Keputusan kajian ini menunjukkan bahawa kombinasi *clinoptilolite*/persulfat adalah proses terbaik diantara ketiga-tiga proses yang telah dikaji dan mempunyai potensi yang lebih baik untuk digunakan dalam menyingkirkan SS, warna, dan COD dari air sisa tekstil mentah. Walaubagaimanapun, rawatan yang lebih lanjut adalah dicadangkan untuk menyingkirkan COD sepenuhnya.

**REMOVAL OF COLOR, SUSPENDED SOLIDS AND COD FROM TEXTILE
WASTEWATER USING CLINOPTILOLITE AND PERSULPHATE,
IN BATCH SYSTEM**

ABSTRACT

The supply of clean water is limited by various sources of pollution such as the dye and textile industries. Previous studies have shown that textile wastewater is toxic, carcinogenic and mutagenic. Its most obvious characteristics are the strong color, high chemical oxygen demand (COD) and suspended solid (SS) caused by unfixed dyes and stuff remaining in the wastewater after production. One of the textile industries in the northern region, Malaysia, is experiencing difficulties in complying with the standard discharge limit of effluent against these parameters. Hence they were selected as the focus of this study. Because textile wastewater is recalcitrant to conventional treatment techniques, chemical based pretreatment have been suggested to degrade and make treatable by biological means, where necessary. In the light of this, the treatment potential of each of clinoptilolite (CPL), persulfate (PS) and a combination of both were investigated in this study by adsorption, oxidation, and adsorption-oxidation processes. A series of batch preliminary experiments were conducted to determine the range of each independent process variable that favours, the three processes (treatments via; CPL, PS, and CPL/PS). Having predetermined the range of each working (operational) variable, they were optimized in another series of main experiments using the classical method. The response surface methodology (RSM) was applied to show the interrelationship between the dependent and independent process variables. Also, the process variables,

especially dosage of media, initial pH of reaction and reaction time were optimized alongside the response parameters (color, SS, and COD). The effect of thermal activation of PS at temperatures of 40°C, 50°C and 60°C was investigated in the PS oxidation process. In the final analysis, the performances of each optimized system were compared to determine the most efficient system. Results indicated that, at the predetermined optimum conditions (particle size: <75µm-250µm, agitation speed: 150rpm, pH: 2, dosage: 8g and **contact** time: 100minutes) of treatment via CPL, the optimum removals for color, SS and COD in terms of percentages (%) were; 90, 90 and 79 respectively. While PS oxidation (at room temperature) had 90%, 78% and 50% removal of color, SS and COD respectively at the optimum conditions (agitation speed: 150rpm, dosage: 1/4 (i.e. contaminant/oxidant ratio), pH: 3 and contact time in minutes: 360 (color), 420 (SS) and 60 (COD)). The combined CPL/PS treatment achieved 98%, 99% and 74% for removal of color, SS and COD at t optimum conditions (CPL dosage: 8g, PS dosage: 1/4, pH: 4 and contact time in minutes: 300 (color), 210 (SS) and 30 (COD)). A comparison of the three processes showed a better performance of the combined CPL/PS which achieved an almost complete decolorization and SS removal. However, it achieved less for COD removal while the sole CPL performed best in COD removal. The performance of thermal activated PS was found better than the PS oxidation at room temperature. The findings of this study have shown that the combination of clinoptilolite/persulfate is the best of the three processes that were investigated and potential to be used to remove SS, color and COD from raw textile wastewater. However, since all parameters except COD met the discharge limit, a further treatment is suggested to completely remove the COD.

CHAPTER 1

INTRODUCTION

1.0 Background

Environmental pollution has been considered to evolve from the era of industrial revolution, with the emergence and growth of many great factories. Industrial production activities result in large volumes of waste discharges including chemical waste which pollute the environment either directly or indirectly.

The textile industry is one of the small and medium scale industries (SMIs) in Asia and also an important sector in the economy and environmental indicators of concerned nations. Textiles are very important primary materials required for the production of clothes and clothing materials. But production also brings about very significant environmental concerns, particularly on the wastewater discharges. The textile industries extensively use synthetic dyes for dyeing and printing (Khatri et al., 2015; Shah et al., 2013; Yao & Geng 2015). The wastewater thus consist of very large quantity of complex chemical substances (as shown by the characterization) which remained as unused materials in the wastewater from various stages of textile processing (Cheung et al., 2009; Divya et al., 2013; Verma et al., 2012; Yonar et al., 2005).

Associated environmental concerns with the clothing, textile, dye and intermediate industries include the quantity and quality of water used and wastewater discharges. The earlier textile finishing industry uses about 100 liters of water to produce about 1 kg of textile material, but the technologies based on the closed-loop

could help in reducing this enormous water use and pollution (Shah et al., 2013). The closed-loop technology is based on recovery and reuse (Stindt and Sahamie, 2014).

Azo dyes are considered the largest group of dyes and industrial colorants, which currently represents 60-70% share of the world dye market (Mahne, 2012; Singh & Arora, 2011; Wu et al., 2012). However, many of these dyes are toxic, carcinogenic and mutagenic, (Salman et al., 2012; Shah et al., 2013). Also, their bonds are resistant to break down, hence, they exhibit the potential for persistence and accumulation in the environment (Shah et al., 2013). However, the use of dyes by the textile industry has steadily grown because they react well with fibers, and their color is stable. Literatures have discussed dyes more because of their high solubility in water and as effluents containing environmentally problematic compounds (Papić et al., 2009) in (Guimaraes et al., 2012). Colors due to unfixed dyes are visible in small quantities due to their brilliance (Robinson et al., 2001).

Several techniques have been used to treat industrial effluents, including textile wastewater which are broadly categorized into physical, chemical and biological methods (Anjaneyulu et al., 2005), or a combination of the methods. The traditional techniques for treating textile wastewater use a combination of physical, chemical and biological methods, although again the traditional methods are becoming insufficient (Lin and Peng, 1996).

Among the previous techniques used, adsorption has gained popularity and considered a very effective physicochemical technique for the treatment of textile wastewater. Its simplicity of application, effectiveness, and universal availability are the

desired properties. It has been found to be about 99.9% effective in the removal of soluble and insoluble organic pollutants hence, its emergence as a major industrial separation technique (Richardson et al., 2002). Its popularity is due to their large surface area in the range of 900m²/g and 1100 m²/g (Ahmad et al., 2013; Bokil et al., 2013). Activated carbon; the most familiar and often used adsorbent has been very efficient, but its relative high cost has necessitated the development of alternative adsorbents (Ahmed and Hameed, 2009; Al-Degs et.al., 2009; Sarici-Özdemir & Önal, 2014), therefore the need for a cost-effective adsorbent (Qiu et al., 2009).

The use of natural zeolites in water purification processes is often times based on the uniqueness of cation-exchange that it exhibits, in which dissolved cations may be removed from water by exchanging with cations on zeolite exchange sites (Kalló, 2001). Although ion exchange is a significant characteristic of zeolite, it also has adsorptive and catalytic properties, a combination of which is tapped in this study.

On the other hand, the advanced oxidative process (AOP), has also been considered effective and environmentally friendly unlike other techniques; it does not transfer pollutant from one phase to another but destroys them to prevent consequent secondary pollution. AOPs have emerged as an important destructive method for eliminating most of the organic and inorganic pollutants including reactive dyes. AOPs have been used to enhance the bio-treatability of wastewaters containing various organic compounds that are non-biodegradable and noxious to common microorganisms. AOPs are therefore in this sense are pretreatment methods (Chan et al., 2011; Divya et al., 2013; Rizzo, 2011). The technique has been effective for the degradation of contaminants like dyes into the inorganic compounds, CO₂, and water.