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Supercritical Carbon-dioxide Assisted Dyeing of Textiles: An Environmental Benign Waterless Dyeing Process

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Abstract*—The textile industry is among the industries with the highest water consumption; water is being utilized at all stages during chemical wet processing of textiles. The water effluent contains dyes as well as dispersing agent and various chemicals. The treatment of these effluents leads to the increase in the ultimate cost. Since costs for water and waste water are continually rising, and the legislator lays down increasingly stringent limits for the pollution of waste water, textile dyeing and finishing methods have to be used in future which will use no or very little water. Various new techniques, such as plasma dyeing, e-control method, solvent induced dyeing method, have been developed to overcome the present deficiency in the conventional dyeing system. One such method is the use of supercritical carbon dioxide (SC-CO2) instead of water for the dyeing of textiles, particularly made from synthetic fibres (polyester, acetate, nylon). Carbon dioxide is available in abundance, ecologically harmless, non -toxic and non-explosive. When placed above the critical point (31.1°C and 73 atmospheres), CO2 becomes a remarkable solvent for many natural and synthetic dyes, which are utilized for the colouration of cotton and various synthetic fibres. The dye solution in the supercritical CO2 is carried to the fibre to be dyed. Under certain conditions, the gas-like diffusion of supercritical CO2 disperses the dye evenly into the small pores and crevices of the fibre. In the dyeing process, the dyestuff powder is fed into the autoclave. The dyeing equipment is flushed with liquid CO2 and preheated liquidified CO2 picks up the dye and performs dyeing of the package as in solvent dyeing. This dye gets absorbed onto the fiber. When the pressure is released CO2 becomes gaseous and loses its dissolving ability and the dye residues are separated after liquidification. Carbon dioxide, free from dye, goes back into the collecting tank after completion of the dyeing process. The circulation of CO2 is stopped, dyeing autoclave is depressurized and the unused dye powder gets deposited at the bottom of the machine. Thus, super-critical dyeing does not produce any drainage and may be considered as an eco-friendly dyeing approach.

Keywords— Supercritical, Carbon dioxide, Dyeing, Solvent, Eco-friendly.

I. INTRODUCTION

The textiles industry is also one of the biggest consumers of water with conventional textile dyeing using large amounts of fresh water, which is disposed of as waste water containing dyestuffs as well as dispersing agent and various chemicals. A vast investment has to be done for the treatment of the textile effluents before it is being disposed of in the water streams. In USA alone, the textile dyeing industry has invested more than one billion dollars in past decade on environment technologies, which are designed to ensure that by-products of textile manufacturing do not pollute the environment [1-4].

Colouration of textiles is the aqueous application of colour, mostly with synthetic organic dyes, to fibre, yarn or fabric in the form of dyeing and printing. It involves the utilization of varieties of dyes and numerous processing auxiliaries/chemicals to the textile to obtain a uniform depth of colouration with colour fastness properties suitable to the end use [5]. Dyeing involves application of dyestuffs (natural as well as synthetic) to textiles by various forms of continuous pad applications, or exhaust dyeing in batch processing equipment. Knit fabrics are dyed by exhaust techniques in batch equipment and woven fabrics are most often dyed continuously.

Water scarcity and increased environmental awareness are worldwide concerns, which are causing a sharp rise in prices for intake and disposal of water. New legislation will even endanger the continuity of textile industries in the near future. The chemical wet processing of textiles continues to expand each year as older products and processes are replaced by the technological diffusion of novel products and innovative processes. Elimination of process water and chemicals would be a real breakthrough. Although there have been efforts to reduce the water input such as altering conventional equipment, recycling water and reusing wastewater—water usage is still high in the textile industry. Non-aqueous systems of dyeing can reduce or completely eliminate the amount of water used. Reducing water use provides environmental benefits as well as cost savings. Application of ultrasonic waves, microwave dyeing, plasma technology, supercritical carbon dioxide, and electrochemical dyeing of textiles are some of the revolutionary ways to advance the textile wet processing [6-12]. Supercritical carbon dioxide assisted dyeing system is one such advanced technique which offers a water-free solution. The use of supercritical fluids as a solvent in the dyeing process has attracted considerable attention in the recent years. The advantages of the fluid are both economic and ecological. Supercritical carbon dioxide (CO2) is an alternative dyeing technology that eliminates the use of water while achieving results comparable to current dyeing processes. This method of dyeing synthetic fibers replaces water from the dyeing process and also reduces the air effluents.

II. Basic Concepts Of Supercritical Fluid Carbon Dioxide

Water and carbon dioxide are our two most popular benign solvents; however, the knowledge of water's behavior as a solvent still dwarfs that of CO2. The scarcity of water in the recent times has led to the development of new technologies, for textile chemical wet processing, based on minimum utilization of water. One such technology is based on the use of supercritical carbon dioxide for dyeing of synthetic and several natural fibres. Carbon dioxide has been investigated extensively as a nonflammable, environmentally benign, inexpensive solvent – both as a liquid and also in its supercritical state. In the 1980s, supercritical CO2 (scCO2) was being hailed as a medium with solvent properties similar to those of n-alkanes, and may be considered as a simple drop-in replacement for a wide variety of organic solvents. The concept of dyeing textiles with supercritical CO2 could be considered as green from the environmental as well as economic perspectives.

For the last four decades, supercritical fluids, which are characterized by exceptional physical-chemical properties, have been used in extraction processes. These fluids have been used to extract natural substances for the production of drugs, cosmetics and spices. In 1994, a German patent was granted for a process in which a substratum was dyed using a supercritical fluid. Due to environmental regulations, research of supercritical fluids as a reaction medium and as a solvent medium for textiles has recently resurged.

Supercritical fluids are highly compressed gases which possess valuable properties of both a liquid and gas. Any gas above its critical temperature retains the free mobility of the gaseous state but with increasing pressure its density will increase towards that of a liquid. The properties, which are intermediate between gases and liquids, are controlled by pressure.

Supercritical fluids do not condense or evaporate to form a liquid or a gas. The fluids are completely miscible with permanent gases, which leads to higher concentrations of dissolved gases than can be achieved in conventional solvents. Supercritical fluids offer advantages in textile processing as they combine the valuable properties of both a gas and liquid. These fluids have solvating power or the ability to act as a solvent as well as a solute, making them desirable in the dyeing process in which disperse dyes are utilized.

Carbon dioxide is the most investigated and used gas in the supercritical fluid dyeing process. It is a naturally occurring, chemically inert, physiologically compatible, relatively inexpensive and readily available for industrial consumption [13-14].

A liquid can be converted to a supercritical fluid by increasing its temperature and simultaneously increasing pressure. A supercritical fluid may be characterized best by referring to a phase diagram as shown for carbon dioxide in Figure 1. A liquid can be converted to a supercritical fluid by increasing its temperature (T) (and consequently its vapour pressure) and simultaneously increasing pressure (p). A closed system thus reaches critical values where no boundary between the liquid and gaseous state can be distinguished, i.e., the supercritical state [15].

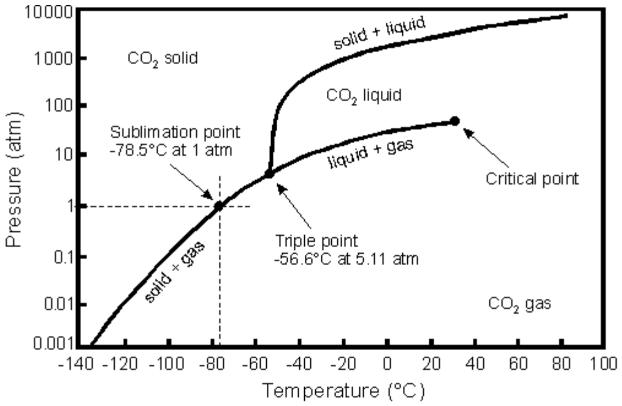

Fig. 1. Pressure-temperature phase diagram for carbon dioxide

The carbon dioxide gas is converted in to the supercritical fluid when the pressure is 60 bar to keep carbon dioxide in liquid state. However the pressure of 74 bar is necessary to keep carbon dioxide in a supercritical condition. Above these critical points (31o C and 74 bar pressure), carbon dioxide displays the solvent properties similar to these of liquid hydrocarbons. Carbon dioxide is the best choice because it is non-toxic, nonflammable, used in the food and beverage industry, and supplied in large amounts either from combustion processes or volcanic sources without the need of producing new gas and it can be recycled in a closed system. The low viscosity of supercritical fluids and the rather high diffusion properties of the dissolved molecules are especially promising aspects for dyeing processes. A supercritical dyeing fluid should easily dissolve solid dyestuffs and should penetrate even the smallest pores without the need of vigorous convection procedures.

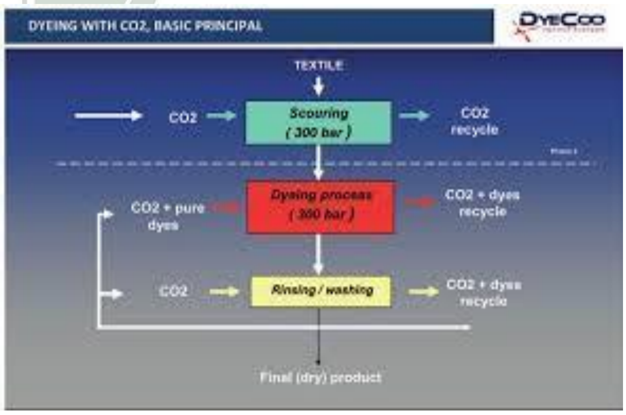

Fig. 2. Dyeing principle with scCO2 (Courtsey: DyeCoo® Textile Systems)

The principle of dyeing with supercritical carbon dioxide was invented in Germany in 1994. However, developing a well-functioning machine for such a dyeing system turned out to be too expensive. DyeCoo Textile Systems' parent company, Feyecon, in the partnership with the Delft University of Technology and Stork, ultimately resulted in DyeCoo (which was formed in 2008), which literally means "dyeing with CO2" (Figure 2). From an environmental point of view, the new dyeing machine developed by DyeCoo is revolutionary and it had won the Herman Wijffels Innovation Award for the best innovative eco-based product for 2009/2010. The final partner of DyeCoo to make history is Tong Siang Co. Ltd (Thailand), part of the Yeh Group. This polyester textile producer was the first textile industry to implement the commercial-scale supercritical fluid CO2 machine into production, branding the process as DryDye. Supercritical fluid CO2 enables polyester to be dyed with modified disperse dyes. It causes the polymer fibre to swell, allowing the disperse dye to diffuse and penetrate the pore and capillary structure of the fibres. The viscosity of the dye solution is lower, making the circulation of the dye solutions easier and less energy intensive. This deep penetration also provides effective colouration of polymers. Furthermore, dyeing and removing excess dye can be carried out in the same vessel; the residual dye is minimal and may be extracted and recycled. Currently, the process is limited to dyeing of scoured polyester fabric run in batches of 100–150 kg, although DyeCoo and its partners are developing reactive dyes for cellulosics to be available for use in this process in the not too distant future [16].

The dyestuff/supercritical carbon dioxide/fiber system represents a three-component/ three-phase system, namely the gas, the dyestuff and the fiber polymer. In their solid state, dyestuff and polymer are present in the form of three separate phases besides the supercritical mixture. The dyestuff is dissolved in the supercritical fluid, transferred to, absorbed by and diffused into the fiber. In the first approximation the system is described as the distribution equilibrium of the dyestuff between fluid and fibers. A more exact definition of the thermodynamic processes involved in this system will have to consider the solubility of carbon dioxide in the polymer and in the solid dyestuff as well as the solubility of the polymer in the fluid [17].

III. DYEING EQUIPMENT USING SUPERCRITICAL FLUIDS

A prospective dyeing apparatus for supercritical liquors is a plant which can be designed to meet special requirements [18]. The machine is an extraction plant modified for processing with the supercritical fluids. In contrasts to conventional extraction plants, the dyestuff are applied to the substrate instead of being removed, i.e. the fluid will have to be loaded with dyestuff prior to coming in contact with the goods to be dyed. This can be done in two manners – (i) the dyestuff is filled into the pressure vessel in defined quantities; and (ii) the dyestuff is filled into an additional small autoclave in the desired (surplus) quantity regulating the carbon dioxide content via pressure, temperature and/or flow control instruments. The absorption of the dyestuff by the fibre, i.e. the diffusion into the inner parts of the fibre, has to meet high levelness standards.

The necessary convection of the liquor can be achieved by an agitator within the dyeing autoclave or by moving the substrate. Another option is to penetrate the goods, either by the circulation of the liquor or by utilizing the current produced by continuous replenishment of carbon dioxide. In the latter case, the flow of replenished carbon dioxide will have to be continuously loaded with dyestuff. The residues of dyestuff or fiber admixtures to be extracted prior to dyeing will be collected in a conventional separator. The separation of phase will in this case be initiated by expansion or by raising the temperature.

A. Dyeing Apparatus

An apparatus for dyeing in supercritical carbon dioxide consists of a temperature controller, a vessel heater which surrounds the vessel, a stainless steel dyeing vessel of 50 ml capacity (with a quick release cap), a manometer, a Varex HPLC carbon dioxide pump and a cooler for cooling the head of the carbon dioxide pump (Figure 3).

Fig. 3. A typical dyeing apparatus for CO2 assisted dyeing

The apparatus was pressure-tested for use up to 350 bars and 100o C. A side arm connects the top and the bottom of the cell outside the heater to allow the supercritical carbon dioxide to circulate by thermal convection.

B. Dyeing Procedure

The fabric to be dyed is wrapped around a perforated stainless steel tube and mounted inside the autoclave around the stirrer (as shown in Figure 4a). The autoclave is then closed, evacuated and cooled with ice water. Liquid carbon dioxide is filled into the autoclave in condensed form, weighing the filled-in quantity. As soon as the autoclave has reached room temperature again, polyglycol, a heat carrier, is added to the tempering bath. The pressure rises to 250 bars within about 7 minutes, an isochoric process achieved by heating the glycol bath to 130o C. Following a dye time of 10 minutes the pressure within the autoclave is reduced to atmospheric temperature within about 2-3 minutes, the carbon dioxide being routed through a separating vessel in order to recuperate precipitated residual dyestuff. Dyestuff order is placed in the bottom of the vessel; the apparatus is sealed, purged with gaseous carbon dioxide, and preheated. When it reaches working temperature, carbon dioxide is isothermally compressed to the chosen working pressure under constant stirring. The pressure is maintained for a dyeing period of 0 - 60 minutes and afterwards the fabric is rinsed with acetone to remove residual dyestuff.

(a)

(b)

Fig. 4. (a) Fabric roll (grey/undyed) inserted in the scCO2 dyeing machine, and (b) Polyester fabric after dyeing with disperse dye using scCO2 dyeing system

The compressed carbon dioxide is recycled and used again for the dye application on polyester substrate. The complete dyeing process is schematically represented in Fig. 5.

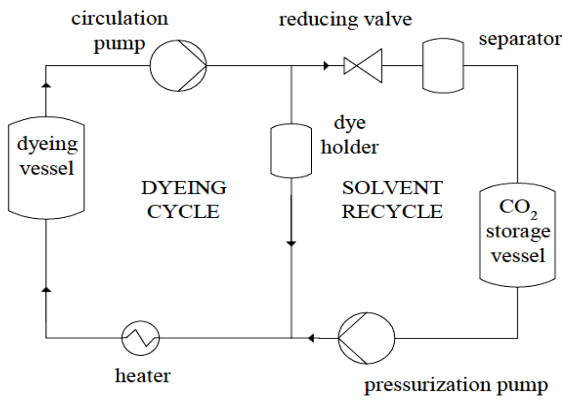

Fig. 5. Simplified flow diagram for dyeing of polyester using supercritical CO2 dyeing system

IV. Merits & Demerits Of Dyeing In Supercritical Carbon Dioxide

Table I compares conventional dyeing to dyeing with supercritical CO_2.

TABLE I. Comparison Of Conventional Dyeing And Scco2 Dyeing System

Conventional dyeing	Dyeing in $scCO_2$
Huge amount of water is required for wet processing technology of textile material during processing	No water is required for wet processing technology of textile material during processing
High volumes of waste water with the residual dye and chemicals	No waste water at all. The dye remains as powder
High-energy requirements	Only 20% energy requirement
Dyeing/washing, drying times is 3-4 hours	Only 15- 60 minutes are required for dyeing/washing

Other possible advantages of this process, claimed for textiles, are:

- Contaminated waste water streams are not produced.
- No effluents.
- Low energy consumption for heating up the liquor.
- Energy preservation because drying processes are no longer required (conventional dyeing processes consume about 3,800 kJ per Kg of water evaporated).
- No air pollution due to recycling of the carbon dioxide (the gas is not contaminated by the processes).
- Substantially shorter dyeing times.
- Penetration of voids between fibres is fast because of the absence of the surface tension and the miscibility of air with carbon dioxide under pressure.
- Environmentally acceptable formulations of dyestuff - no dispersants or adulterants are necessary.
- No chemicals such as leveling agents, pH regulations etc. have to be added.
- No need for auxiliary agents, disposing agents, adulterants, etc.
- For polyester, no reduction clearing (treatment with caustic and sodium hydrosulphite for removal of superficial unfix disperse dye) is needed.
- Very less dyeing time.
- Higher diffusion coefficients lead to higher extraction or reaction rates.

A. *Demerits of $scCO_2$ dyeing system for commercialization*

There are some drawbacks associated with the $scCO_2$ dyeing system. These are-

- Dyeing of multiple packages in the same bath.
- High pressures required for dye solubility.
- During polyester dyeing, the trimer is produced, which is usually removed using aqueous cleaning. However, in waterless $scCO_2$ system, it is a problem to eliminate this trimer.
- Impact of dyeing machine weight is related to circulation.
- There is little data about dyestuff solubility in $scCO_2$.

V. Other Applications Of Supercritical Fluids In Textiles

The supercritical system can be used in other textile processes such as:

- The UV stabilizer or even perfumes may be transferred to fibre.
- Beside polyester, the process can also be used for dyeing of protein and cellulose fibres.
- Nylon and cotton fabrics were scoured using with scCO2 and showed extraction efficiencies more than 95%. Scouring of cotton with scCO2 is also comparable and has been found better than conventional water based scouring. The scCO2 scoured fabrics have been tested for mechanical properties and for dyeing by conventional means and are found to be acceptable.

- The liquid carbon dioxide is non-polar and has a large quadruple moment. Considering this, new classes of polymeric compounds have been developed having good solubility in liquid CO2. These compounds are applied for non-aqueous sizing.
- The use of CO2 has also been investigated for desizing operation. Formulation based on fluorinated compounds quantitative desizing using super critical extraction.
- Supercritical NH3 can be used for mercerization of cellulosic materials.
- Supercritical carbon dioxide can also be used as a more environmentally friendly solvent for dry cleaning as compared to more traditional solvents such as hydrocarbons and perchloroethylene.

VI. Future Prospects Of Dyeing Textiles With Sc-Co2 Dyeing System

The supercritical carbon dioxide technology has become a commercially viable system for dyeing polyester, elastomeric and nylon. However, there are still certain hurdles which need to be overcome before the system can be used on a large scale. Currently, supercritical dyeing requires higher pressures than are currently available in conventional jet dyeing machines. To obtain the required temperature and pressures, autoclaves with large holding capacities must be used in the dyeing process. This type of equipment is still considered state-of-the-art and not readily available on commercial scale presently. The high cost of the system compared with conventional dyeing represents another obstacle. One way of offsetting the capital cost could be for supercritical CO2 to be extended to include pre-treatments such as sizing and desizing.

At present, supercritical dyeing with CO2 is confined mostly to synthetic fibers. For natural fibers, the diffusion of scCO2 is hampered by its inability to break the hydrogen bonds present in many natural fibers, including cotton, wool and silk. A further problem is that reactive dyes, direct dyes and acid dyes, which are suitable for the dyeing of these natural fibers, are insoluble in scCO2. Extended research is required for the process to work with natural fibers; either the fibers have to be modified or a new fixation mechanism need to be developed.

The major attraction of scCO2 is that it is a means of saving substantial amounts of water and energy in the dyeing of textiles. This benefit is particularly important given that water supplies are becoming increasingly scarce, especially in the textile producing regions of China, India and other Asian countries. However, there are still challenges regarding equipment cost, equipment maintenance and the dyeing of natural fibers, which have to be met with in coming future to make the technology successful commercially.

Conclusion

Supercritical fluids have special properties that could lead to substantial improvements when utilized as replacements for water in wet processing of textiles. These fluids have densities and solvating powers similar to liquid solvents combined with viscosity values and diffusion coefficients like those observed for gases. In particular, these properties make supercritical carbon dioxide (scCO2) one of the most beneficial and environmentally acceptable solvents used in manufacturing processes today. Therefore, it is anticipated that commercial textile processes using scCO2 will have many advantages when compared to conventional aqueous processes. Successful commercialization of scCO2 processing will improve the economics of dyeing and other textile chemical processes by eliminating wastewater discharges, reducing energy consumption, eliminating drying, and reducing air emissions. As a result, the use of scCO2 is expected to make textile processing more economical and environmentally friendly. Dyeing in super critical carbon dioxide can be considered as one of the best alternatives to water-based dyeing but this favourable concept is waiting for its commercial implementation. The successful commercialization of the above said concept will definitely improve the economics of dyeing by the way of elimination of wastewater discharges. This method of dyeing synthetic fibers replaces water from the dyeing process and also reduces the air effluents and may be considered as a 'Green Technology' for the future.

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