DEGRADATION OF AZOIC CONGO RED DYE BY USING ULTRASONIC IRRADIATION WITH ADDITIVE

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ABSTRACT

The pollution due to textile dye effluents has been a major concern and the investigations involving various efficient techniques are being carried out to overcome this problem. This study presents the degradation of Congo red, an azo dye, using ultrasound and the degradation process was optimized by addition of ferum powder and salt or sodium chloride. Besides, adsorbent which was carbon paper also was used to enhance more degradation process. This method was called sonosorption method. The dye solution was subjected to ultrasound cleaner of 60 Hz at various initial concentrations, pH and temperature. The time set up for every sonication process was accurately thirty (30) minutes. The absorbance of Congo red dye before and after sonication process was analysed spectrometrically using UV-Vis Spectrophotometer to get the distinct values. The results showed that the initial dye concentration, pH and temperature of dye solution influenced the % decolourisation and lower initial values resulted in high % decolourisation. Additionally, the studies were carried out with addition of ferum powder and sodium chloride (salt) to increase the efficiency of Congo red degradation. The high concentration of salt and ferum powder that were both 2.0 M ended with high percentages of degradation, 49.88 % and 96.42 % respectively. The sono-sorption method studies were conducted with presence of adsorbent (carbon paper) in the dye solution consequently means that the paper was put in the dye solution first before sonication started. The result came out positively compared with degrading of dye in absence of adsorbent. The outcomes of the present work indicate that ultrasound/Fe and sono-sorption method process are efficient for the degradation of Congo red in aqueous solution.

ABSTRAK

Pencemaran akibat sisa pewarna tekstil telah menjadi fokus utama dan kajian melibatkan pelbagai kaedah untuk mengatasi masalah ini. Penelitian ini mengolah penurunan warna daripada *Congo red*, sejenis zat warna azo menggunakan ultrabunyi dan proses degradasi dioptimumkan dengan penambahan serbuk ferum, garam. Selain itu, adsorben ataupun kertas karbon digunakan untuk meningkatkan proses degradasi. Kaedah ini dipanggil kaedah sonosopsi. Penyelesaian pewarna menjadi sasaran Ultrasonik Radiasi 60 Hz di berbagai kepekatan awal, pH dan suhu. Waktu ditetapkan untuk setiap proses sonikasi adalah tiga puluh minit. Absorbansi *Congo red* sebelum dan selepas proses sonifikasi dianalisis menggunakan spektrofotometer UV-Vis untuk mendapatkan nilai yang berbeza. Keputusan kajian menunjukkan bahawa kepekatan pewarna awal, pH dan suhu larutan pewarna mempengaruhi kualiti peratusan degradasi dan nilai-nilai parameter yang lebih rendah menghasilkan peratusan degradasi yang tinggi. Selain itu, kajian diteruskan dengan penambahan serbuk ferum dan sodium klorida (garam) sebagai aditif untuk meningkatkan keefektifan degradasi Congo merah. Kepekatan aditif yang tinggi berakhir dengan peratusan yang tinggi iaitu 49.88% untuk garam manakala 96.42% untuk serbuk ferum. Penelitian kaedah sono-sorpsi dilakukan dengan kehadiran adsorben (kertas karbon) secara serentak dengan pewarna, bermaksud bahawa kertas itu dimasukkan ke dalam larutan pewarna sonikasi terlebih dahulu sebelum eksperimen bermula. Hasilnya menunjukkan positif berbanding dengan menurunkan *Congo red* dalam ketiadaan adsorben. Hasil dari kajian ini menunjukkan bahawa kombinasi di antara USG / Fe dan proses sonosopsi berkesan untuk degradasi *Congo red*.

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LIST OF SYMBOLS

SYMBOLS	**TITLE**
°C	Degree Celsius
mg/L	Concentration
g	gram
ml	mililitre
%	Percentage
kHz	kilo hertz
M	Molarity

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CHAPTER ONE

INTRODUCTION

1.1 Background of Study

In recent decades, the pollution of water sources by industrial effluents has been a major concern and the investigations involving various techniques are carried out to successfully face this problem. Effluents discharged by textile dyeing, food additives, cosmetics and printing industries are rich in colour and this create an aesthetic problem to the public. The colour is mainly due to the usage of dyes and they differ in their classification primarily based on their functional groups. Azo dyes, an important class of dyes, contribute about 70 % of the total dye used and are found to be genotoxic and mutagenic to human population and other living beings. Government agencies are enforcing strict rules and regulations, especially in the developed countries, with respect to the treatment of industrial effluents containing dyes.

By definition dyes can be said to be coloured, ionising and aromatic organic compounds which shows an affinity towards the substrate to which it is being applied. It is generally applied in a solution that is aqueous. Dyes may also require a mordant to better the fastness of the dye on the material on which it is applied. One characteristic of dye is that the dyes must get completely or at least partially soluble in which it is being put to.

The azo dyes containing azo bonds (-N=N-) have complex structure to resist biodegradation under aerobic conditions. On the other hand, the reduction reaction of azo bond gives colourless aromatic amines which are known to be carcinogenic and toxic. In such cases, the treatment of azo dye containing effluents by aerobic degradation yield aromatic amines and for which the final fate in the environmental is almost unknown.

At the very basic level the use of colour in identifying individual components of tissue sections can be accomplished primarily with dyes. Although there are other means, dyes are however, the largest group that can easily be manipulate to our liking. Dyes are applied to numerous substrates for example to textiles, leather, plastic, paper etc. in liquid form. Precisely, types of dyes applied in textile industries classified as; reactive dyes, direct dyes, disperse dyes, acid dyes, basic dyes and vat dyes.

As mentioned before, instead of their well known in industries, azo dyes also contribute to environmental pollution; aesthetic pollution, eutrophication, and perturbation in aquatic life. It occurs due to the release of coloured wastewater from fabric and yarn (thread) dyeing. Because of their colour, potential toxicity, carcinogenic or mutagenic, they extensively spread serious problems to the ecosystem of earth. Thus, it is ecologically essential to degrade azo dyes in water to ensure a healthy environment to humans.

This paper presents a critical review of recent research focuses on azo dyes. One example of azo dye is Congo red dye which is commonly used in textile industry as shown in Figure 1.1. Brightly colored dyes such as the shimmering Congo red commonly used in silk clothing manufacture are notoriously difficult to dispose of in an environmentally benign way. It is toxic to many organisms and is a suspected carcinogen and mutagen. To give it its full name it is the disodium salt of 3,3'-(1E,1'E)-biphenyl-4,4'-diylbis(diazene-2,1-diyl)bis(4-aminonaphthalene-1 sulfonate). It is a benzidine-based anionic disazo dye. Benzidine and Congo red are, however, banned in many countries because of health concerns. But, it is still widely used in several countries.

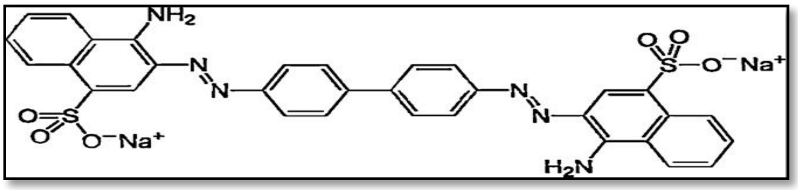

Figure 1.1: Structure of Congo red Dye

Apparently it is used not only to dye silk a gorgeous red, but cleverly adds a second shimmering color and rending the red silk shot through with yellow. It also represents a significant effluent problem along with related dyes from textiles, printing and dyeing, paper, rubber, and plastic industries. Its structural stability makes it highly resistant to biodegradation, and obviously its bright color and toxicity are entirely undesirable in the environment.

Over the past few years, various advanced oxidative processes and many hybrid technologies; to completely or partially degrade the azo dyes into non-toxic end products are reported. Advanced oxidation processes (AOP) are currently being developed for remediation of contaminated effluent because they generate no hazardous sludge. Oxidative degradation is based on free radical attack using powerful oxidants. One of a feasible method to achieve both decolourisation and degradation of azo dyes is sonolytic degradation or else ultrasonic irradiation. Sonochemicals reactions are induced by directing frequency waves around 50 kHz into liquids thereby producing cavitation bubbles (formation of free radicals) known as micro-bubbles and the adiabatic collision of such bubbles creates extreme pressure and temperature, which induce pyrolytic fragmentation reactions. Carbon dioxide and water are the usual products, although with the case of azo dyes, nitrogen would also feature in the byproducts. Several of OH radical formed are as listed in reactions (1.1) to (1.5):

$H_2O \rightarrow H^{\cdot} + {}^{\cdot}OH$ (1.1)

$O_2 \rightarrow 2O$ (1.2)

$H^{\cdot} + O_2 \rightarrow {}^{\cdot}OOH$ (1.3)

$O + H_2O \rightarrow 2{}^{\cdot}OH$ (1.4)

$H^{\cdot} + O_2 \rightarrow {}^{\cdot}OH + O$ (1.5)

In absence of any solutes, these primary radicals of sonolysis mostly recombine to form hydrogen peroxide that is released in the medium (reactions (1.6) to (1.7)). However, when aqueous sonolysis is conducted in the presence of organic solute, a number of chemical processes can occur, depending on the physical and chemical nature of the solute.

$$2\cdot OH \rightarrow H_2O_2 \quad (1.6)$$

$$2\cdot OOH \rightarrow H_2O_2 + O_2 \quad (1.7)$$

1.2 Problems Statement

1.2.1 Environmental pollutions

It is estimated that 10-15 % of the dyes lost in the effluent during dyeing process thus become pollutant to environment. Dye pollutants in wastewater are the principal source of environmental contamination. As a result, wastewater become toxicity and bring dramatic source of aesthetic pollution, eutrophication, and aquatic life disordered.

1.2.2 Improve existed researches

Many methods are presently available in existed researches for the treatment of wastewater discharged from various industries. Most of them succeeded their researches by degrading dye pollutant in wastewater. However, the rate of degradation achieved is still inadequate. Therefore, this research will improve higher degradation rate that existed researchers cannot obtained.

1.2.3 Increasing of energy and cost consumptions.

When wastewater discharged from industries has been polluted with dye (organic waste compound), the energy and cost consumed to clean the wastewater increased. In order to reduce energy consumption, it is required for the treatment of polluted wastewater before it flows out through the piping system and goes to the seas or rivers. The target of this research is to employ a very low cost of wastewater treatment for dye removal.

1.2.4 Human health problems

When pollution occurs, human health also will be infected. Even though dye brings back and forth benefits to the industries, we have to be aware of the harmful elements inside it. Many worst and worst diseases exist around the world until it is hard to cure because of untraceable pollutants such as dye. That is why we need to treat this pollutant so that our humanity is taken care of.

1.3 Objectives

Based on problem statements, the purposes of this research are:

1.3.1 To obtain optimum condition in Congo red dye degradation process using ultrasonic irradiation in presence of additive.

1.3.2 To study the dye degradation using ultrasonic irradiation with addition of newspaper which is called sonosorption method.

1.4 Research Scopes

In implementing this research, the scopes involved are:

1.4.1 To study the effect of pH (3-12), initial concentration (50-100 mg/L) and temperature (45±2-75±2°C) to the degradation of Congo red dye using ultrasonic irradiation facilitated with additive (ferum powder and sodium chloride).

1.4.2 To compare the percentage of degradation in appearance of newspaper and non appearance of newspaper.

1.5 Contributions to Society and Environment

1.5.1 Preserving and protecting environment.

It is good that dye manufacturers and dyeing units have finally recognized the profoundity of environmental impact of using dyes. By applying this degradation process in treating this pollution, we can preserve and protect our environment nature.

1.5.2 Reduce energy and cost consumptions.

By treating the waste water containing dyestuff organic compound at the textile finishing industry, cost consumptions and energy used have been reduced to minimum. Improvement of dyes and dyeing units is needed in order to overcome this problem. As the matter of fact, this low cost consumptions method can replace the expensive treatment of dye pollutant such as photo catalytic method and activated carbon unit which are widely used in waste water treatment process now days. This improvement not only helps reduce the cost and energy but also give benefits to industries in financial aspect particularly.

1.5.3 Remove harmful element of dye which is dangerous to human health.

As stated in problem statement, it is important to remove these harmful elements of dye which is dangerous to human health. Although industries that develop countries but humanity also need to be protect. Thus, this degradation process enhancing with new method will preserve both human health and industries.

CHAPTER TWO

LITERATURE REVIEW

2.1 Definition of dye

A dye can generally be described as a coloured substance that has an affinity to the substrate to which it is being applied. The dye is usually used as an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber. (In contrast, a pigment generally has no affinity for the substrate, and is insoluble). A mordant is a substance used to set dyes. A mordant is either inherently colloidal or produces colloids and can be either acidic or basic. Mordants include tannic acid, alum, chrome alum, and certain salts of aluminum, chromium, copper, iron, iodine, potassium, and tin.

Archaeological evidence shows that, particularly in India and the Middle East, dyeing has been carried out for over 5000 years. The dyes were obtained from animal, vegetable or mineral origin with no or very little processing. By far the greatest source of dyes has been from the plant kingdom, notably roots, berries, bark, leaves and wood, but only a few have ever been used on a commercial scale.

2.2 Types of dyes

2.2.1 Natural dyes

Table 2.1: Types of Natural Dye

Animal Origin	
Tyrian purple	Vat dye
Kermes	Mordant dye
Cochineal	Mordant dye
Techelet	unknown
Vegetable Origin	
Safflower	Direct (substantive) dye
Turmeric	Direct (substantive) dye
Indigo	Vat dye
Woad	Vat dye
Alizarin (Madder)	Mordant dye
Dyer's Broom	Mordant dye
Logwood	Mordant dye
Brazilwood	Mordant dye
Quercitron bark	Mordant dye
Weld	Mordant dye
Old Fustic	Mordant dye

2.2.2 Inorganic Dyes

The first man made organic dye, mauveine, was discovered by William Henry Perkin in 1856. Many thousands of dyes have since been prepared and because of vastly improved properties imparted upon the dyed materials quickly replaced the traditional natural dyes. Dyes are now classified according to how they are used in the dyeing process.

2.2.3 Acid Dyes

Acid dye is water soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers from neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulose fibers.

2.2.4 Basic Dyes

Water soluble cationic dyes that are mainly applied to acrylic fibers but find some use for wool, and silk. Usually acetic acid is added to the dye bath to help the take up of the dye onto the fiber. Basic dyes are also used in the coloration of paper.

2.2.5 Direct (Substantive) Dye

Dyeing is normally carried out in a neutral or slightly alkaline dye bath, at or near the boil, with the addition of either sodium chloride (NaCl) or sodium sulphate (Na_2SO4). Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

2.2.6 Mordant Dye

As the name suggests these dyes require a mordant. This improves the fastness of the dye on the fiber such as water, light and perspiration fastness. The choice of mordant is very important as different mordants can change the final color significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. The most important mordant dyes are the synthetic mordant dyes (chrome dyes) used for wool, these comprise some 30% of dyes used for wool and are especially useful for black and navy shades. The mordant used is potassium dichromate applied as an after-treatment.

2.2.7 Vat Dye

These dyes are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye. In this leuco form these dyes have an affinity for the textile fiber. Subsequent oxidation reforms the original insoluble dye.

2.2.8 Reactive Dye

It is first appeared commercially in 1956, after their invention in 1954 by Rattee and Stephens at the ICI Dyestuffs Division site in Blackley, Manchester, UK. They are used to dye cellulose fibers. The dyes contain a reactive group, either a haloheterocycle or an activated double bond, that, when applied to a fiber in a weakly alkaline dye bath, forms a chemical bond with a hydroxyl group on the cellulose fiber. Reactive dyeing is now the most important method for the colouration of cellulose fibers. Reactive dyes can also be used to dye wool and nylon, in the latter case they are applied under weakly acidic conditions.

2.2.9 Disperse Dye

It is originally developed for the dyeing of cellulose acetate. They are substantially water insoluble. The dyes are finely ground in the presence of a dispersing agent then sold as a paste or spray dried and sold as a powder. They can also be used to dye nylon, triacetate, polyester and acrylic fibers. In some cases a dyeing temperature of 130°C is required and a pressurized dye bath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fiber. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

2.2.10 Azoic Dye

Azoic dye is a dyeing technique in which an insoluble azo dye is produced directly onto or within the fiber. This is achieved by treating a fiber with a diazo component and a coupling component. With suitable adjustment of dye bath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique in that the final color is controlled by the choice of the diazo and coupling components.

2.2.11 Food Dye

This is a special class of dyes of very high purity. They include direct, mordant and vat dyes. Their use is strictly controlled by legislation. Many are azo dyes but anthraquinone and triphenylmethane compounds are used for colours such as green and blue. Some naturally occurring dyes are also used.

2.3 Colourisation of dyes

This is a very common question that occurs in everybody's mind. The answer to which is explained by the presence of a substance called *Chromophore* in the dyes. By definition dyes are basically aromatic compounds. Their structures have aryl rings that has delocalised electron systems. These structures are said to be responsible for the absorption of electromagnetic radiation that has varying wavelengths, based upon the energy of the electron clouds. It is actually because of this reason that chromophores do not make dyes coloured. Rather it makes the dyes proficient in their ability to absorb radiation. Chromophores acts by making energy changes in the delocalised electron cloud of the dye. This alteration invariably results in the compound absorbing radiation within the visible range of colours and not outside it. Human eyes detect this absorption, and responds to the colours. Another possibility is that if the electrons are removed from the electron cloud, it may result in loss of colour. Removing electrons may cause the rest of the electrons to revert to the local orbits. A very good example is the Schiff's reagent. As sulphurous acid reacts with pararosanilin, what happens is that a sulphonic group attaches itself to the compound's central carbon atom. This hampers the conjugated double bond system of the quinoid ring, and causes the electrons to become localised. As a consequence the ring ceases to be a chromophore. As a result, the dye becomes colourless. To conclude chromophores are the atomic configurations which has delocalised electrons. Generally they are represented as carbon, nitrogen, oxygen and sulphur. They can have alternate single and double bonds.

2.4 Dyes colour alteration

The answer lies in the Modifiers. Colour modifiers like methyl or ethyl groups can actually alter the colour of dyes. They do so by altering the energy in the delocalised electrons. It has been found that by addition of a particular modifier there is a progressive alteration of colour. An example can be given for methyl violet series in Figure 2.1 until Figure 2.4.

Step A: When no methyl group is added the original dye *Pararosanil* as it is called red in colour.

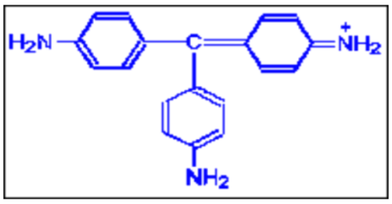

Figure 2.1: Structure of Pararosanil

Step B: As Four Methyl groups are added the reddish purple dye *Methyl Violet* is got.

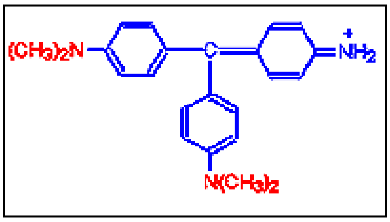

Figure 2.2: Structure of Methyl Violet

Step C: With the addition of more groups a purple blue dye *Crystal Violet* is obtained. It has in it six such groups.

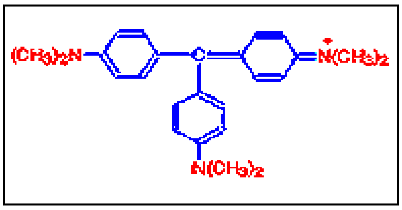

Figure 2.3: Structure of Crystal Violet

Step D: Further addition of a seventh methyl group the dye that is got is called *Methyl green.*

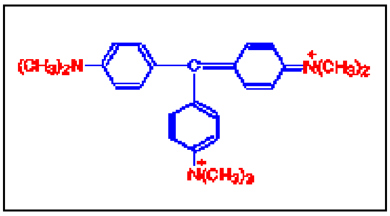

Figure 2.4: Structure of Methyl Green

2.5 Solubility and cohesiveness of dyes

The answer to this riddle lies in substance called Auxochrome. Moreover the Auxochromes has also the abilty to intensify colours. It is a group of atoms which attaches to non-ionising compounds yet has the ability to ionise. Auxochromes are of two types, positively charged or negatively charged. Several types of auxochromes are illustrated in Figure 2.7.

-OH	**-NHR**	**-Cl**
-Br	**$-CH_3$**	**$-NO_2$**
-COOH	**$-NH_3$**	**$-SO_3H$**

Figure 2.7: Types of Auxochromes

2.6 Fundamentals of ultrasound treatment

According to Darinka Brodnjak Voncina *et al.*, (2003), the part of the sonic spectrum, which ranges from about 20 kHz to 10 MHz, is called ultrasound. Ultrasound waves, like all sound waves, consist of cycles of compression and expansion. Compression cycles exert a positive pressure on a liquid, pushing the molecules together; expansion cycles exert a negative pressure, pulling the molecules away from one another. If a large negative pressure is applied to a liquid (here it is the acoustic pressure on expansion), so that the distance between the molecules exceeds the critical molecular distance R (the value R for water is 10.8 cm) necessary to hold the liquid intact, the liquid will break down and voids will be created (i.e. cavitation bubbles will form). Cavitation bubbles are much more consist of $^{\cdot}OH$ radicals which are the main reactions character in ultrasound treatment. These radicals will decide what the experiment turned out to be.