

Recent advances in determination of herbicide paraquat in environmental waters and its removal from aqueous solutions: A review

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ABSTRACT: Herbicide paraquat is widely used in agriculture for weed control. The United States Environmental Protection Agency (U.S. EPA) has set a goal of 3 µg/L for it in drinking water. Also, the European Union Directive (98/83/EC) is more restrictive and has set a maximum admissible concentration at 0.1 µg/L for it in drinking water. Besides, the World Health Organization (WHO) has set an advisory value of 10 µg/L for it in drinking water. To protect the human health and environment from the harmful effects of this herbicide, simple and effective sample preparation, sensitive analytical methods are necessary for determining paraquat in environmental waters and powerful and practical treatment processes for its removal from water matrices are required. In this study, different analytical techniques such as spectrophotometry, capillary electrophoresis (CE) with ultraviolet (UV), optical immunosensor, electrochemical batch-injection analysis (EBIA), liquid chromatography (LC), liquid chromatography/mass spectroscopy (LC/MS), and liquid chromatography/mass spectroscopy/mass spectroscopy (LC/MS/MS) for determination of this herbicide in water samples, and recuperative processes like adsorption, membrane filtration, combination of adsorption and membrane filtration processes, and destructive processes like advanced oxidation processes (AOPs) i.e. ozonation, photocatalytic, Fenton's reaction and electrochemical processes for its removal from aqueous solutions have been reviewed. Also, the future developments of removal methods of this herbicide have been discussed.

Keywords: Paraquat, Determination, Removal, Adsorption, Advanced oxidation.

INTRODUCTION

Paraquat is 1,1'-dimethyl-4,4'-bipyridinium ion, also known as the 1,1'-dimethyl-4,4'-bipyridylium ion (Pico et al., 2000; Lock and Wilks, 2010). The molecular formula of the cation is $C_{12}H_{14}N_2^+$ with a molecular weight of 186.3. The dichloride salt has the formula $C_{12}H_{14}Cl_2N_2$ and a molecular weight of 257.2 (Lock and Wilks, 2010). The chemical structure of paraquat is shown in Figure 1 (Pavlovic et al., 2014). Paraquat dichloride forms colorless, hygroscopic crystals which decompose at 300°C. It is practically non-volatile with a vapor pressure of 0.1 mPa. It is very soluble in water (700 g/l at 20 °C (Lock and Wilks, 2010), 625 g/L at 25 °C (Santos et al., 2011), 620 g/L (Oliveira et al., 2012)) and practically insoluble in most other organic solvents. It is stable in neutral and acidic media, but readily hydrolyzed in alkaline media. Paraquat is photochemically decomposed by ultraviolet radiation in aqueous solution (Lock and Wilks, 2010).

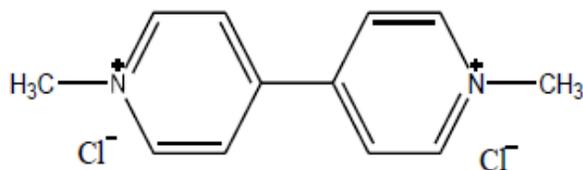


Figure 1. Chemical structure of paraquat (Pavlovic et al., 2014).

Paraquat was first described in 1882 by Weidel and Russo. In 1933, Michaelis and Hill discovered its redox properties and called the compound methyl viologen. The herbicidal properties of paraquat were first described by

Brian et al. (Lock and Wilks, 2010) and since 1962 paraquat has been marketed in over 130 countries as a highly effective contact herbicide. The bipyridinium herbicide paraquat was introduced by Imperial Chemical Industries in 1958. It is very quick-acting herbicide that is absorbed by plants and translocated, thus causing desiccation of the foliage. It is strongly adsorbed by clay constituent soil, and is effectively deactivated as soon as it comes into contact with soil (Pico et al., 2000; Weber et al., 1993).

This non-selective contact herbicide is widely used in agriculture for weed control. The paraquat usage has become abusive and has generated a great concern due to its damage for aquatic environment and human health, as a consequence of its large availability, low toxic dose and relatively low cost. For these reasons this herbicide is now forbidden in Europe although its use has continued in other continents, and therefore the paraquat quantity in water has grown. A great concern also exists related to the possibility of its presence in water, particularly drinking water, for instance due to a deliberate contamination event (Oliveira et al., 2012). Also, it may be present as residues in environmental, food and biological samples (Pico et al., 2000; Galceran et al., 1994; Zen et al., 1996). As a result there is a need for analytical procedures for its isolation and determination (Pico et al., 2000). Generally, various methods for the determination of paraquat has been reported using spectrophotometry (Kato et al., 1999; Kuo, 1990; Matsuoka and Okuda, 1993), capillary electrophoresis (CE) (Acedo-Valenzuela et al., 2004; Núñez et al., 2001; Song and Budde, 1996), immunoassay (Dankwardt, 2000), square wave voltametry (Mhammedi et al., 2007), gas chromatography-mass spectrometry (GC-MS) (de Almeida and Yonamine, 2007) and high performance liquid chromatography (HPLC) with UV, fluorescence, diode array and mass spectroscopy detection (Brunetto et al., 2003; Fuke et al., 2002; Hara et al., 2007; Madhu et al., 1995; Castro et al., 2001; Trobbiani, 2010).

The United States Environmental Protection Agency (U.S. EPA) set a goal of 3 µg/L for paraquat in drinking water and proposes the method 549.2 for its determination in drinking water. The European Union (EU) Directive (98/83/EC) is more restrictive and sets a maximum admissible concentration at 0.1 µg/L for this herbicide in drinking water (Rial-Otero et al., 2006; Carneiro et al., 1994). The World Health Organization (WHO) has set an advisory value of 10 µg/L for paraquat in drinking water (Cullum and Stephens, 2002). Public health concerns are the driving force for the continued legislation aimed at providing a cleaner water and safer environment. Furthermore, EPA goals suggest destruction levels up to 99.9999% of some compounds and use of totally enclosed treatment facilities. The increased environmental constraints and unfavorable public opinion have challenged the continuing application of conventional water and wastewater techniques (Bambang and Jae-Duck, 2007; Li et al., 1991; Sabet et al., 2014; Jafarinejad, 2015a; 2015b; 2015c; Gonza'lez-Pradas et al., 2000; Farabi Barna, 2011; Zahoor, 2013a; Tsai et al., 2005; Oliveira et al., 2014; Zahoor, 2013b). In this study, recent advances in determination of herbicide paraquat in environmental waters and removal of it from aqueous solutions have been reviewed.

Determination Techniques Of Paraquat In Water

To overcome the requirements of the environmental program, based on goals and limitations of the U.S. EPA and the European Union, simple and effective sample preparation and sensitive analytical methods are necessary for determining paraquat in environmental waters (Dionex Corporation, 2011).

Because of the toxicity and significance of paraquat, several methods, based on different analytical techniques have been reported for the detection and determination of this compound in water (Khatoon et al., 2013). Paraquat in water samples can be determined by many different analytical techniques such as spectrophotometry (Khatoon et al., 2013), capillary electrophoresis with ultraviolet (Acedo-Valenzuela et al., 2004; Chu and Chang, 2011; Fuke et al., 2002; Paixão et al., 2002; Nagayama et al., 1987; Pico et al., 2003; Carneiro et al., 2000; Buchberger and Schöftner, 2003; Núñez et al., 2002; Kanlansky et al., 1994), optical immunosensor (Mallat et al., 2001), electrochemical batch-injection analysis (EBIA) (Simoões et al., 2007; de Souza and Machado, 2003), liquid chromatography (LC) (U.S. EPA, 1997; Waters Corporation, 2007; Dionex Corporation, 2010; Raquel et al., 2006; Tuzimski, 2008; Ibáñez et al., 1996; Chen et al., 2002), liquid chromatography/mass spectroscopy (LC/MS) (Cullum and Stephens, 2002), liquid chromatography/mass spectroscopy/mass spectroscopy (LC/MS/MS) (Trobbiani, 2010; Mallet, 2013; El Aribi, 2006; El Aribi, 2010; Núñez et al., 2004; Marr and King, 1997).

Spectrophotometry

Many of the earlier reported spectrophotometric methods are less sensitive and suffer from many drawbacks (Pico et al., 2000; Khatoon et al., 2013). Khatoon et al. (2013) have developed an extractive, sensitive spectrophotometer method for the detection and determination of paraquat using glucose as easily available reducing agent. Paraquat was reduced with glucose in alkaline medium to give a blue colored ion with an absorbance maximum at 610 nm. Beer's law is obeyed in the range 0.5-5.0 µg of paraquat in 10ml of the final

solution (ppm). This method has been successfully applied to the determination of paraquat in water, grain, plant material and biological sample.

Capillary Electrophoresis (CE) with ultraviolet (UV)

Capillary electrophoresis with UV detection has been proved to be a promising alternative for the analysis of paraquat in water (Acedo-Valenzuela et al., 2004). Solid phase extraction (SPE) using commercial SPE cartridges were the most common procedure for extraction/preconcentration of paraquat (Pico et al., 2000; Chu and Chang, 2011). Non-polar phases such as C₈ and C₁₈ (Fuke et al., 2002; Paixão et al., 2002) after addition of an ion pair reagent for concentration of this herbicide was the most widely employed for drinking waters (Chu and Chang, 2011). Cation-exchange resins (Nagayama et al., 1987), silica and porous graphitic carbon (PGC) have been reported as adsorbent materials for the extraction and pre-concentration of paraquat from tap and river water; and concentration factor and limits of detection (LOD) have been 250 and 0.2 ppb, respectively (Pico et al., 2003; Carneiro et al., 2000). Moreover, CE/MS has also been used for the determination of this herbicide in water samples (Buchberger and Schöftner, 2003). Nevertheless, CE coupled with UV detection has lower concentration sensitivity than High-Performance Liquid Chromatography (HPLC) due to its low injection volume and short optical pathlength. To improve the sensitivity of CE methods, several sample stacking techniques have been reported (Chu and Chang, 2011; Núñez et al., 2002; Kanlansky et al., 1994).

In recent years, nanoparticles have been used as concentrating probes to extract paraquat from aqueous solution because of their high surface area-to-volume ratio and ease of surface modification. Chu and Chang (2011) have used silica nanoparticles (SiNPs) as concentrating probes to extract paraquat from aqueous solution before capillary electrophoretic analysis. Adsorption of paraquat onto SiNPs is mainly through electrostatic interaction. After extraction and centrifugation, the analytes were eluted from the surface of SiNPs by rinsing with acetic acid solution. The extract was directly analyzed by capillary electrophoresis with UV absorption detection. Using SiNPs to concentrate the analytes from 10 mL of aqueous solution, the enrichment factors for paraquat was 75. The limit of detection at signal-to-noise ratio of 3 was 0.03 µM for paraquat.

Optical immunosensor

Biosensors seem to be a promising tool to obtain fast, sensitive, specific and reproducible measurements. The combination of immunoassay and flow through sensors led to the development of flow through immunosensors. These devices combine the powerful of antibodies as recognizing agents, an appropriate physicochemical transducer to convert the recognition success to a readable signal and a flow injection system to perform continuous measurements. Reported immunosensors have used to perform indirect measurements by means of competitive immunoassay configurations or labels such as enzymes, fluorescent chemicals or electrochemically active substances. Mallat et al. (2001) selected a solid-phase fluoroimmunoassay combined with an optical transducer to achieve excitation and collection of fluorescence from fluorescently labelled antibodies locally bound at the planar interface. Excitation and collection of fluorescence from fluorescently labelled anti-paraquat antibodies locally bound at the planar interface allows the measurement of the fluorescent signal which is indirectly related to the paraquat concentration of the sample. Matrix effects on the immunosensor response have been observed, thus leading to the following detection limits, 0.06 µg/L, when analyzing paraquat in river water. The validation of the biosensor has been carried out analyzing paraquat samples by capillary zone electrophoresis with ultraviolet detection (CZE-UV) at 214 nm. Preconcentration of the samples prior to their injection in the capillary electrophoresis have been performed using the automated solid-phase extraction system (ASPEC-XL). Paraquat samples have been adjusted at pH 9 and have been percolated through a silica cartridge, subsequent elution has been carried out using a mixture of hydrochloric acid and methanol and afterwards samples have been evaporated and injected. Mallat et al. have explained that this optical immunosensor, also called RIVER ANALYZER (RIANA) with an optical immunosensor can be applied for fast monitoring of paraquat in river water samples being the total analysis time of 15 min.

Electrochemical Batch-Injection Analysis (EBIA)

Batch injection analysis (BIA) has represented an innovative injection approach for performing rapid electroanalysis. The method involves the injection of a small volume of a liquid sample directly over a detector that is immersed in a large volume of blank solution. The potentialities and applications of BIA have shown that it can be used with a large variety of detectors, such as electrochemical, optical and thermal (Simoões et al., 2007; Quintino et al., 2002). Electrochemical BIA presents a number of advantages from the analytical point of view such as small sample injection volume (≤100 µL which reduces the amount of adsorption blocking of the electrode surface), high reproducibility and sensitivity, real time and extremely fast analysis, the possibility of making many

successive determinations without changing the supporting electrolyte as well as a special attraction for environmental monitoring due to the possibility of the use of portable instruments for in situ analysis. It is possible to carry out a square wave or cyclic voltammetric scan either during or immediately after the period of injection (Simoões et al., 2007; Brett et al., 1994).

According to Monk et al. (1999) and Simoes et al. (2007) the electrochemical behaviour of paraquat shows two reversible reduction peaks on sweeping the applied potential in the negative direction. The first, at around 20.7 V vs SCE, is attributed to radical cation formation ($PQ^{2+} \leftrightarrow PQ^+$) and the second at approximately -1.2 V to formation of the neutral species ($PQ^+ \leftrightarrow PQ^0$) which is probably followed by a chemical dimerisation step. Nafion-coated glassy carbon electrode has been utilized to detect paraquat in river water and urine by differential pulse voltammetry, with an accumulation time of 5.0 min at open circuit. The detection limit has been about 0.7 µg/L and recoveries between 87 and 106% were obtained for spiked river water and urine samples (Simoões et al., 2007; de Oliveira et al., 2004). Also, gold, platinum and carbon fibre microelectrodes have been used in the determination of paraquat in pure electrolyte by square wave voltammetry (SWV) with detection limits of 3.9, 6.2, and 20.4 µg/L, respectively (Simoões et al., 2007; de Souza and Machado, 2003). Simoes et al. (2007) have applied the BIA technique with removal of any pre-treatment steps, to the electroanalytical detection of the herbicide paraquat by square wave voltammetry during sample injection. The results obtained have shown that the herbicide can be detected at µg/L levels with small injection volumes (<100 µL) and times (<two seconds).

Liquid Chromatography (LC)

High-performance liquid chromatography (HPLC) is one commonly used technique for the analysis of paraquat in water. Solid phase extraction (SPE) is the typical method for sample extraction and enrichment in the analysis of diquat and paraquat in water samples by HPLC. The baseline separation of paraquat and dequat is difficult on conventional reversed-phase (RP) columns (C_{18} or C_8) due to their weak retention on those columns. Therefore, ion-pairing reagents are added to the mobile phase. This addition may also improve peak shape. The U.S. EPA published EPA Method 549.2 for monitoring diquat and paraquat in aqueous samples. C_{18} stationary phase with an ion-pairing reagent in the mobile phase and photodiode array (PDA) detection is used in this method. HPLC conditions were given in Table 1 and method detection limits (MDL) for paraquat and diquat were 0.68 and 0.72 µg/L, respectively (U.S. EPA, 1997; Dionex Corporation, 2011). Also, a stationary phase that may be used in the hydrophilic interaction liquid chromatography (HILIC) mode was reported for the separation in the absence of an ion-pairing reagent (Dionex Corporation, 2011; Waters Corporation, 2008). An improved separation with resolution (R_s) of 3.2 has been achieved using the Acclaim® Mixed-Mode HILIC-1 column (Dionex Corporation, 2010; 2011).

Table 1. HPLC conditions and photodiode array (PDA) detector settings in EPA method 549.2 (U.S. EPA, 1997).

HPLC conditions	
Column	Phenomenex spherisorb, 3µ, 4.6 mm x 100 mm
Column temperature	35.0° C
Flow rate	2.0 mL/min., ion-pair mobile phase (mobile phase is made by adding the following to 500 mL of deionized water: 13.5 mL of orthophosphoric acid; 10.3 mL of diethylamine; 3.0 g of 1-hexanesulfonic acid, sodium salt. Then it is mixed and diluted with deionized water to a final volume of 1 L.)
Injection volume	200 µL
Photodiode array detector settings	
Wavelength range	210 - 370 nm
Sample rate	1 scan/sec
Wavelength step	1 nm
Integration time	1 sec
Run time	5.0 min
Wavelengths for paraquat	257 nm
Wavelengths for diquat	308 nm

For water sample preparation, Off-line SPE (Raquel et al., 2006; Tuzimski, 2008; Taguchi et al., 1998) is usually used, and EPA Method 549.2 also describes it for water sample preparation, which is improved compared to Method 549.1, but still complex (Dionex Corporation, 2011; U.S. EPA, 1997). Compared to off-line SPE, on-line SPE offers the advantages of full automation, the absence of operator influence, time savings, and strict process control (Dionex Corporation, 2011). Several applications of on-line SPE to the determination of diquat and paraquat in water samples by HPLC have been reported (Ibáñez et al., 1996; Chen et al., 2002; Ren et al., 2001). Also, to eliminate interferences sufficiently and fulfill the simple and sensitive determination of diquat and paraquat in tap and pond water, an improved on-line SPE system has been used. In this improved on-line SPE system, two SPE

cartridges have used. One has been the Acclaim Mixed-Mode WAX-1 cartridge for the elimination of anionic interferences; the other one has been the Acclaim Mixed-Mode WCX-1 cartridge for the enrichment of diquat and paraquat, and the elimination of co-enriched cationic interferences. The analysis has been completed by baseline separation of diquat and paraquat on the Acclaim Trinity™ P1 column. The Dionex UltiMate® 3000 Dual HPLC system have been used as an efficient platform to fulfill the on-line SPE and separation. The conditions have given in Table 2 and chromatograms have shown in Figure 2. The complete analysis only requires 16 min, and method detection limits have been 0.12 µg/L for diquat and 0.10 µg/L for paraquat, which meets the requirement of EPA Method 549.2 (Dionex Corporation, 2011).

Table 2. The conditions of the improved on-line SPE method (Dionex Corporation, 2011).

Item	Description
SPE cartridge 1	Acclaim Mixed-Mode WAX-1 (guard), 5 µm, 4.6 × 10 mm
SPE cartridge 2	Acclaim Mixed-Mode WCX-1 (guard), 5 µm, 4.6 × 10 mm
Analytical column	Acclaim Trinity P1, 3 µm, 3.0 × 50 mm
Mobile phase	A: 250 mM CH ₃ COONH ₄ (pH 5.2) B: MeOH C: Water
Gradient	0.0 – 6.0 min, A: 10%, B 5%; 6.1 – 9.5 min, A: 55%, B: 45%; 9.6 – 16 min, A: 10%, B: 5%
Column temperature	For separation, 500 mM (NH ₄) ₂ SO ₄ – CH ₃ OH –Water, 60 : 15 : 25, (v/v) 25 °C
Flow rate	0.7 mL/min for on-line SPE; 0.6 mL/min for separation
Injection volume	2500 µL onto SPE cartridge 1
Detection	At 260 nm for paraquat, 311 nm for diquat

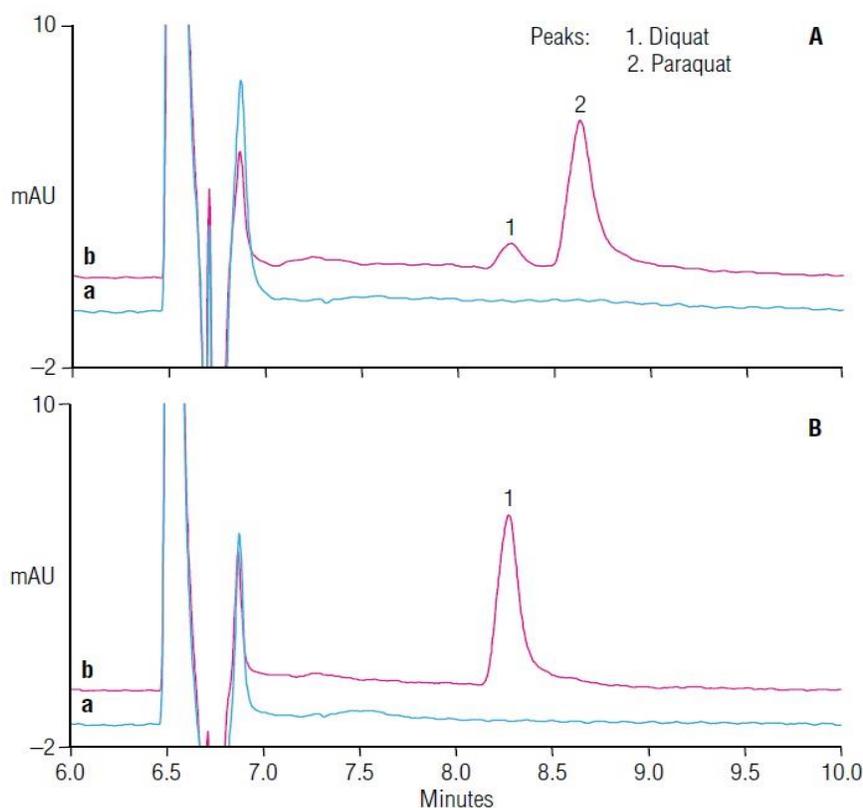


Figure 2. Determination of diquat and paraquat in pond water using the improved on-line SPE mode. Chromatograms: (a) pond water and (b) the same sample spiked with diquat and paraquat standards (2.5 µg/L each) with Panel A showing detection at 260 nm and Panel B at 311 nm (Dionex Corporation, 2011).

Liquid Chromatography/Mass Spectroscopy (LC/MS)

A rapid and sensitive method has been used for the analysis of paraquat using LC/MS, electrospray ionization (ESI), positive ion mode, selective ion monitoring (SIM) large volume injections, and minimal sample

preparation. No trace enrichment was required to obtain LOD below 1 µg/L. Analysis has been done using Agilent 1100 LC/MSD quadrupole coupled to an Agilent 1100 series LC system. HPLC conditions, MS conditions, and SIM parameters have been given in Table 3 and extracted ion chromatogram of paraquat in raw borehole water have been shown in Figure 3 (Cullum and Stephens, 2002).

Table 3. HPLC conditions, MS conditions, and SIM parameters for the analysis of paraquat using LC/MS (Cullum and Stephens, 2002).

HPLC conditions	
Column	Zorbax extend C ₁₈ , 150 mm long × 2.1 mm id, 3.5 µm particles, 60 °C
Flow rate	0.4 mL/min
Injection volume	250 µL
Mobile phase	Isocratic elution A: 5 mM tridecafluoroheptanoic acid (TDFHA) in water (75%) B: Acetonitrile (ACN) (25%)
MS conditions	
Ionization mode	API-ES, Positive
Drying gas flow	13 L/min
Nebulizer gas pressure	30 psig
Drying gas temperature	350 °C
V _{cap} voltage	3500 V
SIM parameters	
SIM ion	185
Fragmentor voltage	140

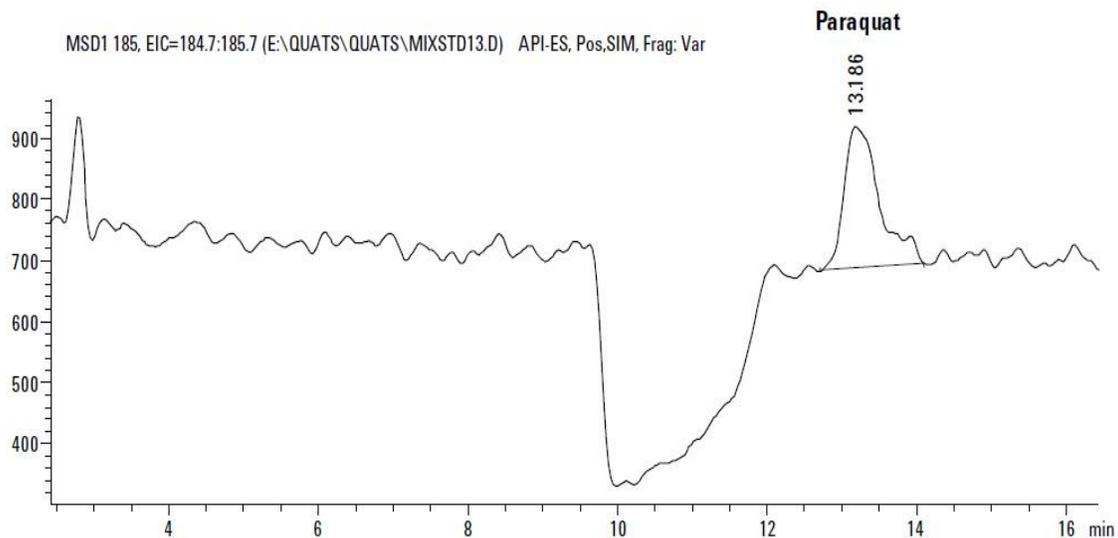


Figure 3. Extended ion chromatogram of 1 µg/L of paraquat in raw borehole water (Cullum and Stephens, 2002).

Liquid Chromatography/Mass Spectroscopy/Mass Spectroscopy (LC/MS/MS)

As it has been noted, the U.S. EPA method 549.2 utilizes reversed-phase chromatography with ion pairing for the separation of diquat and paraquat using UV detection (U.S. EPA, 1997; Mallet, 2013). Ion pairing agents are typically avoided with ESI-MS applications owing to suppression of the ionization in the MS source. For MS applications, HILIC has provided suitable chromatography without the requirement of ion pairing agents. However, recent advances in MS sensitivity have made the direct analysis of trace-level contaminants in water attainable and very attractive. The possibility of removing laborious and time-consuming solid phase extraction and sample concentration is highly desirable. Direct injection of an aqueous sample for RP chromatography is ideal as the sample matrix is similar to the initial mobile phase conditions (Mallet, 2013). Several works have been done for the analysis of paraquat in water samples using LC/MS/MS (Trobbiani, 2010; Mallet, 2013; El Aribi, 2006; El Aribi, 2010; Núñez et al., 2004; Marr and King, 1997). For example, conditions of LC/MS/MS analysis of paraquat and diquat, using an API 3200™ mass spectrometer and an Ultra Quat HPLC column have been given in Table 4 and the chromatograms of these compounds have been shown in Figure 4 (El Aribi, 2006).

Table 4. Conditions of LC/MS/MS analysis of paraquat and diquat, using an API 3200™ mass spectrometer and an Ultra Quat HPLC column (EI Aribi, 2006).

Item	Description
Sample	Injection: 10 µL, concentration: 5 µg/mL each component, sample diluent: DI water, sample temperature: ambient
Column	Ultra Quat, dimensions: 50 × 2.1 mm, particle size: 3µm, pore size: 100 Å
Mobile phase	10 mM heptafluorobutyric acid:acetonitrile, 95:5 (v/v)
Flow	0.3 mL/min
Temperature	Ambient
Detection	Applied Biosystems API 3200™
Interface	Electrospray
Ion mode	Positive
Temperature	600 °C
Ion spray™ voltage	5500 V
Collision exit potential	3 V
Curtain Gas™	15 psi
Gas supply 1	70 psi
Gas supply 2	60 psi
Quantitation	MRM
Q1/Q3	Unit resolution
Dwell time	200 ms
Precursor Ion (amu)	93 (2+) for paraquat and 183+ for diquat
Fragment Ion (amu)	171+ for paraquat and 157+ for diquat
DP (V)	20 for paraquat and 30 for diquat
Collision energy (eV)	20 for paraquat and 30 for diquat

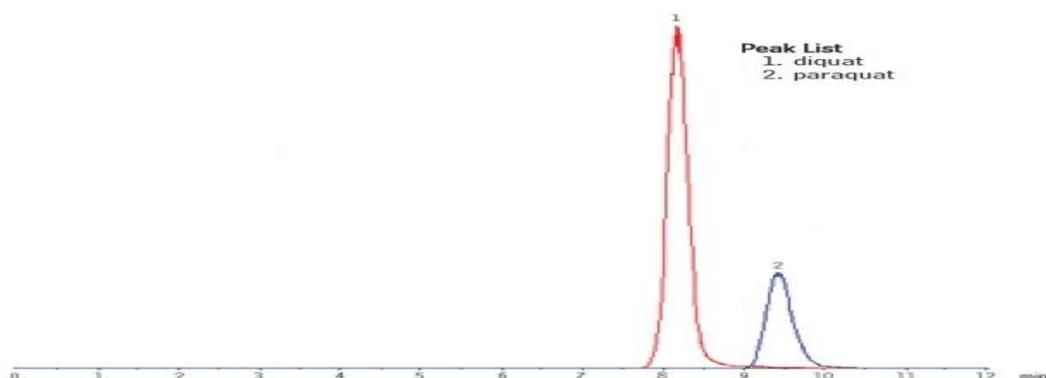


Figure 4. The chromatograms of LC/MS/MS analysis of paraquat and diquat, using an API 3200™ mass spectrometer and an Ultra Quat HPLC column (EI Aribi, 2006).

Removal Of Paraquat From Water

To protect the human health and environment from the harmful effects of herbicide paraquat, powerful and practical treatment processes for its removal from water matrices are required. A number of classical treatment processes are in use for the removal of herbicide paraquat from water. They have broadly classified into two categories (Zahoor, 2013); recuperative processes like adsorption on porous solids, membrane filtration, and combination of adsorption and membrane filtration processes (Pavlovic et al., 2014; Gonza'lez-Pradas et al., 2000; Farabi Barna, 2011; Zahoor, 2013; Weed and Weber, 1968; Aouada et al., Lerdsirivichai, 2011), and destructive processes like advanced oxidation processes (AOPs) i.e. ozonation, photocatalytic, Fenton's reaction and electrochemical processes (Santos et al., 2011; Oliveira et al., 2012; Oliveira et al., 2014; Lee et al., 2003).

Recuperative processes

Adsorption process

Weed and Weber (1968) have investigated the effect of adsorbent charge on the competitive adsorption of paraquat and diquat by three-layer clay minerals. The results have shown that two factors controlled the positions of the diquat vs. paraquat competitive adsorption isotherms in the systems studied: (1) adsorbent surface charge density and (2) prevalence of opposing, i.e., interlayer surfaces in an adsorbent particle. Paraquat has preferentially adsorbed on all montmorillonites and on the external surface of vermiculite whereas diquat was preferentially adsorbed on the internal surface of vermiculite and on the external surface of non-expanded mica. At a surface charge density of about 8×10^4 esu/cm² adsorption of diquat and paraquat on external surfaces appeared

to be equal. At lower surface charge densities, the widely spaced charge centers (7 °Å) on paraquat could most effectively counter the adsorbent charge and this cation was preferentially adsorbed over diquat. With increase in surface charge density, adsorption sites are more closely spaced, and diquat was preferentially adsorbed due to the shorter separation of its charge centers (3.5 °Å). Also, results have indicated that structural charge on layer silicates is expressed as discrete adsorption sites rather than a smear of surface charge.

González-Pradas et al. have used two montmorillonite-(Ce or Zr) phosphate cross-linked compounds at different temperatures (288K and 308 K) by batch experiments for removal of paraquat from water. They have classified adsorption isotherms obtained for paraquat on both adsorbents as H-type of the Giles classification (Giles et al., 1960), which suggests that paraquat molecules are strongly adsorbed on the samples. Also, they have noted that increase in temperature from 288K to 308K did not have any clear effect on the adsorption process of paraquat on either adsorbent. The Ce-montmorillonite adsorbent has shown a higher adsorption capacity than the Zr-montmorillonite adsorbent (González-Pradas et al., 2000).

Tsai et al. (2005) have used spent and treated diatomaceous earth for removal of herbicide paraquat from an aqueous solution. The results have shown that base-activated clay mineral from spent diatomaceous earth has had a larger adsorption capacity at a higher pH value over the range of 3–11 and at lower temperature. The adsorption kinetics have been well described by the pseudo-second-order model equation. Furthermore, the Freundlich model has appeared to fit the data better than the Langmuir model for describing the adsorption behavior of paraquat from an aqueous solution on spent diatomaceous earth and its activated product (activated by sodium hydroxide at about 100 °C).

Aouada et al. have studied the effect of acrylamide concentration on capability of hydrogels constituted by poly (acrylamide) (PAAm) and methylcellulose (MC) for removing paraquat dichloride from aqueous solution using UV-Vis technique. PAAm-MC hydrogel has been produced by acrylamide (AAm) monomer polymerization in aqueous solution in the presence of MC, N-N'-methylene-bisacrylamide (cross-linker) and N,N,N',N' tetramethylenediamine (catalyst agent). The AAm concentration ranging set at 3.6, 6.0 and 9.0 % (in-wt) with constant MC concentration (0.5 in-wt %). Results have shown that the concentration of AAm has been an important factor that has affected the maximum amount of paraquat adsorbed (q_{eq}). They have concluded that the q_{eq} values decreased when the AAm concentration increased: 13.1, 8.9 and 6.7 mg/g for hydrogels synthesized with 3.6, 6.0 and 9.0 % AAm, respectively. The adsorption trend in these hydrogels was that greater compaction decreases the paraquat adsorption capacity. These results have suggested that PAAm-MC hydrogels are potential materials that can be applied as adsorbents for removal of contaminants materials from aqueous solution.

Lerdsirivichai has tested four adsorbents (powdered activated carbon (PAC), chitosan, alumina, and soil) for paraquat sorption from agriculture run-off water. PAC was the best of them to remove paraquat. Lerdsirivichai has explained PAC adsorption with Langmuir isotherm, which indicates formation of paraquat monolayer on PAC surface. The sorption capacity of PAC with paraquat was 116.28 mg/g. Paraquat adsorption on PAC was very fast at initial period. The initial sorption rate was 0.0011-0.0211 g/mg/min. The steady state of paraquat sorption (99%) has been obtained after 15 hours (Lerdsirivichai, 2011).

Pavlovic et al. have investigated spent coffee grounds as adsorbent for removal of herbicide paraquat from its aqueous solutions in the batch sorption mode. Adsorption capacity (mg/g) has been found to be 27.87 ± 1.57 mg/g, while the removal efficiency has resulted of 32.25 ± 1.79 %. Adsorption rate has been found to be very fast, whereby the time required for equilibrium adsorption occurred within first 20 minutes. The process behavior has been predicted using the second-order kinetic model (Pavlovic et al., 2014).

Membrane process

Lerdsirivichai (2011) has tested two nanofiltration (NF) membranes (TS80 and NX45) and an Ultrafiltration (UF) membrane (UE10) for paraquat removal from agriculture run-off water. Flow diagram of membrane experimental set up is shown in Figure 5. TS80 membrane with highest salt rejection and lowest molecular weight cut-off (MWCO) was the most effective membrane for paraquat removal (95%) among membrane tested. In case of permeate flux, the lower permeate flux (0.04-0.13 m³/(m².d.b.)) presented at high concentration applied (30 mg/L of paraquat) that was resulted from the effect of concentration polarization and membrane fouling. For NX45 membrane, lower salt rejection and higher MWCO than TS80 membrane, have presented 75-81% of paraquat removal. UE10 membrane has removed paraquat in range of 15-51%. The results have depicted that the membrane having less MWCO showed higher removal efficiency.

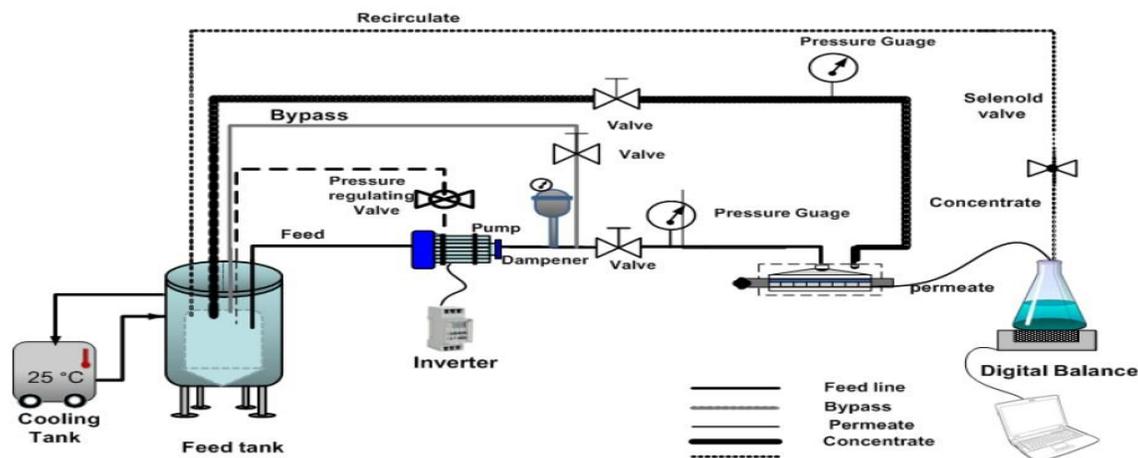


Figure 5. Flow diagram of membrane experimental set up in Lersirivichai's work (2011).

Farabi Barna (2011) has conducted a feasibility study of using silica supported catalysts as membrane materials to treat wastewater containing paraquat dichloride. Both adsorption and decomposition kinetics have been explored utilizing different analytical techniques such as liquid chromatography mass spectrometry and UV-Vis spectrometry. The results have demonstrated strong adsorption by the contaminant onto silica surfaces. Competitive binding model predictions have been found to be consistent with experimental adsorption data. Addition of an exogenous agent (e.g. H_2O_2) was also attempted to assist paraquat decomposition; however, investigation of paraquat- H_2O_2 interaction both in presence and absence of the catalysts indicate that peroxide functionality was not effective for chemical decomposition of paraquat. As radical generation was key to mineralization of organic contaminants, the findings have suggested that alternative techniques triggering generation of hydroxyl or single charged paraquat radicals need to be explored.

Combination of adsorption and membrane filtration processes

Lersirivichai has studied a hybrid process containing adsorption on PAC and membrane filtration for paraquat removal from agriculture run-off water. In combined experiment, hybrid ultrafiltration UE10 process has shown higher paraquat removal (64%) than adsorption and direct filtration. In hybrid nanofiltration processes, paraquat removals were 95% in hybrid TS80 and 65% in hybrid XN45; that these were slightly lower than direct filtration. Moreover, high permeate flux has been observed in all the hybrid processes due to low fouling, scouring effect, and assisting layer. Higher paraquat removal in hybrid NF (TS80) membrane process with the presence of humic acid in feed than that of without humic acid can be expected because of co-fouling. As presence of PAC normally decreases membrane fouling, permeate flux of the hybrid membrane, should show higher than direct filtration. Lersirivichai has concluded that hybrid process is the interesting option for application in terms of time used for operation (removal) and maintenance (membrane cleaning) (Lersirivichai, 2011).

Zahoor (2013) has prepared magnetic activated carbon (MAC) and has compared it with PAC for their adsorptive properties, and has used them in combination with UF membrane in a hybrid manner for the removal of linuron and paraquat. The comparison of PAC/UF and MAC/UF hybrid processes has shown that percent retention of paraquat and linuron was high for PAC due to its high surface area. However due to cake formation over membrane surface the decline permeate fluxes and long backwash times for PAC have been observed. PAC also has caused blackening of pipes and flow meter. MAC (an iron oxide and PAC composite) has been removed from slurry through magnet thus no cake formation and secondary problems observed for PAC was not encountered. Also the backwash times were minimum for MAC/UF process. Zahoor concluded that MAC can be used as alternative to PAC in membrane water treatment hybrid reactors [36]. In other work, Zahoor has used granular activated carbon (GAC) as an alternative of PAC in order to minimize secondary problems associated with the use of PAC in the UF membrane processes, cake formation, long backwash times and blackening of pipes. The designed pilot plant for GAC/UF hybrid system has shown in Figure 6. Secondary problems have not been observed for GAC/UF process. The GAC had high adsorption capacity and their particles were larger than PAC which can be kept from flowing with effluents into the membrane system. Langmuir and Freundlich adsorption have been used to describe the adsorption of 2,4-Di-chlorophenoxyacetic acid (2,4-D) and paraquat on GAC. Adsorption capacity of adsorbent was high for 2,4-D as compared to paraquat. Also, the R_2 value was high for Langmuir model as compared to Freundlich model. Retention percentage of 2,4-D by membrane was high and thus the decline in

permeate flux was high as compared to paraquat in UF membrane process. 100% retention of 2,4-D was achieved in GAC/UF hybrid system. Improved permeate fluxes have been observed for both contaminants in the hybrid system. From economical point of view, the use of PAC in the membrane systems is expensive as compared to GAC, which reduces backwashing time and do not causes blackening of the pipes.

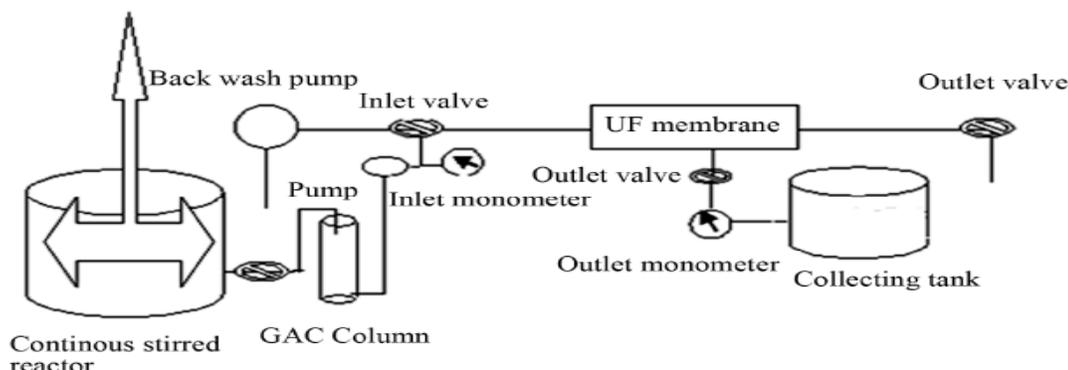


Figure 6. Granular activated carbon (GAC)/Ultrafiltration (UF) pilot plant (Zahoor, 2013).

Advanced oxidation processes (AOPs)

To reduce the paraquat and other herbicides impact, powerful and practical treatment processes for its degradation in environmental water are needed. The traditional treatment techniques are not sufficiently effective for most pesticides and herbicides (Santos et al., 2011; Esplugas et al., 2002). On the other hand, in some physical processes there is a simple transfer of the pollutants from one phase to another, not being destroyed. The advanced oxidation processes are clean technologies based on the generation of extremely reactive and non-selective hydroxyl radicals, with very high oxidative power ($E_0=2.8$ V). Due to their powerful capability to oxidize numerous organic compounds into CO_2 and H_2O , AOPs have been selected for various applications (Santos et al., 2011; Sabet et al., 2014; Jafarinejad, 2015a; 2015b; Esplugas et al., 2002; Mota et al., 2008). Among them, ozonation process (Kearney et al., 1985; Andreozzi et al., 1993), photocatalytic process (Lee et al., 2003; Tennakone and Kottegoda, 1996; Moctezuma et al., 1999; Kang, 2002; Florêncio et al., 2004; Cantavenera et al., 2007; Kanchanatip et al., 2011), the Fenton's reaction (Oliveira et al., 2012; Santos et al., 2011; Oliveira et al., 2014; Dhaouadi and Adhoum, 2010) and electrochemical processes (Dhaouadi and Adhoum, 2009) have been used for paraquat removal from aqueous solutions.

Ozonation process

As action mechanism of ozonation does not produce chlorinated compounds that may originate in the chlorine disinfection process, in recent years, use of it has grown in treatment of drinking water (Mota et al., 2008; Augugliaro et al., 2006). However, its use in wastewater treatment is limited, owing to the high demand of energy to generate ozone (Mota et al., 2008; Titus-Pera et al., 2004). Furthermore, the efficiency of ozone is extremely dependent on gas-liquid mass transfer, which is impeded by the low solubility of ozone in aqueous solution (Mota et al., 2008; Gogate et al., 2004). Ozone has a high reduction potential (2.07V), and can react slowly and directly with an organic substrate (Mota et al., 2008; Augugliaro et al., 2006). However, the use of ozone is only characterized as an AOP when it decomposes to generate hydroxyl radicals (Eq. (1)), and can be catalyzed by hydroxyl ions (HO^-) in alkaline medium or by transition metal cations (Mota et al., 2008; Augugliaro et al., 2006; Pera-Titus et al., 2004).



The efficiency of ozone in degrading organic compounds is improved when combined with H_2O_2 , UV radiation or ultrasound.

Kearney et al. have used UV/ozonation for removal of paraquat under operating conditions: paraquat concentration= 1500 mg/L, 32 g O_3 /h, and 66 low-pressure mercury vapor lamps (254 nm). Significant oxidation of paraquat has not been occurred in the presence of oxygen during 7 h. But, when O_3 has been fed, 32.8% of it has been destroyed during 7 h [80]. Also, Andreozzi et al. have studied ozonation of paraquat under operating conditions: paraquat concentration= 231–2057 mg/L, 38.6 L O_3 /h, and pH = 4.2–8.0. Paraquat has been degraded after 120 min of reaction at pH=8.0. N-methylisonicotinic acid, N-formyloxamic acid, ammonia, oxamic acid and nitrate have been proposed for intermediate compounds of paraquat oxidation (Andreozzi et al., 1993).

Photocatalytic process

According to Mota et al. (2008), the principle of heterogeneous photocatalysis is based on the activation of a semiconductor particulate material (CdS, TiO₂, ZnO, WO₃ etc.) by the action of radiation with an appropriate wavelength. With the absorption of photons by the semiconductor particle possessing enough energy to promote the conduction of an electron (e⁻) from its valence band (VB) to the conduction band (CB) (a transition called bandgap energy), activation is achieved and creating holes in the valence band (h⁺) that will act as oxidizing sites. On the other hand, according to Hoffmann et al., UV illumination onto a photocatalyst excites to produce electron and hole pair (e⁻/h⁺) with high-energy state, which migrate to the particle surface and initiate a wide range of chemical redox reactions. The valence band potential (+2 eV) is positive enough to generate hydroxyl radicals at the surface and the conduction band potential (-0.2 eV) is sufficiently negative to reduce molecular oxygen. The hydroxyl radical is used as a powerful oxidizing agent to convert organic pollutants into CO₂ and less toxic by-products (Lee et al., 2003; Hoffmann et al., 1995).

Tennakone and Kottegoda (1996) have reported that 50 mg paraquat/L was decomposed in aqueous solutions, when in contact with TiO₂ affixed on a polymer film on irradiation for 6 h with a 400 W medium-pressure mercury lamp. They have found that paraquat could be mineralized to CO₂, NH₃, HCl and small quantities of NO₂⁻/NO₃⁻ by solar or artificial irradiation of contaminated water in the presence of TiO₂-coated film (Santos et al., 2011; Lee et al., 2003; Tennakone and Kottegoda, 1996).

Moctezuma et al. (1999) have used UV light over commercial TiO₂ to remove paraquat under operating conditions: paraquat concentration= 10, 20 and 40 mg/L, UV (365 nm), 50 mL O₂/min, 200 mg TiO₂/L, pH = 4, 6.6, 7 and 9. They have reported that paraquat is slowly degraded by direct photolysis in the presence of dissolved oxygen (paraquat concentration= 20 and 40 mg/L; pH=6.6). Direct photolysis with UV light destroyed 60% of paraquat in less than 3 h of reaction (paraquat concentration= 10 mg/L; pH=6.6). In the presence of TiO₂, all species were consumed after three hours of reaction at high pH values (Moctezuma et al., 1999; Santos et al., 2011). Also, Kang (2002) has prepared TiO₂ photocatalyst film using hydrothermal method and investigated its catalytic performance for paraquat decomposition under operating conditions: paraquat concentration=1000 mg/L, 0.5 L air/min, TiO₂ film (three-time coating), UV-light intensity: 36 W/m². About 100% of paraquat has been degraded after 15 h of reaction (Kang, 2002; Santos et al., 2011). Lee et al. (2003) have removed paraquat in aqueous suspension of TiO₂ in an immersed UV photoreactor. The schematic diagram of photoreactor with suspended TiO₂ in Lee et al. work is shown in Figure 7. They have reported that the required time for 90% removal of paraquat was 18, 12, and 2 h at the UV light intensities of 12, 24, and 36W/m², respectively. The removal rate of paraquat in the reactor was 0.54 mg/L/h with only air-sparging. The removal rate in 24 h with both the UV radiation and air-sparging was 50% higher than that with only the UV radiation. Variations of the paraquat concentration at the UV intensities of 4 and 8 W/m² decreased slowly with time, but that at 12 W/m² decreased more rapidly. The removal efficiency at the air-sparging flow rate of 1 L/min increased as a UV light intensity increased. pH value in the reactor at the UV intensity of 12W/m² decreased with time until 12 h and then increased with time over 12 h (Lee et al., 2003; Santos et al., 2011).

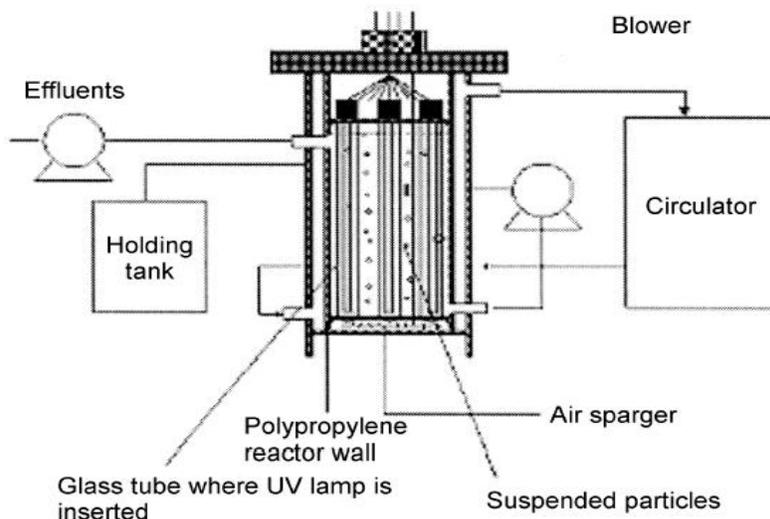
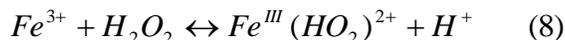
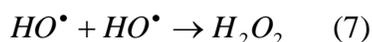
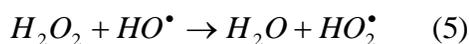
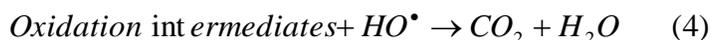
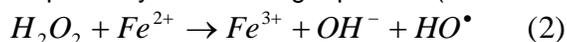


Figure 7. Schematic diagram of photoreactor with suspended TiO₂ in Lee et al. work (2003).

Florêncio et al. (2004) have investigated photodegradation of diquat and paraquat in aqueous solutions by TiO_2 . Operating conditions have been: paraquat concentration = 7.5 mg/L, 200 mg TiO_2 /L, and pH = 4, 7 or 9. Under alkaline medium, paraquat degradation was almost complete after 30 min of reaction (Florêncio et al., 2004; Santos et al., 2011). Moreover, Cantavenera et al. (2007) have studied photocatalytic degradation of paraquat under paraquat concentration = 20 mg/L, 0.04 and 0.4 g TiO_2 /L, UV-light intensity: 140 W/m². Near complete mineralization of paraquat have been achieved after ca. 3 h of irradiation by using 0.4 g/L of catalyst amount at neutral pH (ca. 5.8) (Cantavenera et al., 2007; Santos et al., 2011). Also, Kanchanatip et al. (2011) have worked on degradation of paraquat under visible light over fullerene modified V- TiO_2 with paraquat concentration = 15–50 mg/L, 1 g catalyst/L. They have reported 70% degradation within 4 h (Kanchanatip et al., 2011; Santos et al., 2011).

Fenton's reaction

Fenton's reaction is a non-expensive and environmental friendly oxidation method, which appeared in 1894 when Fenton strongly improved tartaric acid oxidation by the use of ferrous ion and hydrogen peroxide (Fenton, 1894; Santos et al., 2011). This process is widely used in wastewater treatment. Fenton's reagent is a solution of hydrogen peroxide and ferrous ions and this process has a complex mechanism, which can even though be simplified by the following equations (Santos et al., 2011; Mota et al., 2008; Sun et al., 2007; Jiang et al., 2010):



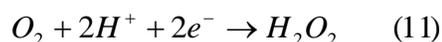
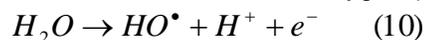
Briefly, the reaction between iron and hydrogen peroxide produces hydroxyl radicals with high oxidative power (Eq. (2)), which attack the organic matter present in the water (Eq. (3)). Unfortunately, some parallel reactions occur (Eqs. (5)–(7)), and so the hydroxyl radicals are not only consumed to degrade the organic matter but also to produce other radicals, with less oxidative power, or other species (scavenging effect of HO^\bullet). Besides, this leads to the undesired consumption of hydrogen peroxide (Eq. (5)). On the other hand, Eqs. (8) and (9) indicate a generation of Fe^{2+} by the reaction between H_2O_2 and Fe^{3+} (Fenton-like process); this way ferrous ion is restored, acting as catalyst in the overall process (Santos et al., 2011).

Dhaouadi and Adhoum (2009) have used four different activated carbons as catalysts in paraquat degradation by the heterogeneous Fenton's process under paraquat concentration=20 mg/L, 1 g catalyst/L, T= 70 °C, hydrogen peroxide concentration=12.5 mM. 71.4% of chemical oxygen demand abatement (COD) has been obtained under the conditions indicated. Moreover, Santos et al. (2011) have studied paraquat removal from water by oxidation with Fenton's reagent. Under selected conditions (T = 70.0 °C, $[Fe^{2+}] = 5.0 \times 10^{-4}$ M, $[H_2O_2] = 3.4 \times 10^{-2}$ M, and pH = 3.0) nearly all the initial paraquat dichloride present in the reactor was degraded after 60 min and 60% of the organic matter has been totally mineralized into CO_2 and H_2O , after 240 min. Under the optimum conditions (T = 30.0 °C, $[Fe^{2+}]_0 = 5.0 \times 10^{-4}$ M, $[H_2O_2]_0 = 1.6 \times 10^{-2}$ M, and pH₀ = 3.0, for $[paraquat]_0 = 100$ mg/L), complete paraquat degradation and about 40% of mineralization have been reached after 4 h of reaction (batch reactor). In the other work, Oliveira et al. (2012) have used real pipe deposits as peroxidation catalysts (heterogeneous Fenton-like oxidation process) to degrade the herbicide paraquat in water; the process is essentially catalytic, being negligible the role of adsorption. However, the contribution of the homogeneous process by dissolved iron and other ions depends on the type of deposit used. This provides a useful application of these solid wastes that result from either cleaning or maintenance operations in water distribution systems. The deposits are quite complex and the reasons for their completely different performances are not yet completely clear. Even so, it has been anticipated that the iron oxides present in each sample played a role, although the presence of other metals should not be ruled out. The pH_{pzc} (point of zero charge) of the deposits have been also of concern, as they inherently affected the medium pH when the deposits were added to a paraquat solution. For the solids tested, the effect of particle size was almost negligible. A better degradation has been achieved when the pH of 3.0 was used. Nevertheless, the possibility of using higher pHs has been evidenced, up to values of at least 7, due to the

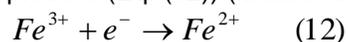
acidification of the water along oxidation/solids addition. This way, the need of acid consumption in the pre-acidification stage was avoided, as commonly required in the Fenton's process. The calcium rich deposit was only useful as catalyst when the medium pH was adjusted to the required acidic values of Fenton's reaction. They have concluded that, depending on the types of solids present in given water network, in situ treatment can be made without insertion of chemicals apart from the oxidant, in case of a contamination event. Also, Oliveira et al. (2014) have investigated paraquat degradation in the pilot loop system, achieving similar results to those obtained in a lab scale reactor. Initial pH has been proven to be a very important factor for Fenton reaction. Results have shown complete paraquat degradation (nearly 100% within 8 h) if initial pH was 3 and little degradation rate (30% within 24 h) if initial pH was 5. For the first time, they have shown that distribution system pipes can work as a catalyst for Fenton reaction providing also complete paraquat degradation; the installation of old cast iron segments with length from 0.5 to 14 m into PVC pipe loop system had a significant positive effect on degradation rate of paraquat, even without addition of iron salt; the larger the pipe, the bigger is the contribution of the heterogeneous process. They have reported that once iron pipes work as catalysts, water decontamination can be done in-situ, using the appropriate operating conditions. Loose deposits can be used as catalysts, but special care must be taken to their composition. The gradual addition of H₂O₂ showed to be the best option in the oxidation process, allowing reaching higher mineralization degrees, up to 60% in only 24 h.

Electrochemical process

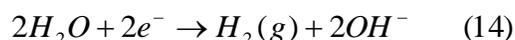
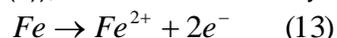
In electrochemical processes, hydroxyl radicals can produce by two means: anodic oxidation (AO) (direct form) and mediated electro oxidation (indirect form). In anodic oxidation, the hydroxyl radical is generated in the anode (Pt, PbO₂, doped with SnO₂ etc.) of an electrochemical cell from water oxidation (Eq. (10)). In mediated electro-oxidation, chemical species, such as H₂O₂, are continuously generated in the cathode by the reduction of two electrons of dissolved oxygen (Eq. (11)) (Mota et al., 2008; Brillas et al., 1998; Brillas et al., 2002):



The generated H₂O₂ can act as a reagent for Fenton's system, with the addition of iron, leading to the formation of hydroxyl radicals (Eq. (2)) (electro-Fenton (EF) process) [79, 98]. If the Fe³⁺ obtains with Fenton's reaction (Eq. (2)) or add to the solution, can be continuously reduce to Fe²⁺, creating an electrochemical catalysis process (Eq. (12)) (Mota et al., 2008; Oturan and Brillas, 2007).



With the introduction of UV to help reduce Fe³⁺ to Fe²⁺, the oxidation power of the system can also be increased (photoelectron-Fenton (PEF) process) (Mota et al., 2008; Wang, 2008). Fenton's electrochemical process can also be used by means of an electrochemical cell with iron electrodes (cathode and anode), in which the anode has the function of transferring iron to the solution and the cathode functions as an inert electrode for water reduction, as shown in Eqs. 13-14. The Fe²⁺ transferred by the cathode acts in the Fenton's reaction (Eq. (2)), with the addition of hydrogen peroxide to the system (Mota et al., 2008; Saltmiras and Lemley, 2002).



Dhaouadi and Adhoum (2009) have studied degradation of paraquat by electrochemical methods; in fact, they have tested and compared four different advanced oxidation methods in the degradation of paraquat: anodic oxidation, electro-Fenton, photoelectro-Fenton and classic Fenton (CF). The operating conditions was: paraquat initial concentration= 10.50 mg/L, T = 25 °C, pH = 3, [Fe²⁺]₀ = 0.1.2 mM, [H₂O₂]₀ = 20 mM, current intensity: 50, 100 and 200 mA. The paraquat concentration versus time plot has indicated that the fastest initial degradation rate was attained for CF method but after 20 min no paraquat degradation was observed. Dhaouadi and Adhoum (2009) have concluded that CF has a significantly lower oxidative ability as compared to other systems. However, this may be due to the insufficient peroxide quantity used in the operation. The photoelectro-Fenton has been the most efficient treatment method (Santos et al., 2011; Dhaouadi and Adhoum, 2009).

Future Perspectives

In current state, different analytical techniques have been applied for determination of herbicide paraquat in water samples, and several treatment processes such as adsorption, membrane filtration, combination of adsorption and membrane filtration processes, ozonation, photocatalytic, Fenton's reaction and electrochemical

processes have been used for its removal from aqueous solutions. In the future, several works can be done in these directions:

- Economical comparison of these different methods for removal of herbicide paraquat from aqueous solutions
- Suggestion of new adsorbents (natural, nano-materials, etc.) with a large adsorption capacity and combination of this method with the other separation techniques for removal of herbicide paraquat from water matrices
- Use of Dispersive Liquid-Liquid Micro-Extraction (DLLME) for separation of herbicide paraquat from water samples and comparison of it with the other techniques
- Investigation of Supercritical Water Oxidation (SCWO) for removal of herbicide paraquat from environmental waters

CONCLUSION

To overcome the requirements of the environmental program, based on goals and limitations of the U.S. EPA, the European Union and World Health Organization, simple and effective sample preparation and sensitive analytical methods are necessary for determining paraquat in environmental waters. Paraquat in water samples can be determined by many different analytical techniques such as spectrophotometry, CE with UV, optical immunosensor, electrochemical batch-injection analysis, LC, LC/MS, and LC/MS/MS. Many of the reported spectrophotometric methods are less sensitive and suffer from many drawbacks. Solid phase extraction was the most common procedure for extraction/preconcentration of paraquat. The BIA technique with removal of any pre-treatment steps, to the electroanalytical detection of this herbicide by square wave voltammetry during sample injection, have shown that it can be detected at $\mu\text{g/L}$ levels with small injection volumes ($<100 \mu\text{L}$) and times (<2 seconds). The U.S. EPA method 549.2 utilizes reversed-phase chromatography with ion pairing for the separation of diquat and paraquat using UV detection. Ion pairing agents are typically avoided with ESI-MS applications owing to suppression of the ionization in the MS source. For MS applications, HILIC has provided suitable chromatography without the requirement of ion pairing agents. However, recent advances in MS sensitivity have made the direct analysis of trace-level contaminants in water attainable and very attractive. The possibility of removing laborious and time-consuming solid phase extraction and sample concentration is highly desirable. To reduce the paraquat impact, powerful and practical treatment processes for its separation from environmental waters are needed. The removal methods of paraquat from water samples have broadly classified into two categories; recuperative processes like adsorption on porous solids, membrane filtration, combination of adsorption and membrane filtration processes, and destructive processes like advanced oxidation processes i.e. ozonation, photocatalytic, Fenton's reaction and electrochemical processes. In physical processes there is a simple transfer of the pollutants from one phase to another, not being destroyed; but in advanced oxidation processes there is a capability to oxidize organic compounds into CO_2 and H_2O .

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