Chapter 2

Microwave Coloration

Microwave dyeing takes into account the dielectric and the thermal properties of matter. The dielectric property refers to the intrinsic electrical properties that affect the dyeing by dipolar rotation of the dye and influences the microwave field upon the dipoles. The aqueous solution of dye has two components which are polar, in the high frequency microwave field oscillating at 2450 MHz. It influences the vibrational energy in the water molecules and the dye molecules.

The heating mechanism is through ionic conduction, which is a type of resistance heating. Depending on the acceleration of the ions through the dye solution, it results in collision of dye molecules with the molecules of the fiber. The mordant helps and affects the penetration of the dye and also the depth to which the penetration takes place in the fabric. This makes microwave superior to conventional dyeing techniques.

Microwave promoted organic reactions are known as environmentally Benign methods that can accelerate a great number of chemical processes. In particular, the reaction time and energy input are supposed to be mostly reduced in the reactions that are run for a long time at high temperatures under conventional conditions [39]. Microwave is a volumetric heating (fast), whereas conventional is a surface heating (slow), as shown in Fig.10. This fact has been realized in textile coloration by many authors [40].

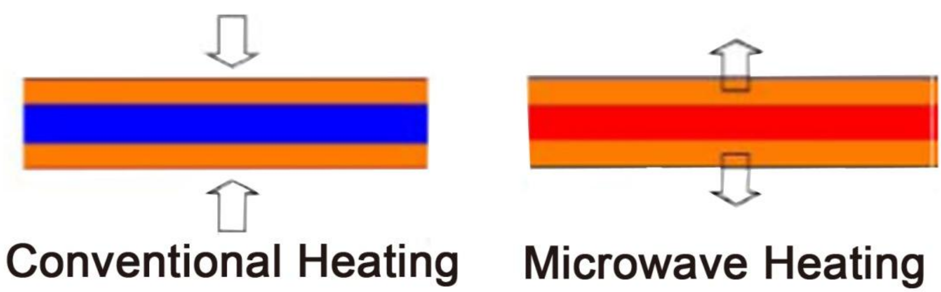


Fig. 10. *Microwave heating (volumetric) versus conventional heating (surface).*

2.1 Flax

Owing to the poor dyeability of flax fibres, a method based on microwave treatment of flax fiber with urea to improve its dyeability with reactive dyes was recently developed. It was found that the treated flax fibers had significantly improved dyeability. The causes to the improvement of the dyeability of the flax fiber were found to be the increased absorption of dye on the fiber and the increased reaction probability between the dye and the fibre [41,42].

2.2 Polyester

2.2.1 Dyeing of Polyester Fabric

The possibility of coloration of polyester fiber using microwave irradiation was studied [43]. An investigation was undertaken to assess the effect of microwave heating on aqueous and solvent-pretreatment (perchloroethylene), as well as dyeing polyester fibers with disperse dyes. Microwave irradiation and solvent-pretreatment allow a high increase in dye uptake and dyeing rate acceleration. Performance of dye leveling and color homogeneity was achieved, which was found to be better than that obtained by conductive heating. The rate of dyeing with microwave heating is much faster than the rate of dyeing with conductive heating. In the case of microwave heating equilibrium can be reached within a few minutes, whereas in the case of conductive heating equilibrium was established after a few hours. Of course, this depends upon conditions of pretreatment (time, temperature and nature of solvent, as well as temperature of the dyeing bath). In other words, the heating technique is the main factor in this respect. Polyester dyeing rates were also evaluated; the result showed that the rate of dyeing with microwave heating is much faster than the rate of dyeing with conductive heating. In the case of microwave heating equilibrium can be reached within a few minutes, while in the case of conductive heating equilibrium was established after a few hours. The half dyeing time ($t_{1/2}$) was reached in a few second when using microwave irradiation versus four hour in case of conductive heating [43].

A study on the effect of microwave irradiation on the extent of aqueous sodium hydroxide hydrolysis of PET fibre and the impact of this treatment on its coloration with disperse dyes was investigated. Comparison of the results obtained from the microwave irradiation and the conventional heating methods showed that the rate of hydrolysis was greater using microwave irradiation. The treated fabric was then dyed using microwave irradiation to heat the dye bath. Increased levels of dye uptake were observed with increasing weight loss of the hydrolyzed polyester fabric [44-46].

The rates of dyeing of polyester fibre with amino – and hydroxy – substituted anthraquinones in aqueous N, N – dimethylformamide (DMF) using microwave and conductive heating have been compared. Structural changes, commonly associated with interactions between DMF and polyester fiber, were limited and minimal shrinkage occurred due to the low DMF to water ratio and short dyeing times. Tensile properties reflected this minimal shrinkage through increased elongation at break, and differential scanning calorimetry also indicated that structural changes were minimal. Microwave radiation increased dye diffusion, shrinkage, and elongation at break compared to conductive heating. It is believed that molecular oscillation within the microwave–irradiated dyebath increases the rate of migration of dye to the fibre interface and enhances the plasticization of the polymer by DMF, thereby increasing the rate of dye diffusion within the fiber. Localization of energy associated with the use of microwave radiation is believed to be the predominant cause of increase in the rate of dyeing [47].

2.2.2 Effect of Microwave Pretreatment on the Dyeing Behavior of Polyester Fabric

Polyester fabric (filament by filament) was pretreated in a microwave oven in the presence of solvent and subsequently dyed with commercial disperse dyes {Dispersol Red C-B (CI Disperse Red 91) and Dispersol blue B-G (CI Disperse Blue 26} at different temperatures and for different durations of time. It was observed that the solvent interaction with the polyester could be enhanced by using microwave heating. Solvent molecules interact rapidly, not only with the surface of the fiber but also with the interior parts. Scanning electron microscope results showed that structural modifications take place, which produce surface roughness and voids; this enhances the dye uptake by threefold in comparison to conventional methods [48].

2.2.3 The Research Progress of the Physical Technology on the Polyester Fabric Dyeing

Some new physical methods were introduced to solve the problems in dyeing polyester process. Methods such as ultrasonic, low temperature plasma, supercritical carbon dioxide, microwave, microcapsules, radiation and electronic pre-illuminates are introduced on the point of ecology. Dyeing ability of polyester fiber and dyeing system is improved and quality is increased. Waste water discharge is reduced, no water or non water dyeing is realized to save energy and protect environment [49].

2.2.4 The Level Dyeing Technology of Polyester Fabric by Microwave

Microwave fixation method was used with seven solvent systems (i.e., 100% water, 10, 30, 50% urea and 10, 30, 50% DMF) in promotion of dyeing of polyester. In the respective pad-baths, the padded polyester fabrics were exposed over a boiling water bath to maintain sufficient moisture content during irradiation. The colour strength values were used to determine the depth of shade or concentration of the dye associated with the seven dyeing methods. DMF, as a strong interacting solvent, causes plasticization of polymer chains by weakening interchain cohesive forces in the amorphous and in the ordered non-crystalline regions of the polymer. When the crystallites formed are large, the swollen polymer structure is rigid, causing formation of voids upon removal of the solvent. Dye uptake will then be greater due to the voids within the polymer increasing the internal surface area [50].

2.3 Polyamide

Many authors have investigated the feasibility of using microwaves for a variety of textile processes including heating, dyeing, finishing, fixation, printing, and drying [51-53]. This application allows some possibilities of energy conservation, reduction of processes, time and chemicals used, production increment and minimization of environmental pollution. The effect of microwave irradiation on dyeing of polyamide fibers (nylon-6) with reactive dyes was studied and the influence of microwave irradiation on the polymer characteristics was compared with conventional heating [54]. The result showed that there are increases in rate of dyeing, and dye uptake levels with high decrease in shrinkage value when using microwave if compared with traditional heating, and this decrease increased when adding alcohols. There are increases in tensile strength as well as elongation. The results show also that microwave heating has no solublizing effect on nylon-6 fabric either in presence or absence of alcohols. Influence of microwave irradiation on nylon-6 molecular weight (M.W.), intrinsic viscosity (η), degree of polymerization and end groups content ($-NH_2$, -COOH) was also evaluated. It was observed that there is an increase in terminal end groups ($-NH_2$, -COOH) with increasing boiling time, and there was also an increase when microwave irradiation was used if compared with traditional heating. However the value of intrinsic viscosity (η), molecular weight (MW) and degree of polymerization (DP) were decreased as the boiling time increased [55].

2.4 Cotton

2.4.1 Microwave Dyeing of Cotton

A recent method based on microwave dyeing of cotton and cotton/wool blend fabric with microwave irradiation to improve its dyeability with reactive dyes was recently reported. A high increase in dye uptake and acceleration in the dye rate was observed. Microwave radiation appears to be an effective technique for dyeing cotton and cotton/wool blend fabrics and is useful in enhancing dye uptake when compared with conventional heating. From the kinetic parameter it was observed that the $t_{1/2}$ value of the dyed samples is shorter when using microwave irradiation than of those dyed by using conventional heating. Additionally, it is shorter when dyed with the two-bath method than the one-bath method; the ΔH for samples dyed with microwave irradiation is less than that of samples dyed with traditional heating. It can be observed also that the $-\Delta\mu^{\circ}$ has a negative value, which indicates that the dyeing process is an exothermic process. The results of the X-ray diffraction pattern as well as those of the scanning electron microscope indicate that the crystallinity of the fibre decreases with increasing exposure time to both types of heat, but with the certainty that the decrease is more significant with the microwave irradiation. This decrease in crystallinity is associated with an increase in fibre diameter. The value of the $t_{1/2}$ is shorter when using microwave irradiation than with conventional heating. The fastness tests for washing, rubbing, perspiration as well as fastness to light are relatively lower than their corresponding samples dyed using microwave heating [56].

The removal of natural impurities from cotton fibres using oxygen microwave low temperature plasma was studied. The influence of treating power, air pressure and time to the removal efficiency, strength and whiteness of bleaching, were evaluated and comparisons were made with conventional pre-treatment. The research results suggested that using oxygen microwave low temperature plasma in place of traditional refining technology to treat cotton knitted fabrics, the capillary effect, bursting strength, whiteness and the K/S value of dyeing are close or better than the conventional pre-treatment [57, 58].

Dyeing and fixation of cotton fabric with reactive dye using microwave was researched and compared with conventional dyeing process. Based on trials, the results showed that the dye uptake and color fastness of microwave dyed fabric were similar or higher than with conventional process. The microwave heating could shorten dye time, and save energy greatly [59].

The cotton reactive dyeing using dip-dyeing method by microwave heating was also studied. The effects of Glauber salt (Na_2SO_4), soda ash (Na_2CO_3) and liquor ratio on microwave dyeing were discussed. The results showed that cotton fabric could be smoothly dyed by reactive dyes using dip-dyeing method and under microwaves. Na_2SO_4, Na_2CO_3 and liquor ratio had effect on dye exhaustion and dye fixation, and the color fastnesses of dyed fabrics were good. The physical properties of microwave dyed fabric were also studied; the results indicated that the tear strength and tensile strength of the fabric were improved and the flexibility of the fabric was little influenced [60].

Using pad-batch method, the effect of batching time on coloration of cotton with monochlorotriazine reactive dyes using microwave irradiation and conventional heating was investigated. The results show that microwave for short time (2 min) was better than 12-h batching time under conventional heating [61, 62].

2.4.2 Microwave Versus Conventional Dyeing of Cotton Fabrics

Microwave irradiation dyeing and conventional dyeing were compared. The results showed that the color depth, color fullness, levelness and crocking fastness of fabrics dyed by microwave irradiation method were comparative to those of conventional dyeing. The effect of microwave irradiation dyeing process on dyeing behavior was investigated through single factor experiment method: the optimal dyeing technique was obtained through orthogonal experiment: the power of microwave irradiation was 595 W, dyeing time and fixation time were 6 min and 5 min, 15g/L of sodium sulfate, 15 g/L of sodium carbonate. The crystallinity of cotton fiber was decreased under microwave irradiation, which was favorable to improve the dyeing behavior of cotton fabric [63].

2.4.3 Application of Microwave Technology in Cotton Fabric Dyeing with Reactive Dyes

The influence of different factors on dyeing depth was explored when the cotton fabric was dyed with K reactive dyes by microwave radiation, and the rubbing fastness and soaping fastness of the fabric by conventional dyeing and microwave dyeing were compared. And the effects of microwave heating on the dyeing properties of different dyes were researched. The results showed that dyeing time of cotton fabric by microwave heating could be greatly shortened, and the dyeing performance was similar to conventional dyeing process [64].

2.4.4 Saturated Steam-Assisted Radio Frequency Fixation of Reactive Printed Cotton Fabrics

Previous study declared that the development of a prototype machine for the processing of fabrics, which can be used as a reactor for the continuous finishing processes. The optimum applicator design for fabrics was developed in accordance with laboratory – scale experimental studies. Reactive printed samples were treated with the combination of radio frequency and steam in order to take advantage of the steam energy and to improve energy absorption. The colour yields of the samples fixated with the combination of radio frequency and steam energy were compared with conventional steaming (10min) and thermofixation (5min) processes. It was observed that steam – assisted radio frequency fixation ensured similar colour yields in a shorter setting time (3min) compared with conventional methods. It was concluded that the new system could be an alternative method of setting, with the advantages of time savings and lower energy consumption [65].

2.4.5 The Use of Microwave Energy for the Fixating of Reactive Printed Cotton Fabrics

The wastes which are formed by the consumption chemical, water and energy, play an important role on the increase of environment pollution in textile industry, like other industries. Assessment of chemical and energy saving potential are of great importance in terms of costs and environmental issues. On this account in this study, application of microwave energy for the fixation of reactive printings was investigated. It was determined that the fixation of the samples could be obtained with only microwave energy without a drying process. Higher color yields were ensured with microwave fixation compared with conventional methods for the small and medium molecular sized (red and blue) reactive dyestuffs. On the other hand lower color yields occurred at microwave fixation process for the dyestuffs with big molecular size (turquoise), compared with conventional methods. The effects of the concentration of urea in the printing paste were also unvestigated and it was shown that adequate color yields could be obtained without using urea, depending on the dyestuff properties [66].

2.5 Wool

2.5.1 Dyeing of Wool Fabrics

The difficulty in dyeing of wool fibre is due to its scale-like surface structure which contains a hydrophobic lipid barrier [67]. This complex structure makes it difficult for the dye molecules to penetrate the fiber molecules, resulting in low level of the dye exhaustion. Improvement in dyeability of wool fabric by microwave treatment was investigated. The color yield of the fabric treated under various conditions, i.e. the microwave time treatment and power were evaluated. It was observed that the color yield of wool fabric was improved after microwave treatment. The treatment time and irradiation power have a greater impact on the color yield of dyed fabric. The color yield of dyed fabric increases with increasing treatment time, but decreases with increasing power from 400W to 700 W. The longer the treatment time, the greater is the color yield of dyed fabric, as a result of the grater dyeability of treated fabric. The microwave treatment causes a slight damage on the surface scale of the wool fiber, this promoting the adsorption and penetration of dye molecules into the wool fibers as well as improving the extent of reaction between reactive dye and wool fibers. The microwave irradiation doesn’t significantly affect the crystallinity and the chemical structure of wool fibers. The tensile strength increased after microwave modification [68-70].

Wool fabric was treated with microwave irradiation. The surface morphological structures and crystallinity of the untreated and microwave-treated wool were investigated with scanning electron microscopy (SEM) and X-ray diffraction (XRD).Wool was treated with microwave and then dyed with Lanasol reactive dyes and Palatin 1: 1 metal complex dyes. Adsorption behavior and diffusion coefficient were also evaluated. A higher dye uptake rate and increased diffusion coefficient of treated fibers were observed in the dyeing test, which was attributed to the damages of wool surface morphological structure under microwave irradiation [71]. Use of microwave heating for dyeing wool fabrics with palatine acid red means saving energy and time was also investigated. The optimum color strength is obtained in minutes, with good leveling and compatible fastness properties with conventional method. The scanning electron microscope examination revealed that microwave helps in physical change of microstructure of the fibre with higher dye diffusion. A kinetic investigation of the dyeing process revealed that the half dyeing time ($t_{1/2}$) of dyed wool using conventional heating was higher than ($t_{1/2}$) of dyed wool when using microwave heating. The opposite holds true for the specific dyeing rate constant (K') and diffusion coefficient (D). Comparison of the values of dye affinity ($\Delta\mu°$) and dyeing heat (ΔH) shows that the affinity of samples dyed using microwave heating is much higher than of those dyed using conductive heating. The heat of dyeing is lower in case of microwave heating; both are exothermic reaction [72].

2.5.2 Microwave Heating for Fixation of Pad-Dyeing on Wool

Microwaves are high – frequency radiation capable of producing very rapid, uniform and efficient heating in suitable materials. In particular, they can be used for the rapid heating and fixation of pad – dyeing on textile. The feasibility of applying certain reactive dyes to wool in fixation times of 30-60s has been demonstrated. Factors influencing the rates of fixation of the dyes have been investigated in some detail [73].

2.6 Silk

The possibility of dyed silk fabric using microwave irradiation was studied. The measurement results showed that when microwave radiation is applied to the treatment of silk the dye uptake, color fastness and the coloring of silk can be improved. It is very prospective when microwave treatment is combined with the traditiona1 dyeing method [74].

Study about the micropore structure of mulberry silk after being refrigerated at super-low temperature and radiated with microwave was evaluated. Through the analysis and research about the micropore morphological structure of the boiled mulberry silk fiber after being refrigerated at super low temperature and radiated with microwave, cracks in the longitudinal surface and many micropores in the horizontal cross-section due to the obvious thermal dilation during treatment appeared [75].

2.7 Application of Microwave Technology in Textile Modification

The mechanism of microwave including thermal effect and nonthermal effect and drying characteristics of microwave was reviewed. The applications of microwave technology in textile dyeing and finishing was introduced: pretreatment (degumming of refining, retting of silk fabric and bleaching), dyeing (by fabric or two mode, microwave could not be applied in dyeing of hydrophilic fiber but in hydrophobic fiber by adding appropriate auxiliaries), printing (the printed fabric was irradiated by microwave, which could prevent the water in the printing paste to outflow, and these water could be applied in the fixation and tintage on the fabric) and finishing (epoxy resin finishing, formaldehyde – free durable press finish, oil repellent and water repellent finish). It was pointed out that the applications of microwave technology in other fields including measuring humidity, drying latex of the carpet, the drying of polyester, treatment of nylon rope and microwave low temperature plasma finishing. The development trend of microwave technology was also prospected [76].

2.8 Acrylic Fiber

Microwave dyeing was carried out under a variety of conditions in terms of the power and time of a microwave to investigate the effects of microwaving on the dyeability of acrylic fibers. The results have shown that, at low concentrations of dye, adsorption using the microwave - based procedure is higher and much faster than conventional methods, but K/S is the same around the saturation point**.** The surfaces of microwave-irradiated acrylic fibers are rougher than conventionally dyed fibers, allowing the dye molecules to permeate and adsorb into the acrylic fibers. As a result, a reaction between the dye molecules and the acrylic fibers would be more probable. Differences in tensile strength and thermal gravity parameters for fibers dyed by conventional and microwave methods are not considered to be a significant cause for concern.

Increased dyeability is related to the local overheating due to microwave irradiation [77] and the increased roughness of the fiber surface. A power of 720 W and microwave irradiation time of 14 minutes have been found to be an optimum dyeing condition for acrylic fibers, although 5 minutes using 720 W microwave irradiation is enough to obtain the same dyeability as conventional methods [78].

2.9 Polypropylene

2.9.1 Acid Dyeing of Polypropylene

A process for making a surface of a non-polar polymeric material receptive to coloration with an acid dye was studied. This study concerns processes comprising treating the non-polar polymeric surface with low temperature microwave plasma wherein a chemical compound has been added, thereby creating receptor sites for acid dye on the surface of the non-polar polymeric material. It was observed that the large volume microwave plasma generator (LMP) treatment enhances acid dyeability of non-polar polymeric material. The result of the evaluations indicates that strongly basic monomers such as amines hexamethylene diamine, acrylamine, hydrazine, acrylic acid and 1, 3-diaminopropane, produce very satisfactory dyeability. Amphoteric, weakly acid or weakly basic monomers, such as the alcohols, and amines formamide, butylamine, ammonia, heptamine, toluidine, acetonitrile and vinylpyrroline are less effective. The amine 1, 3-diaminopropane proved to be the most effective monomer for polypropylene fiber, a woven fabric, or non woven fabric. LMP technology offers a technique for uniformly depositing a layer of plasma product of as yet unspecified chemical nature (depending on the plasma monomer used) onto the surface of a non-polar polymeric material such as polypropylene fiber a woven fabric, or non woven fabric to enhance its dyeability with acid dyes [79].

2.9.2 Disperse Dyeability of Polypropylene Fibers Via Microwave and Ultrasonic Energy

In this study, the dyeability of polypropylene fibers with a disperse dye via microwave and ultrasonic energy was examined. A dye bath having a liquor-to-goods ratio of 20:1, and including dyestuff 2% owf was prepared and dyeing experiments using microwave and ultrasonic energy were carried out. In the case of microwave dyeing, experiments have been carried out at different energy levels (L, M-L, M, M-H and H) and different time ranges (1 to 5 min) while in the case of ultrasonic energy different temperatures (20, 40, 60 and 80 degrees C) and different time range (1 min to 30 min) were used. Additionally, effect of carrier was also investigated. Dyed samples were examined by determining their K/S values. Diffusion coefficients in all methods were calculated using Shibusawa's approximation of Hill's equation. Washing fastnesses of dyed samples were also examined. This study showed that the dyeability of polypropylene fibers was increased by both microwave and ultrasonic energy [80].

2.10 Use of Microwave Fixation in Printing with Natural Color

Until recently, use of microwave in textiles is restricted to drying process. Recently, some researches have studied the feasibility of using microwaves for variety of textile processes, e.g. drying, dyeing, finishing and printing. Owing to the importance gained by microwave heating and natural dyes, researchers studied the effect of microwave fixation time, additives, and mordant in coloring wool fabric with natural dyes (Lawsone, obtained from *Henna*, *Lawsonia alba* Lam. Leaves). They observed that Lawsone (2-hydroxy-1, 4-naphthoquinone), the dye component of henna, can be employed to print the wool fabric by using microwave fixation technique. Orange color and higher K/S compared to that obtained by conventional methods are obtained without the need of drying step on using this technique. The color strength and overall fastness properties of microwave fixed samples are found to be good and the samples acquire soft handle [81].

2.11 Synthesis

2.11.1 Microwave-Assisted Synthesis of Eco-Friendly Binders from Natural Resources

The most widely used technique for printing textiles is the pigment printing. Aqueous formulations for pigments print pastes typically consist of pigment(s), a suitable thickener, binder and cross linking agents. Because the pigments have almost no affinity for the substrate, the binder and cross linking agents bind the pigments to the surface of the substrate during the heat-curing or fixation step. Binders are also responsible for the hand and many performance properties of the printed textile [82,83]. Synthesis of eco-friendly binders from natural resources using microwave irradiation to improve textile printing was studied. The prepared polymers using microwave heating at reaction time of 45-60 min ensures the formation of alkyd resins *versus* 8-10 hrs when using conventional heating. Modified alkyd resins from sunflower oil have been successfully used as binders in the formulation of pigment printing pastes. They were characterized by non-Newtonian pseudo plastic behavior, weight loss as well as water absorption. Tg of the prepared binders was to be found in the range of (+2.5 - +5.7) which indicate the glassy state of binders is typically formed by cooling to very low temperature. It was observed that the roughness and overall properties depend on the type of fabric and binder used in printing pastes. The rubbing, washing and perspiration fastness ranged from good to excellent in case of using prepared binders, while the ranges were from poor to good in case of commercial binder. The printings have excellent fastness to light. In addition, all samples show soft handle, except in commercial binder it shows harsh handle [84].

2.11.2 Microwave-Assisted Synthesis of New Polyfunctionally Substituted Arylazo-Aminopyrazoles

Synthesis of new poly functionally substituted arylazo - aminopyrazoles for utilization in printing via conventional and microwave heating was investigated. This work has been carried out to investigate the synthetic approaches of new heterocyclic azo-dyes via conventional refluxing and microwave heating. As from a sequence of reactions starting from cyanoacetic acid, 4 – arylazo - 2*H* – pyrazol – 3 - ylamines and 4-arylazo-2-phenyl-2*H*-pyrazol-3-ylamines are obtained. Structures of the obtained compounds were established with certainty via inspection of spectroscopic and analytical data. Evaluation of fastness properties and spectral data of these new disperse dyes in printing polyester fabrics were investigated. From the result we can observe that these dyes give brown to orange-red shades on polyester fabrics showing poor to very good fastness properties [85].

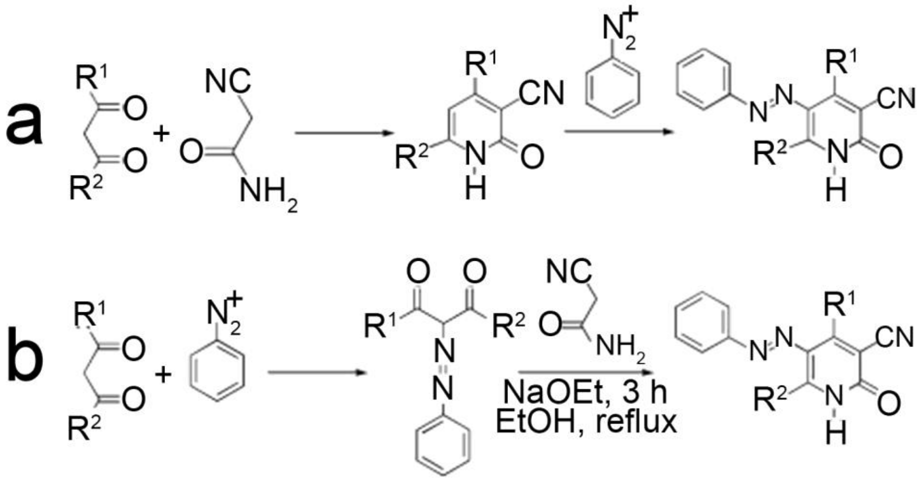
2.11.3 One-Pot Synthesis of Disperse Dyes under Microwave Irradiation: Dyebath Reuse in Dyeing of Polyester Fabrics

A series of 4-hydroxyphenylazopyrazopyrazolopyrimidine disperse dyes were prepared via one-pot reactions of p-hydroxyphenylhydrazone, hydrazine hydrate, and acetylacetone or anaminones using microwave irradiation as an energy source. Structural assignments of the dyes were confirmed by X-ray crystallographic structure determination. Instead of discharging the dyebath after each dyeing cycle, the residual dyebath was spectrophotometrically analyzed and then pH readjusted for a repeat dyeing with longer time. Fastness of the dyed samples was measured after each recycle. Most of the dyed fabrics tested displayed good light fastness and excellent fastness to washing and perspiration. Finally, the biological activity of the synthesized dyes against gram positive bacteria, gram negative bacteria and yeast were evaluated [86].

2.11.4 Microwave-Assisted Synthesis of 5-Arylazo-4, 6-Disubstituted-3-Cyano-2-Pyridone Dyes

Azo compounds are the largest group of colorants in terms of number and production volume of currently marketed dyes and pigments. The importance of azo compounds as colorants is due to the simplicity of their synthesis by diazotization and azo coupling, and to the almost innumerable possibilities presented by variation on the diazo compounds and coupling components, in conjunction with their generally high molar extinction coefficient and moderate / high fastness properties [87]. Arylazo colorants containing pyridone rings can be prepared from β-diketones and various diazonium salts, followed by condensation with cyanoacetamide as follows: [88-90].

The arylazo dyes obtained in such manner do not contain unreacted pyridone material and are generally obtained in higher yields. Long reaction times, the use of a toxic and strong base for the condensation step, are the other disadvantages of conventional method. The possibility of improved method for synthesizing novel, 5-arylazo-4, 6-disubstituted-3-cyano-2-pyridone dyes from β-diketones and various diazonium salts, followed by high speed microwave-assisted condensation with cyanoacetamide was recently reported. It was observed that the synthesis of an important group of azo-based dyes was rapid and efficient via use of microwave heating. The use of controlled sealed vessel microwave heating allowed the preparation of a variety of pyridone colorants in very short reaction times, and high yields, if compared with conventional methods [90].



Scheme 1. *Synthetic methods for the preparation of arylazopyridones.*

2.12 Colour Removal

2.12.1 Microwave-Assisted Degradation of Remazol Golden Yellow Dye Wastewater as well as Enhanced Chlorine Dioxide CLO₂ Catalytic Oxidation Process

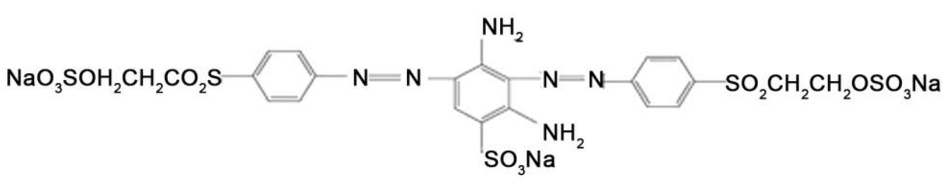


Fig. 11. *Chemical structure of remazol golden yellow RNL.*

The color and high COD of effluents from dye house cause serious environmental contamination problems nowadays. In particular, azo dyes represent about half of the dyes used in the textile industry and, as a consequence, a relevant problem of pollution related to the release of these products in the environment is taking place [91,92]. Although there were several other technologies available for the removal of color and COD from azo dye wastewater such as biodegradation [93], sorption [94-96], electrochemical and oxidative degradation [97-98], and chlorine dioxide (CLO_2) catalytic oxidation was a very attractive and useful technique for treatment of dye house effluents

[99–101]. The removal of remazol golden yellow dye in order to assess the effectiveness and feasibility of microwave enhanced chlorine dioxide (CLO_2) catalytic oxidation process as well as the operating parameters such as the CLO_2 dosage, catalyst dosage, and pH was evaluated [99-101]. The results showed that microwave-enhanced catalytic oxidation process could effectively degrade remazol golden yellow dye with low oxidant dosage in a short reaction time and extensive pH range compared to the conventional wet catalytic oxidation. Under the optimal condition (CLO_2 concentration 80 mg/L, microwave power 400W, contacting time 1.5 min, catalyst dosage 70 g/L, and pH 7), color removal efficiency approached 94.03%, corresponding to 67.92% of total organic carbon removal efficiency. It was found that the fluorescence intensity in microwave-enhanced ClO_2 catalytic oxidation system was about 500 a.u. which verified that there was much hydroxyl radical produced [99].

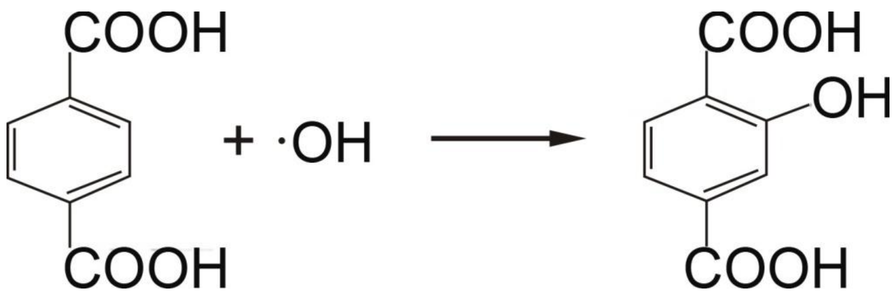


Fig. 12. *Reaction between hydroxyl radical and terephthalic acid.*

Compared with different processes, microwave enhanced ClO_2 catalytic oxidation system could significantly enhance the degradation efficiency. It provides an effective technology for dye wastewater treatment [100-104].

2.12.2 Microwave-Assisted Regeneration Process of Reactive Black 5 Treatments by Combined Electro-Coagulation-Granular Activated Carbon Adsorption

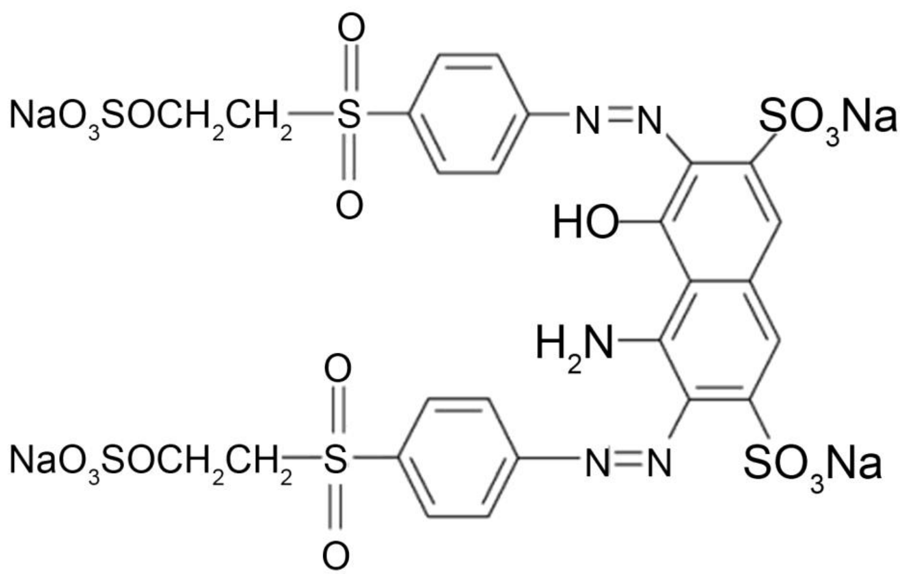


Fig. 13. *Molecular structure of C.I. Reactive Black 5 (RB5, azo dye),* λ_{max} *= 597 nm.*

Textile wastewater is a major water pollution source in developing countries and often contains high concentrations of unfixed dyes (about 20%). Azo dyes are of great concern because of their widespread use, toxic aromatic amine intermediates, and recalcitrance for aerobic wastewater treatment [105]. Several techniques have been applied to remove dyes from wastewater, including adsorption, chemical oxidation, electrochemical degradation, and advanced oxidation processes. However, their low removal abilities or high costs often limit their application [106]. Treatment of an azo dye, Reactive Black 5 (RB5) by combined electrocoagulation-activated carbon adsorption–microwave regeneration process was evaluated. The toxicity was also monitored by the *Vibrio fischeri* light inhibition test. Granular activated carbon GAC of 100 g L^{-1} sorbed 82% of RB5 (100 mgL^{-1}) within 4 h. RB5- loaded GAC was not effectively regenerated by microwave irradiation (800 W, 30 s). Electrocoagulation showed high decolorization of RB5 within 8 min at pH 7, current density of $277Am^{-2}$, and NaCl of 1 gL^{-1}. However, 61% COD residue remained after treatment and toxicity was high (100% light inhibition). GAC of 20 g L^{-1} effectively removed COD and toxicity of electro coagulation-treated solution within 4 h. Microwave irradiation effectively regenerated intermediate-loaded GAC within 30 s at power of 800 W, GAC/water ratios of 20 g L^{-1}, and pH of 7.8. The adsorption capacity of GAC for COD removal from the electro coagulation-treated solution did not significantly decrease at the first 7 cycles of adsorption/regeneration. The adsorption capacity of GAC for removal of both A_{265} (benzene-related groups) and toxicity slightly decreased after the 6th cycle [107].

2.12.3 Regeneration of Acid Orange 7-Exhausted Granular Activated Carbons with Microwave Irradiation

An investigation was performed for the regeneration of three granular activated carbons (GACs) exhausted with acid orange 7 (AO7). The three GACs were made from different materials, i.e. coconut shells, almond nucleus and coal. The AO7 adsorption process was carried out in a continuous-flow adsorption column. After adsorption, the AO7-saturated GAC was dried at 120 ℃, then regenerated in a quartz reactor by 2450 MHz microwave (MW) irradiation at 850 W for 5 min. The efficacy of this procedure was analyzed by determining the rates and amounts of AO7 adsorbed in successive adsorption–MW regeneration cycles. Effects of this regeneration on the structural properties, surface chemistry and the AO7 adsorption capacities of GAC samples were examined. It was found that after several adsorption–MW regeneration cycles, the adsorption rates and capacities of GACs could maintain relatively high levels, even higher than those of virgin GACs, as indicated by AO7 breakthrough curves and adsorption isotherms. The improvement of GAC adsorption properties resulted from the modification of pore size distribution and surface chemistry by MW irradiation [108, 109].

2.12.4 Microwave-Assisted Synthesis of Titania Nanocubes, Nanospheres and Nanorods for Photocatalytic Dye Degradation

Nanomaterials of transition metal oxides have attracted a great deal of attention from researchers in various fields due to their numerous technological applications [110-113]. Among them, nanocrystalline titania has been attracting increasing attention due to its fascinating properties and potential applications. Titanium dioxide is a versatile material which is being investigated extensively due to its unique optoelectronic and photochemical properties such as high refractive index, high dielectric constant, excellent optical transmittance in the visible and near IR regions as well as its high performance as a photo catalyst for water splitting and degradation of organics [114]. With a band gap of

3.0–3.3 eV, titanium dioxide has been photo catalytically active only under ultraviolet light (wavelength k\400 nm) [115]. Titanium dioxide mainly exists in three crystalline phases: anatase, rutile, and brookite [116]. Among the three crystalline forms, anatase titanium dioxide is attracting more attention for its vital use as pigments [117], gas sensors [118], catalysts [119-120], photocatalysts [121-123] in response to its application in environmentally related problems of pollution control and photovoltaic [124]. A simple microwave method to synthesize phase pure anatase and rutile nanotitania with different morphologies *viz*., cubes, spheres, and rods was evaluated. Photocatalytic activity studies of the synthesized samples were carried out using the dye, methylene blue in aqueous solution under ultraviolet light irradiation. The photoluminescence (PL) features of the synthesized titania nanostructures were also compared in the present study. Photocatalytic dye degradation studies were conducted using methylene blue under ultraviolet light irradiation. Dye degradation ability for nanocubes was found to be superior to the spheres and the rods and can be attributed to the observed high surface area of nanocubes. As synthesized titania nanostructures have shown higher photocatalytic activity than the commercial photocatalyst Degussa P25 TiO_2 [125].

2.12.5 Microwave Enhanced-Sorption of Dyestuffs to Dual-Cation Organobentonites from Water

The microwave enhanced-sorption of dyestuffs such as Neutral Red S-BR, Neutral Dark Yellow GL and Acid Blue B onto organobentonites from water was investigated. The decolorization rates of various dyestuffs by organobentonites were increased from 18.0% to 71.8%, the saturate desorption capacity of Neutral Red S-BR and Acid Blue B were increased 83.9% and 76.3 % by microwave irradiation, respectively. The value of the microwave enhanced-sorption parameter R_m increased in the following order: Neutral Red S-BR > Acid Blue B > Neutral Dark Yellow GL, which corresponded with their aqueous solubility. The zeta potentials of particles were decreased greatly by microwave, which is very significant for improving both sorption of dyestuffs to organobentonites from water and the separation of the adsorbents from treated water [126].