# Electrochemical method for Dye industry waste water Treatment

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**Abstract** – *The present study was mainly devoted to evaluate the applicability of differential pulse adsorptive stripping Voltammetry (DPAdSV) for the determination of ultra-trace concentration levels of a range of reactive dyes. The studied reactive dyes were found to adsorb effectively onto the hanging mercury drop electrode (HMDE). This applied electro-analytical method was primarily based on the nonel-electrolytic accumulation (adsorption) of the analyte of interest (reactive dye), followed by a cathodic reduction scan measurement. Consequently, the adsorptive stripping volta-mmo-grams of the analyzed reactive dyes exhibited several useful electrochemical signals, corresponding to the cathodic reduction of the anthraquinone, azo and halo groups. AdSV has been used successfully for monitoring and studying the electrochemical behavior of the anthraquinone-based reactive dye (Reactive Blue 19) via its well-developed AdSV peak associated with the two-electron reversible reduction of the anthraquinone moiety. The stripping voltammogram of this reactive dye in alkaline solution displayed a further AdSV peak at a more negative potential, probably related to the cathodic reduction of anthrone product.*

**Key Words** – **differential pulse adsorptive stripping Voltammetry, HMDE, accumulation, anthraquinone reactive dye, azo and halo groups.**

## INTRODUCTION

Wastewater generation in huge volumes is one of the consequences of uncontrolled demand for textile articles, which causes extreme water consumption by textile industries [1]. Different wet-processing operations in the manufacturing process of textile industry result in the production of effluent which contains various pollutants including dyes, surfactants, detergents, and suspended solids [2]. Azo dyes as the largest group of organic dyes [3] constitute 20–40% of the dyes used in the textile industry [4] and are the most frequent chemical class of dyes applied to industrial scale [5]. The general chemical formula of azo compounds has been shown in the form of R-N = N-R functional group. In the structure of these compounds, the double bond between nitrogen atoms indicates the azo chromophores, while R is the aromatic ring [1] containing groups such as sulfonate and hydroxyl

[3]. The relatively low degree of dye fixation to fabrics especially for the reactive dyes results in the release of unfixed dyes into the effluent [6, 7]. It has been stated that textile industries produce a strongly colored wastewater [8]. It has also been declared that even the presence of inconsiderable dye concentrations in the effluent can reduce

the penetration of light into the receiving water bodies. This leads to devastating effects on the aquatic biota [9] such as photosynthetic activity of aquatic plants [8]. The probable persistence and the long term bioaccumulation of synthetic organic dyes severely damage the health of ecosystems and living organisms [10]. A wide range of technologies for the removal of dyes from contaminated effluents can be found in literature [11]. Conventional treatment methods, i.e., physical, chemical, and biological processes, are still highly used. The physical methods mainly are practical for separating the solid pollutants, since there must be a difference between the pollutant and its media regarding the physical property. It is noticeable that chemical treatment occurs just under conditions that electrostatic property of both pollutant and coagulant is compatible [12]. Undesirable efficiency, high cost, and secondary pollutants are major shortcomings of physicochemical processes [9]. In spite of the fact that synthetic dyes have properties such as stability against light, temperature, and biodegradability [4], which makes de-colorization difficult and incomplete [6], it was stated that azo dyes are non-resistant to biological treatment methods under anaerobic conditions. However, applying this method is not suggested for dye removal as the product resulted from breakdown of azo dyes can be more toxic than the dye molecules [4].the adverse environmental and health effects of dyes and their degradation products have pushed scholars' efforts towards developing powerful and effective treatment technologies[13]

**Current status of dye industry in India**

India has been considered as pioneer in the art of natural dyeing. It is one the world's twelve mega diversity countries and harbors more than 450 dye yielding plants. [19]
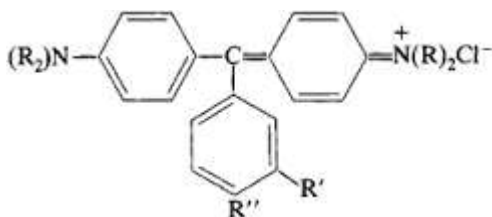
A dye can be defined as a highly colored substance used to impart color to variety of materials like textiles ,wood, paper, varnishes, leather, ink ,fur, foodstuffs ,cosmetics, medicines, toothpaste etc. Dyes are widely used in many industries such as textile dyeing, food, cosmetics, paper printing, leather and plastics, with textiles industry is the major consumer. Natural dyes dyestuffs and dyeing are as old as textiles themselves .Man has always been interested in colors but Color is the most visible pollutant that can be easily recognized in wastewater and it should be treated properly before discharging into water bodies or on land. The presence of color in wastewater either in industrial or domestics needs is considered as the most undesirable. Besides, the occurrence of various coloring agents likes dyes, inorganic pigments, tannins and lignin which usually impart color [18]. Dyes become among the main contributor for this

environmental matter with dyes wastes is predominant. The number of synthetic dyes presently utilizes in textile industry is about 10 000, representing an annual consumption of around 7 x 105 tones worldwide [20].

**Dyes for protein fibers**

All fibers obtained from animals (such as wool and silk) are considered as protein fibers. Proteins are made up of twenty essential amino acids. They are more complex than cellulose which is made of repeated sugar units. High pH denatures proteins and acid dyes are, therefore, used to dye wool, angora, cashmere and silk. These dyes are applied to the fabrics along with acid solutions. The chemical reaction between the dye and the fiber results in the formation of an insoluble dye molecule on the fiber [22] the three most important acid dyes are azo dyes, triarylmethane dyes and anthraquinone.

**Triarylmethane dyes**: Triarylmethane dyes are derivatives of the hydrocarbon triarylmethane a hydrocarbon. Acidic triarylmethane dyes containing at least two $SO_3H$ group are used to dye wool and silk fibers. Dyes containing only one $SO_3H$ group are used as indicators (e.g. phenolphthalein). Basic triarylmethane dyes are used extensively in the manufacture of stamping inks, writing and printing [23] Triarylmethane dye.



**Anthraquinone dyes**: Anthraquinone dyes have a sulfonic acid group which makes them soluble in water. They are used to dye wool and silk due to their affinity towards auxiliary binding agents. A subclass of acid dye called food coloring dyes is used to dye protein fibers and some nylon fibers under high temperature. [24].Another subclass of the anthraquinone dyes is called the fiber reactive dye which is used to dye protein fibers. The most important and distinguishing characteristics of these dyes are the property of forming covalent bonds during the application process with the substrates that is to be colored [25]. Unlike other dye groups, these dyes consist of a known chromophore system which contains various reactive groups. Based on these reactive groups, they are classified into (a) mono anchor dyes, (b) double anchor dyes and (c) multiple anchor dyes [26] are present in a colloidal state with a low water solubility property and are applied under a dye bath condition under the required temperature which depends on the thickness of the fiber to be dyed [27] Direct dyes which are used extensively to dye protein fibers can also be used to dye synthetic fibers like nylon and rayon. These dyes are applied under an aqueous bath containing electrolytes and

ionic salts. Direct dyes lack the property of getting dried-up fast after they are applied on fabrics .Basic dyes are also considered as cationic dyes. They form a colored cationic salt when dissolved in water. These cationic salts are found to react with the anionic surface of the substrate. These dyes are found to be powerful coloring agents for acrylic fibers [28]

**Azo dyes:** Azo dyes in general can be defined as ones which have: A chromophore azo group (-N=N-) attached to an aromatic or heterocyclic nucleus at one end.

An unsaturated molecule of carbocyclic, heterocyclic or aliphatic type at the other end. Azo dyes account for 60-70% of all the dye groups and are found to give out bright and high intensity colors compared to the other classes of dyes [29] .the color of a dye is due to the electronic transition between various molecular orbital, the probability of which determines the intensity of the color of the dye. These dyes are found to contain two groups: the chromophore (N=N, C=C, C=O) and the auxochromes (-OH, -NH2, -NR2) [30].Cotton in general, is not found to bind well with picric acid or other anionic or cationic dyes due to the presence of hydroxylic groups in its structure. Hence, simple azo dyes are found to be not that effective in dyeing cotton [17].These dyes are found to be the largest classification of dyes with the Color Index (CI) of more than 10,000 [31]. Azo dyes are classified into groups (mono, di, tri, tetra etc.) Based on the number of azo groups attached to its center. A mono azo dye has one N=N bond while di and tri azo groups have two and three N=N bonds, respectively. To avoid confusions, the dyes with three or more azo groups are often considered as poly azo dyes [32]. The azo groups are generally connected to benzene and naphthalene rings, but can also be attached to aromatic heterocycles or enolizable aliphatic groups. The side groups attached imparts the color to the dye. Color index (CI) is the systematic arrangement of colors based on their hue, brightness and saturation. The color index of a dye is found to vary depending on the number of azo groups attached.[33]. Azo dyes constitute the largest and the most important class of commercial dyes used in textile, printing, tannery, paper manufacture, and photography industries. These dyes are inevitably discharged in industrial effluents and have a serious environmental impact, because their precursors and degradation products (such as aromatic amines) are highly carcinogenic [34] Numerous biodegradability studies on dyes have shown that azo dyes are not prone to biodegradation under aerobic conditions.(These dyes are either adsorbed or trapped in bioflocs, which affects the ecosystem of streams, so they need to be removed from wastewater before discharge. Removal of dyes from wastewater can be effected by chemical coagulation, air flotation, and adsorption methods.[35] These traditional methods mainly transfer the contaminants from one phase to another phase without effecting any reduction in toxicity. Therefore, advance oxidation is a potential alternative to degrade azo dyes into harmless species.

## literature review

In year 2001 [15], studied on the "Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk" In this study The use of a previously untried bio absorbent, barley husk, for dye removal is compared to corncob. The effectiveness of adsorption as a means of dye removal has made it an ideal alternative to other more costly treatments. This paper deals with two low-cost, renewable bio absorbents, which are agro industrial by-products, for textile dye removal. In to this study Experiments at total dye concentrations of 10, 20, 30, 40, 50, 100, 150, and 200 mg l$^{-1}$ were carried out with an artificial effluent consisting of an equal mixture of five textile dyes. The effects of initial dye concentration, bio absorbent particle size, dose of bio absorbent, effective adsorbent, and dye removal kinetics were examined. One gram (per 100 ml) of ≤600 μm corncob was found to be effective in removing a high percentage of dyes at a rapid rate (92% in 48 h). One gram of 1×4 mm barley husk was found to be the most effective weight and particle size combination for the removal of dyes (92% in 48 h). The results illustrate how barley husk and corncob are effective bio absorbents concerning the removal of textile dyes from effluent.

In year 2003 [21] et al, studied on "Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste" In this study The adsorption of Congo Red by coir pith carbon was carried out by varying the parameters such as agitation time, dye concentration, adsorbent dose, ph and temperature. Equilibrium adsorption data followed both Langmuir and Freundlich isotherms. Adsorption followed second-order rate kinetics. The adsorption capacity was found to be 6.7 mg dye per g of the adsorbent. Acidic ph was favourable for the adsorption of Congo Red. Desorption studies suggest that chemisorption might be the major mode of adsorption.

In year 2007 [42] studied on" Advanced Oxidation Processes for Treatment of Textile and Dye Wastewater" in a review Textile wastewater containing dyes are difficult to treat by conventional biological processes as most of the dyes are non-biodegradable and are toxic to the microorganisms. These dyes can be easily treated if the conventional treatment methods are incorporated with the advanced oxidation process which can break the complex structure of the dye and make it more amenable to bio-degradation. This paper reviewed different Advanced Oxidation Processes (aops) like ozonation, hydrogen peroxide, UV radiation and their combination for comparison of treatment efficiencies for remediation of textile wastewater. The paper revealed that the treatment efficiencies of various options depend on the characteristics of the wastewater to be treated.

In year 2011 [14] studied on textile wastewater treatment" in this paper it was observed that the coagulants poly-

aluminum chloride/ lime (PAI) and polyaluminium ferric chloride (PHFCL) poly ferrous sulphate (PFS) and polyferric chloride (PFCL) these are all novel hydrolyzed coagulants are more effective and was also suggested to used for decolourization and there are some natural coagulants are also used because of there ecofriendly nature.

In year 2012 [16] studied on "Colour Removal of Direct Red Dye Effluent by Adsorption Process Using Rice Husk" it was observed in this study that the rice husk could be employed as economy and effective adsorbent for the removal of direct red 23 from dye effluent and was also studied on the effect of concentration of dye solution and the effect of amount of adsorbent on the percentage removal of dye. Such as Azo dyes and their degradation products like aromatic amines are highly carcinogenic. It was observed that this is the new technology Adsorption of dyes was the most effective treatment for any wastewater which containing different types of dyes. In this experiment study Adsorption process was adopted for removal of direct red 23 dye from the dye effluent by the using rice husk as the adsorbent in treated and untreated form. In there experiment there some process involved like washing and drying of rice husk at 105°C, followed by soaking in 0.6 M citric acid for 2 hours and heated to 120 °C. And was dried and washed continuously to obtain treated rice husk. This treated and untreated rice husk were used for removal of direct red 23 dyes. In this study it was observed that the Dye solutions of different concentrations was prepared and a known amount of adsorbent was added to study the Effect of concentration of dye Solution and effect of amount of adsorbent on the percentage of removal of direct red 23.

In year 2013 [40] Studied on the various treatment process of color removal from dying effluents was show various process. In this paper such as coagulation/flocculation adsorption complex metric technique membrane separation, chemical technique irradiation chemical reduction biological treatment such as aerobic treatment aerobic treatment was used. It was observed that the above techniques are more effective and can use in textile effluent treatment process.

In year 2014 [41] studied on Imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions" In this study it is observed that due to the increasing presence of molecules, refractory to the microorganisms in the wastewater streams, the conventional biological methods cannot be used for complete treatment of the effluent so that author introduce new technologies to degrade these refractory molecules into smaller molecules, which can be further oxidized by biological methods, has become imperative. In this paper experiment work on aims at high lighting five different oxidation processes operating at ambient conditions viz. Cavitation, photocatalytic oxidation, Fenton's chemistry (belonging to the class of advanced oxidation processes) and ozonation, use of hydrogen peroxide (belonging to the class of chemical oxidation technologies). The experiment work highlights the

basics of these individual processes including the optimum operating parameters and the reactor design aspects with a complete overview of the various applications to wastewater treatment in the recent years. In the next article of this two article series on imperative technologies, hybrid methods (basically combination of the oxidation processes) were discussed and the this work forms a useful foundation for the work focusing on hybrid technologies.

In year2015 [43] studied on "A review of electro coagulation Technique in treatment of textile mill Waste water" Wastewater generated by the textile industry is rated as the most polluting among all industrial Sectors considering both quality and quantity. The pollution load is mainly due to spent dye baths, which consist of un reacted dyes, dispersing agents, surfactants, salts, and organics. Dyes are formulated to produce colors that must be resistant to oxidizing and reducing agents, washing, and light exposure. This characteristic of dyes makes them highly resistant to treatment operations. In this paper it was observed used electro-coagulation process in experiment treatment of wastewater of dying industry Electro-coagulation proved to be a innovative technology in treatment of wastewater from Textile industries. This studied carried out that the Electro-coagulation is a complex process with many mechanisms acting simultaneously to remove pollutants. The electro coagulation method showed promising aspects in this study. The electro coagulation treatment provided complete color reduction in all treatment conditions while varying the current and voltage applied along with increasing the area of electrodes. In the results they observed that This method will prove better alternative than the conventional systems.

In year 2017 [44] studied on the coagulation/flocculation process for cationic anionic dye removal using wastewater treatment residuals. In this study aluminum based water treatment residue discharge from water treatment plants was used as coagulant for color removal from a cationic and anionic dye solution .it was observed that this study also represented the cost analysis of reusing that sludge from the water treatment as a coagulant.

**Experimental Procedure**

**Apparatus needed –**

A dsorptive stripping and cyclic voltarnmetric measurements were carried out using a Metrohm E612 voltammetric scanner and E611 voltarnmetric detector (Metrohm, Herisau, Switzerland) with Houston Instruments 2000 X-Y recorder, a Metrohm 663 VA Multimode Electrode stand (MME) was used in the hanging mercury drop electrode (HMDE) mode. The three electrode system was completed by means of a platinum auxiliary electrode and an Ag/AgCI (3M KCI) reference electrode. In addition, Metrohm 646 VA voltammetric processor coupled with a Metrohm 647 VA stand was also used for obtaining adsorptive stripping voltammetric measurements.

**The working electrode:** The working electrode is the characteristic multi-mode electrode (MME) in which three types of mercury electrodes are combined into a single design: Hanging mercury drop electrode (HMDE), dropping mercury electrode (DME) and static mercury drop electrode (SMDE).

**Reference electrode:** The Ag/Agel reference electrode is in many respects the most satisfactory of all reference electrodes and certainly the simplest. It consists of a silver/silver chloride wire in 3 M potassium chloride solution.

**Auxiliary electrode:** The third functional electrode is the auxiliary electrode, which is made of an inert material like platinum or of glassy carbon. This electrode is the current carrying electrode in the three-electrode system It is placed directly opposite the reference electrode.

For differential pulse voltammetry at the HMDE, a scan rate of 5 mVs-1 and pulse amplitude of 50 mV with a pulse interval of 1 s were used. The medium stirring speed was used during accumulation with mercury drop size of O.4 mm'. Usually reactive dyes were monitored over the voltage range from 0.0 to -1.3 V. pH measurements were made using an Orion pH meter, previously calibrated. All glassware, voltammetric cell and electrode systems were cleaned prior to determination and washed three times with de-ionised water. De-ionised water was produced by a Maxima ultra pure water system.

**Reagents**

**(a) Reactive Dyes (samples)**

All chemicals and samples used were of the highest purity available and were used without further purification. Zeneca Specialties (Manchester, UK) kindly provided sample of Reactive Blue -19. Fluorotriazine and chlorotriazine reactive dyes were generously supplied by BASF PLC (Manchester, UK). the reactive dyes used in these studies together with their chemical structures, molecular formula and molecular weight. Stock solutions of each dye of concentration 1 x l 0-2 mol r' in de-ionised water were prepared by dissolving an accurately weighed amount of pure substance. Solutions with lower concentration were prepared daily by diluting the stock solutions with de-ionised water. For obtaining a standard solution of the intermediate form Reactive Blue 19-Vinyl Sulfone (R8 19-VS), a solution of 1x 10-3 mol r' of the original dye was stirred at pH = 11 at room temperature for one hour. The pH was adjusted to pH 7 by the addition of 0.1 M HCt. In order to obtain solutions of fully hydrolysed dye of Reactive Blue 19 (RB 19-0H), or fluorotriazine-based and chlorotriazine-based azo reactive dyes, solutions of original reactive dyes in sodium carbonate at pH 10 were heated for at least one hour or alternatively 1 x l 0-3 mol r' solution of dye solution were refluxed at pH 11 for 3-4 hours.

## (b) Supporting electrolytes

The buffer solutions used in all experiments were prepared using analytical-grade materials (Analar grade) as following: hydrochloric acid (Fisons chemical ltd.), sodium hydroxide (BDH), boric acid (Fisons), glacial acetic acid (Fisons), orthophosphoric acid (BDH), sodium acetate (Fisons), sodium hydrogen carbonate (Fisons), and disodium carbonate (Fisher scientific).

Britton-Robinson buffer (PH - 2; 0.04 M in each constituent) was prepared by dissolving 2.47 gm of boric acid in 500 ml of distilled water containing 2.3 ml of glacial acetic then adding 2.7 ml of orthophosphoric acid and diluting to I L with distilled water. The desired pH of the buffer was adjusted with 4 M sodium hydroxide solution. A 0.02 M acetate buffer was prepared from both acetic acid and sodium acetate. The carbonate buffer was 0. I M in both sodium hydrogen carbonate and disodium carbonate.

## Surfactants

The non-ionic surfactant Triton X-lOO (stock solution: 200 mg r'j was obtained from Sigma (Dorset, UK). The anionic surfactant Aerosol OT (1 mV·I ) and Gelatine (0.5 mV·I ) were purchased from BDH (Poole, England). Glycerol (200 mg rl) and Sorbitol (2 mV·I ) both were supplied by Aldrich (Gillingham, England). Tetraphenyl phosphonium chloride (TPPC) cationic surfactant (I x 10-2 M) was obtained from Janssen chimica (Geel, Belgium). Finally, BDH ( Poole, UK) supplied the complexing agent EDTA (lxIO-4M).

## Metal ion solutions

Standard solutions of metal ions: line (II), Copper (II), Cobalt (II), Lead (II), Tin (II), Iron (II), Indium (III), Titanium (IV), Selenium (IV), Silicon (II), Gold (I), Lithium (I), Sodium (I), Magnesium (II), and Barium (II) were prepared by diluting Fisons spectral atomic absorption standard solutions.

## Working Procedure

The general procedure adopted for obtaining adsorptive stripping voltammograms were as follows. A 20 ml aliquot of an appropriate buffer was placed in a clean dry voltammetric cell and the required stock solution of the test substance was added. Solutions were deoxygenated by bubbling with nitrogen for 5 min initia1ly, while the solution was stirred at medium stirring speed. Adsorptive accumulation was carried out whilst stirring the solution. An accumulation potential at 0.0 V was applied to the working electrode for 2 min (unless otherwise stated). At the end of the accumulation period in stirred solution, the stirrer was stopped and after 20 shad elapsed and the solution had become quiescent, cathodic scans were carried out over the voltage range 0.0 to -1.3 V. Cyclic voltammetry was carried out immediately after forming a new HMDE. A new hanging mercury drop was formed after removing oxygen and after recording of the curves. All measurements were obtained at room temperature.

## CONCLUSION

Electrochemical technologies have been investigated as the effluent treatment processes for over a century. Fundamental as well as engineering researches have established the electrochemical deposition technology in metal recovery or heavy metal-effluent treatment. Electrocoagulation has been used industrially and demonstrated its superior performances in treating effluents containing suspended solids, oil and grease, and even organic or inorganic pollutants that can be flocculated. Electroflotation is widely used in the mining industries and is finding increasing applications in wastewater treatment. The uniform and tiny sized bubbles-generated electrically give much better performance than either dissolved air flotation, sedimentation or even impeller flotation. This process is compact and easy to facilitate with automatic control. With the invention of stable, active and cheap materials for oxygen evolution, this technology will gradually replace the conventional flotation techniques. Indirect oxidation is still a viable technology for treating toxic or biorefractory pollutants although there are concerns about the formation of chlotinated intermediates in the case of using chlorine ions or about the complicated facilities in the case of using electrically formed hydrogen peroxide or ozone. Direct anodic oxidation represents one of the simplest technologies in the pollutant mineralization provided the anode materials are stable and have high overpotential of oxygen evolution. The investigation of various materials so far shows that titanium or other noble metal-based boron-doped diamond film is the candidate for industrial application. It has the widest window for water split and is inert in tough situations. Further improvement in its stability in electrochemical application is required before its industrial acceptance.

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