

Chapter

Green Methods of Chemical Analysis and Pollutant Removal

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Abstract

This chapter deals with chemical analysis and pollutant removal methods that follow some of the 12 principles of Green Chemistry. In this chapter, the 12 principles of the Green Chemistry along with the short description are highlighted. Several chemical analysis methods are presented, that are both used for chemical identification and concentration determination, whether conventionally or instrumentally. The conventional chemical analysis methods evaluated in this chapter include volumetric and gravimetric, while the instrumental ones presented are limited to atomic absorption spectrometry (AAS) and X-ray fluorescence (XRF) for determination of the analyte concentration, and Infrared spectrometry (IR) and X-ray diffraction (XRD) for chemical identification. Additionally, the pollutant removal methods involving conventional and advanced processes, are reviewed. The conventional chemical removal methods such as precipitation, coagulation, and adsorption are illustrated. The advanced methods in removing chemical pollutants discussed in this chapter are photocatalytic degradation, photo-oxidation/reduction, Fenton and Photo-Fenton, and ozonation. In the description of the chemical analysis and the chemical pollutant removal methods, the evaluation of the unsuitableness or suitableness toward some of the Green Chemistry principles are also accompanied. In addition, the ways to make the less green methods to be greener are also proposed.

Keywords: green chemistry principles, chemical analysis, pollutant removal, method greening

1. Introduction

The principles of Green Chemistry consist of 12 aspects, including [1–5]:

1. Pollution Prevention/Waste minimization,
2. Atom Economy,
3. Less Hazardous Chemical Synthesis.
4. Designing Safer Chemicals,

5. Safer Solvents and Auxiliaries,
6. Design for Energy Efficiency,
7. Use of Renewable Feedstocks,
8. Reduce Derivatives,
9. Catalysis,
10. Design for Degradation,
11. Real-time analysis for Pollution Prevention, and.
12. Inherently Safer Chemistry for Accident Prevention.

Principle no.1 refers that chemical pollution in the environment has to be prevented by minimizing waste from industrial production, chemical analysis laboratories, hospital activities, and many others. Some believe that it is better to prevent waste generation than to treat or clean up waste after it has been generated.

In principle no.2, it is presented that synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. Hence no waste or minimum waste has resulted.

Principle no.3 suggests that whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Based on principle no.4, it is illustrated that chemical products should be designed to preserve efficacy of the function while reducing toxicity. Green Chemists make sure that the things that we synthesize not only do what they are supposed to do, but they do it safely.

In Principle no.5, it is described that the use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.

It is suggested by Principle no.6, that energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

Principle no.7 refers that raw material or feedstock should be renewable rather than depleting whenever technically and economically practical. Green chemists look for alternative sources for making materials. Renewable feedstocks (corn, potatoes, biomass) can be used to make many products: fuels (ethanol and bio-diesel), plastics, and more.

It is implied by principle no. 8, that unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

Principle no.9 refers that in chemistry and biology, catalysis is the acceleration (increase in rate) of a chemical reaction by means of a substance, called a catalyst, which is itself not consumed by the overall reaction. Using catalysts can reduce energy, increase efficiency, and reduce by-product formation, which further generates energy efficiency and waste minimization.

Principle no.10 expresses that chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation product. Design for degradation means that when green chemists design a new chemical (i.e., a pharmaceutical drug or medicine) or material (i.e., a new plastic) – they design it so that it breaks down at the end of its useful lifetime.

In principle no.11, it is messaged that real-time analysis for a chemist is the process of checking the progress of chemical reactions as it happens. Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances. Knowing when your product is “done” can save a lot of waste, time, and energy.

Principle no.12 infers that substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

The 12 principles of the Green Chemistry enable people to protect the planet from chemical threats and energy crisis, as well as to find creative ways to reduce chemical waste, conserve energy, and replace hazardous substances [2]. Hence, all human activities should be based on or considered to the all or some of the 12 principles of the Green Chemistry. Some of the activities involving chemicals are material production/synthesis, chemical analysis, and chemical pollutant removal/treatment. In this Chapter, only chemical analysis and chemical pollutant removal or treatment methods are presented.

Many chemical analysis methods are recognized that are frequently used in a variety of fields including environment, health, food, mining, even archeology [6]. The analysis of chemical methods is usually conducted for identification of a certain chemical or some chemicals as well as for determination of the chemical concentration in the sample(s) [6–12]. The chemical analysis methods widely used involve simple as well as advanced technologies [6–12]. The conventional methods usually use more chemicals and auxiliaries [11], hence further resulting in the toxic chemical waste and wastewater, which create pollution [8, 9]. In contrast, the instrumental chemical analysis methods need less chemicals but may consume more energy [9, 10, 12]. The chemical waste and wastewater and inefficient energy are opposite to the principles of the Green Chemistry, which are waste minimization or pollution prevention, safer solvents and auxiliaries, and efficient energy [8, 9].

In order to reduce chemical waste, conserve energy, and replace hazardous substances, evaluation of some chemical analysis methods is required. It is important, therefore, to recognize the chemical analysis methods that are less suitable and suitable to the principles of the Green Chemistry. The ways to make the chemical analysis methods to be green are also essential to be explored and further to be used.

In addition, a lot of human activities involving chemical processes such as industry, mining, medical, and transportation, always result in chemical waste, that can be formed as gas/particulate, liquid and solid. The chemical waste or wastewater disposed of into the environment without any proper treatment lead to serious pollution [13–18].

The high air pollution can generate a variety of adverse health outcomes. It increases the risk of respiratory infections, heart disease, and lung cancer [13, 14]. The sources of air pollution vary from small units of cigarettes and natural sources such as volcanic activities to large volume of emissions from motor engines of automobiles and industrial activities. Both short and long-term exposure to air pollutants have been associated with health impacts. The most health-harmful pollutants – closely associated with excessive premature mortality – are fine PM_{2.5} particles that penetrate deep into lung passageways [14].

The serious water pollution due to the inadequately treated or treated industrial wastewater effluents may cause eutrophication in the receiving water bodies and also form a favorable condition for toxin-producing waterborne pathogens [15–18]. The chemicals in wastewater usually comprise of heavy metals and organic compounds [14, 17].

The release of heavy metals into wastewater through human and industrial activities has become a major problem both for humans and aquatic lives. Some negative impacts of heavy metals on aquatic ecosystems include the death of aquatic life, algal blooms, habitat destruction from sedimentation, debris, increased water flow, and other short- and long-term toxicity from chemical contaminants [17, 18]. Severe effects on human health may include reduced growth and development, cancer, organ damage, and nervous system damage [17, 18]. Among the heavy metals, hexavalent chromium is ranked among the top sixteen toxic pollutants that have harmful effects on human health. High chromium dosage has been reported to cause damage to human kidney and the liver, and at low concentration, it causes skin irritation and ulceration. Exposure to high chromium concentration also causes cancer in the digestive tract and lungs [18].

Persistent organic pollutants (POPs) are organic compounds of anthropogenic origin that resist degradation and accumulate in the food chain, and in extreme cases, death [13, 14]. Owing to their toxicity, they can pose a threat to humans and the environment. Some of the POPs polluting water are pentachlorophenol, DDT, hexachlorocyclohexanes, hexachlorobenzene, heptachlor, polychlorinated dibenzo-p-dioxins, polycyclic aromatic hydrocarbons, polychlorinated terphenyls, polybrominated diphenylethers, polybrominated dibenzo-p-dioxins, dibenzofurans, and short-chain chlorinated paraffins [14].

Therefore, removal of chemicals from wastewater before reaching ecosystem is urgent. Many methods for waste treatment are frequently reported, including conventional and advanced methods [19–21]. The conventional methods usually need more chemicals and so that dispose of chemical waste than the advanced methods [21]. The advanced methods use more energy such as light and high temperature than the conventional methods [21].

Using many chemicals and high energy is unexpected because these against the principles of the Green Chemistry [1–5]. It is still necessary to expose the chemical pollutant treatment methods that do not fully follow and follow the principles of the Green Chemistry. By knowing the greener pollutant removal methods, people can choose to use them, and further can prevent the environmental pollution and energy crisis.

Under the circumstances, in the following sections, some chemical analysis and pollutant removal methods that have unsuitableness or suitableness procedures toward some of the Green Chemistry principles are described, and the ways to substitute the less green with the greener methods are also presented. The chemical analysis and pollutant removal methods discussed are presented in the table below (Table 1).

2. Green chemical analysis methods

Green chemical analysis is an analysis procedure that avoids or reduces the undesirable environmental side effects of chemical analysis while preserving the classic analytical parameters of accuracy, sensitivity, selectivity, and precision [9, 10]. The

No	The methods	Function	Greenness
1	Volumetric	Quantitative chemical analysis	Less
2	Atomic absorption spectrophotometric	Quantitative chemical analysis	Less
3	X-Ray Fluorescence	Quantitative chemical analysis	Green
4	X-Ray diffraction	Identification	Green
5	Fourier Transform Infrared	Identification	Green

Table 1.
The chemical analysis and pollutant removal methods.

goal of green analytical chemistry is to use analytical procedures that generate less hazardous waste and that are safer to use and more benign to the environment. The main analytical result is related to an increase in analysis reliability, higher precision, and time-saving, which very positively combines with a substantial reduction of waste [9, 10]. The Green chemical analysis should apply at least four Green Chemistry principles, from the 12 principles [10], which are:

1. waste minimization or pollution prevention or prevention of waste generation (no. 1).
2. safer solvents and auxiliaries (no. 5),
3. design for energy efficiency (no. 6), and
4. safer chemistry to minimize the potential of chemical accidents (no. 12).

The chemical analysis methods can be categorized into conventional and instrumental methods, which are used whether for identification and concentration determination purposes [6, 7, 11, 12]. In this section, the conventional analysis method that is evaluated regarding greenless or greenness is volumetric, since it is widely used in environmental and food fields. Meanwhile, the instrumental methods discussed are limited to atomic absorption spectrophotometric the (AAS), X-ray fluorescence (XRF) Infrared spectrometry (IR), and X-ray diffraction (XRD), due to their intensively use in various fields.

2.1 Volumetric method

Volumetric is a chemical analysis method based on the reaction between analytes with the respective standard solution placed in a burette. This method is usually performed with large volume, and sometimes uses hazardous auxiliary. The solutions both standard and analyte, at the end of the process, become harmful wastewater. Although categorized into old or conventional method, volumetric is still frequently used as a standard method in environmental, food, and mineral analysis [8, 11].

In the environmental field, volumetric is placed as a standard method for chemical oxygen demand (COD) assay. COD level represents the quantity of organic and oxidizable inorganic chemicals polluting sample water. A commonly used oxidant in the COD assay is potassium dichromate ($K_2Cr_2O_7$) in combination with boiling sulfuric acid (H_2SO_4) [11]. It is clear that this procedure uses the toxic and carcinogenic

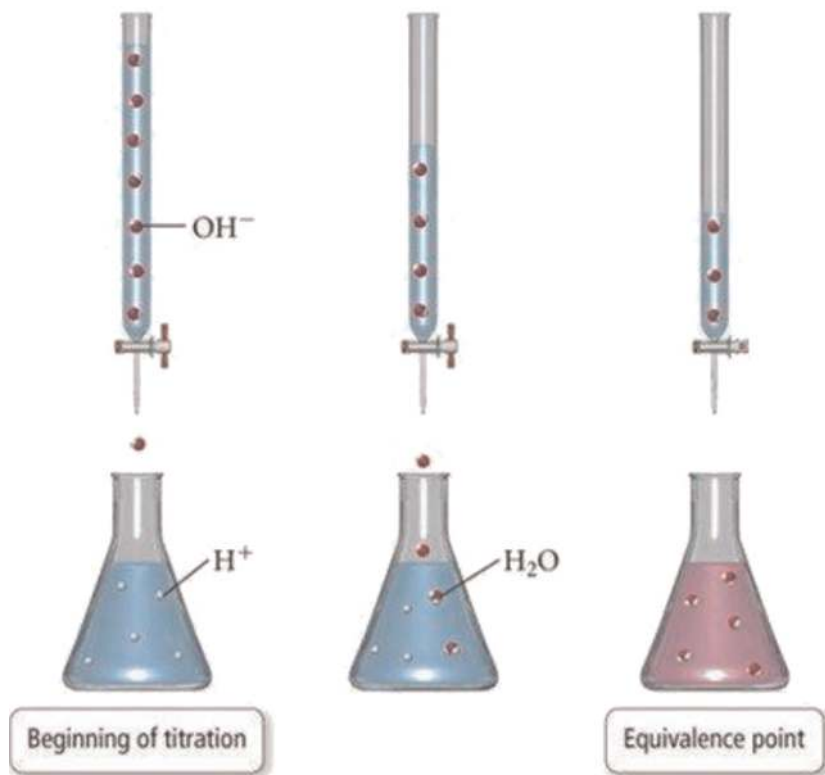


Figure 1.
Titration technique [8].

$\text{K}_2\text{Cr}_2\text{O}_7$ and corrosive sulfuric acid as the auxiliaries, which is against the Green Chemistry Principle number 5 [1–5]. Further, a large volume of $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{H}_2\text{S}_2\text{O}_4$ solutions are usually used, which results in a large volume of the corresponded chemical wastewater. This resultant of the wastewater will advance to create environmental pollution, which clearly is not suitable to the Green Chemistry Principle number 1 (Figure 1) [1–5].

Volumetric method is also used in food analysis, that is to determine saponification number. The saponification number represents an indication of the nature of the fatty acid's constituent of fat in coconut oil, olive oil, and sesame oil. In this procedure, KOH or NaOH, HCl, ethanol, and ether have to be used in large volumes. The use of the corrosive NaOH/KOH will leave the poison waste, which is unsuitable with principle no 1. In addition, since the procedure also uses the hazardous solvents, the procedure is contradiction with principle no 5.

The COD measurement is essential in monitoring the environmental quality and the determination of saponification number has an important role in food quality, so greenings the procedures are required. Greening analysis methods generally can be conducted in several ways [9, 10], such as:

1. modifying an old method to incorporate procedures that either use less hazardous chemicals or use lesser amounts of hazardous chemicals.
2. developing new analytical methodologies; instrumental methods in analysis is a decrease in sample volume needed for analysis.

3. use of direct techniques of analysis,

- i.e., different laser-spectroscopic methods
- or solventless processes of analysis

In the case of COD determination, the greening procedure can be conducted by reducing the quantity or volume of the reagent or substituting the toxic reagent with the safer or less toxic one. The strong oxidant but toxic $K_2Cr_2O_7$ can be substituted with $KMnO_4$ [4]. The other way is by applying a smaller volume of the reagents, which hence results in low volume of the wastewater or minimize the wastewater. Using instrumental method to determine saponification number, such as gas chromatography [6], which is greener, is also possible.

2.2 Spectrophotometric methods

2.2.1 Atomic absorption spectrophotometric (AAS)

Atomic absorption spectrophotometric (AAS) method provides concentration data of metals dissolved in the solution. Accordingly, solid samples such as soils, food, minerals, etc. have to be destructed to form a clear solution containing dissolved metal ions [12, 13].

In the AAS method, the dissolved metals have to exist in atomic form. The atomization of the metal ions requires high temperature, which can be from flame or from electric thermal, and flameless conditions [13]. In AAS method, chemicals are not required [12, 13] that can prevent waste generation, following principle no.1 [1–5]. It is clearly suggested that the method falls into a green chemical analysis method.

The atomization of most metal ions usually takes place at high temperature, about 2000–2500°C which can be provided by flame [13], as illustrated by **Figure 2**, and also can be from electric from graphite furnace. The high-temperature flame, in addition to consumes high energy also generates potential accidents, which are contrary to the principle number 6 and 12, respectively. The high electricity consumption is not in accordance to the principle no 6. It is concluded that based on the energy aspect, AAS is included as a less green method. Additionally, among the

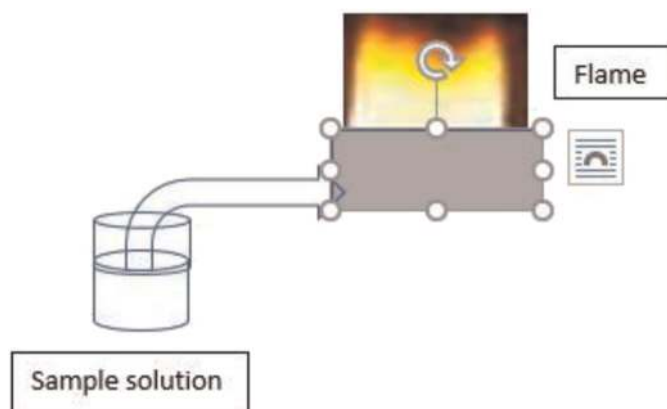


Figure 2.
Flame for atomization in AAS analysis.

metal ions, mercury is the liquid metal at room temperature allowing it to evaporate at high temperature. Accordingly, the atomization of mercury cannot be conducted at high temperature, but to be performed by reducing it to form an atomic phase at room temperature, then called flameless atomization [13]. Accordingly, flameless AAS seems to be greener than the flame one in terms of energy efficiency.

2.2.2 X-ray fluorescence (XRF) and X-ray diffraction (XRD)

XRF method is used for the determination of the elemental concentration, whether metals, metalloids, and non-metals. This method can be used for measuring solid, liquid, and aqueous solutions. The solid samples can be directly measured, and no needs to be prepared into the aqueous solutions, and hence no chemicals are used. Additionally, all metals, metalloids, and non-metals in the samples can be directly measured without any atomization to form elements [13]. It is clear hence that XRF is greener method than AAS to get the same information.

XRD can only be used for crystalline solid samples and that can be directly measured. In this method, chemicals are not required, avoiding it to result in waste. The samples have to be powdered with 100–250 mesh in size. The information given by this instrument is the type of crystal samples [13]. This method does not result in any chemical waste preventing environmental pollution.

However, some believe that the X-ray is a hazardous ray, but in the XRF and XRD instruments, the ray is strictly prevented to irradiate objects including people surrounding. Hence, these methods are in accordance with the principle of Green Chemistry no 12.

2.2.3 Fourier transform infrared (FTIR)

FTIR is a spectrophotometric method required to detect the characteristic bonds in molecules, which can further be used for the identification of the molecules. The samples analyzed can be liquid or solid. In the analysis proses, the liquid samples are placed in cuvettes, while the solid powdered is pelleted with KBr matrix [13]. This method does not need any chemicals and is operated with the low energy infrared. It is obvious that this spectrophotometric method meets the principles no. 1 and no. 6 of the green chemistry.

3. Green methods for pollutant removal

Human activities in hospitals, mining, variety of industries, and other fields almost always result in chemical waste and wastewater. The chemical waste can be toxic heavy metals, hazardous dyes, and persistent organic compounds. These unexpected chemicals adhere human health and ecosystem, which are essential to be treated or removed before entering the environment [14–18].

Several pollutant treatment/removal methods are recognized that are related to conventional and advanced technologies [20–23]. The conventional methods are represented by coagulation and adsorption, and the advanced methods discussed in this chapter consist of photocatalytic -degradation and photo-oxidation, categorized into advance oxidation processes (AOPs).

3.1 Coagulation

Coagulation is essentially a chemical process. It is the destabilization of colloids by the addition of chemicals to neutralize the negative charges of the colloids and to consolidate suspended contaminants for easy removal from water [23–26]. The chemicals are known as coagulants that fall into two categories that are inorganic and organic materials. Frequently used inorganic coagulants include aluminum sulfate, aluminum sulfate, aluminum chloride, and ferric sulfate [24]. Examples of common organic coagulants are polyamines, melamine-formaldehyde, and tannins [25]. Generally speaking, anionic coagulants are suitable to catch mineral particles, while cationic coagulants can capture organic colloids. Inorganic coagulants are usually cost-effective and can be used in a wider variety of applications [24–26]. However, the inorganic coagulants are usually health hazardous and transferred into hazardous sludge in large volume. This is used for removing particles, colloids, or oily materials in suspension. The process of coagulation is illustrated in **Figure 2**. From figure, it can be seen that at the end of the process, large amount of toxic sludge is produced, from the colloidal pollutant and the chemical coagulant. This sludge can be categorized as solid toxic waste. Hence coagulation is opposite to the principle of Green Chemistry no 1.

To make the method greener, the toxic solid waste has to be treated properly, such as by solidification method. In the solidification, the solid waste is mixed with limestone and cement to form a compact and stable solid. The compact and stable solid waste can be avoided from releasing into the environment (**Figure 3**).

3.2 Adsorption

Adsorption is a process that leads to transfer of a molecule or an ion from a fluid bulk to solid surface. This can occur because of physical forces or chemical bonds. In the simple term, adsorption is the attraction of ions or molecules onto the surface of a solid [27, 28]. Adsorption takes place when ions or molecules in a liquid bind themselves to the surface of a solid substance. The solids are called adsorbents, which have a very high internal surface area that permits adsorption. The adsorbent materials known are natural or synthetic zeolites, natural clay minerals, silica gel, activated aluminum, and silicic acid [28].

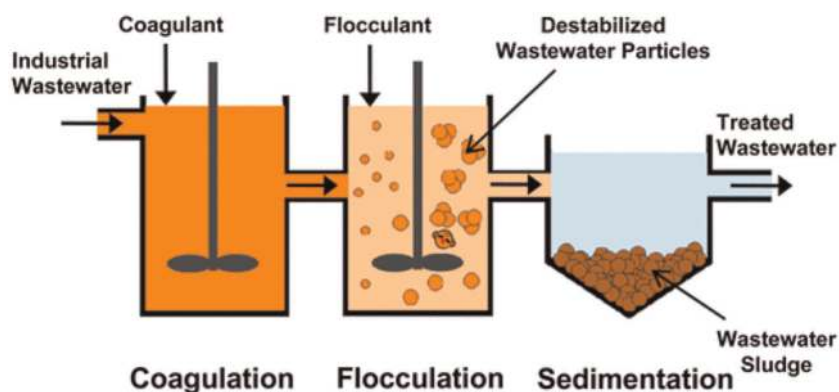


Figure 3.
Coagulation process [24].

Adsorption is believed as a simple and effective method to remove chemical or toxic pollutants. This method is most commonly implemented for the removal of low concentration of non-degradable organic compounds from groundwater, drinking water preparation, process water or tertiary cleansing after, for example, biological water purification [28, 29].

Furthermore, green adsorbents have also been developed, including bio sorbents prepared from Andean Sacha inchi (*Plukenetia volubilis* L.) shell biomass [30] and agricultural waste [31]. The adsorbents were prepared from the waste that are hazardous material free and low cost. It is obvious that such adsorbents well agree with the Green Chemistry principle no. 1, no. 3, and no. 5.

The adsorbents are usually non-toxic and low-cost materials. However, after a period of time (from minutes to hours) of the adsorption process, the adsorbent has been saturated with toxic pollutants, generating hazardous sludge or solid waste (**Figure 4**). It is clear as well that adsorption is less green method. The greening method can be conducted by converting the hazardous solid waste into a compact and stable solid material, preventing it to release into the environment.

3.3 Advance oxidation processes (AOPs)

Advanced oxidation processes are based on the generation of OH radicals that are very reactive, non-specific, and strong oxidant. The strength of the OH radical is indicated by the high standard reduction potential (E), as 2.80 V, which is higher than the standard reduction potential (E) of ozone (2.07 V), known as strong oxidizing agent [32]. AOPs are considered powerful methods for degradation of various organic pollutants due to their ability for removing almost any organic contaminant. A great number of methods are classified under the broad definition of AOPs based on the oxidizing agents applied [32–50].

Most of them use a combination of strong oxidizing agents (e.g., H_2O_2 , O_3) with catalysts (e.g., transition metal ions) and irradiation (e.g., ultraviolet, visible) [32–47]. A combination of H_2O_2 and Fe(II) ion transition metal known as Fenton agent is used Fenton process. When the Fenton process is accompanied by ultraviolet or visible light, the process is named as photo-Fenton. The process involving TiO_2 photocatalyst and ultraviolet light irradiation is drawn as a photocatalysis process. Using O_3 as oxidant in the degradation process is called ozonation. Oxidizing agents from metals, metal oxides, and graphene can also be included in the AOPs.

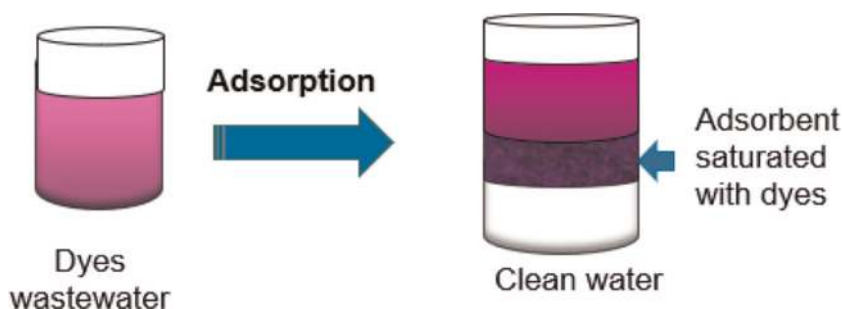
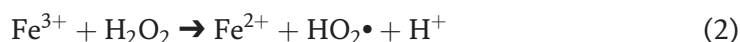


Figure 4.
Simple illustration of adsorption process.

3.3.1 Fenton/photo-Fenton processes

Fenton oxidation process is a catalytic reaction of H₂O₂ with ferrous ions, that predominantly produces OH radicals as the central oxidizing species, and ferric ions as shown in Eq. (1). Then the ferric ions are reduced back by H₂O₂ into ferrous ions, as presented by Eq. (2) [32–36].



The above reaction results in the continuous support of Fe²⁺ iron for the direct Fenton reaction, thus minimizing the required Fe²⁺ concentration, enhancing the catalytic oxidation cycle, and providing additional •OH [33].

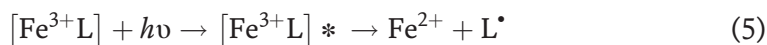
Photo-Fenton process involves a combination of Fenton reagents (Fe²⁺ + H₂O₂) and UV-visible radiation (λ < 600 nm) that gives rise to extra OH radicals by two additional reactions. The reaction of OH radicals' formation due to the photodecomposition of H₂O₂ by UV light, as presented in Eq. (3) [33].



Fenton, as well as Photo-Fenton type processes, are favored by acidic pH conditions, in the range of pH 2.8–3.0. However, the Fenton process produces a large amount of ferric hydroxide sludge at higher pH, which requires additional separation and disposal of solid waste (9). Accordingly, for the wastewater with higher pH in many cases, the acidification of the reaction medium is a necessity.

The application of UV-C and even UV-A (near UV) radiation during the Fenton (= photo-Fenton) process causes a dramatic increase in the •OH formation efficiency [33–36]. A large number of the •OH enables the use of lower ferrous catalyst concentrations, preventing the solid waste of the ferric hydroxide sludge. It seems that the photo-Fenton process is greener, in terms of waste minimization (principle no.1), and the effect of using UV light on the prevention of precipitation is found to be significant.

The low efficiency affecting photo-Fenton processes at neutral pH is mainly due to iron precipitation, and can be therefore prevented by properly adding iron complexing agents. As pointed out in reaction Eq. (5), such compounds (L) should be able to form stable complexes with Fe(III), which (i) significantly absorb UV-vis light and (ii) undergo photochemical reductions leading to Fe(II) ions [34–36]:



Iron complexing agents used for preventing precipitation of ferric hydroxide are Polycarboxylates and amino polycarboxylates that can form stable complexes with Fe(III), absorb light in the near-UV and the visible regions more efficiently than aquo-complexes [35, 36], and undergo photoreduction through a ligand-to-metal charge transfer (LMCT) generating Fe(II) ions [36]. The iron complexing compounds should be photo-degraded during photo-Fenton process, to avoid chemical waste formation. It is clearly seen that the addition of complexing compound can make Fenton and photo-Fenton greener.

3.3.2 Photocatalysis over TiO_2

The photocatalytic process using TiO_2 photocatalyst is very promising for application in water purification and wastewater treatment because many organic compounds can be decomposed and mineralized by the proceeding oxidation and reduction processes on TiO_2 surface [37–47]. The most commonly tested compounds for decomposition through photocatalysis are phenols, chlorophenols, pesticides, herbicides, benzenes, alcohols, dyes, pharmaceuticals, humic acids, organic acids, and others [37]. Additionally, photocatalysis process over TiO_2 for reducing the toxic Cr (VI) into the harmless Cr(III) as well for oxidizing the hazardous Pb(II) into the safer PbO_2 are also assessed [37].

TiO_2 is the most commonly used photocatalyst, because it is non-toxic, chemically stable, cheap, and very efficient. In photocatalysis, light of energy greater than the bandgap of the semiconductor excites an electron from the valence band to the conduction band. In the case of anatase TiO_2 , the bandgap is 3.2 eV, therefore UV light ($\lambda \leq 387$ nm) is required [37–47]. The absorption of a photon excites an electron to the conduction band (e^-_{CB}) generating a positive hole in the valence band (h^+_{VB}) and an electron in the valence band (e^-_{CB}), as presented as Eq. (6). The hole can interact with a water molecule, as seen in Eq. (7).



However, it has some disadvantages: one of these is a relatively high value of the bandgap, around 3.2 eV, which limits its use under UV light. The other weaknesses are: high dispersion in the water which causes difficulties in sedimentation, and sensitive to the recombination of photoinduced electrons and holes, which decreases its photocatalytic activity [39–47]. The weakness of using UV light allows it to consume high energy (ignores principle no. 6) and the hazardous UV light is potential to cause an accident if exposes to a person for long time (less suitable to the principle no 12). Clearly, the method has not followed fully the principles of the Green Chemistry.

Therefore, an effort has been focused to overcome this deficiency of using UV light, by doping TiO_2 crystal structure with either metal elements [38–44], or non-metal elements [45–47]. Doping process is hoped to narrow the bandgap that falls into visible region. Metal elements that have been doped into TiO_2 include Ag [38–40], Au [41], Cu [42], and Fe [43, 44], while non-elemental dopants are N [45], S [46], and C [47]. The doping TiO_2 has been frequently reported to be able to decrease their bandgap from 3.2 to smaller than 3.0 eV. The narrowing gap is illustrated in **Figure 5**.

The gap decrease is able to enhance its photoactivity significantly under visible light irradiation. The use of visible light for replacing the UV light, enables photocatalysis process to be greener method. The photocatalysis process for complete degradation of organic pollutants will form smaller and saver molecules, which is in line with waste minimization. It is clear that this method obeys principle no. 2, and is in line with the green method.

3.3.3 By using nanomaterial oxidizing agents

Several metal [48] and metal oxide nanomaterials including iron oxide [49], graphene oxide [48], as well as graphene bounded with metals [50] have shown strong

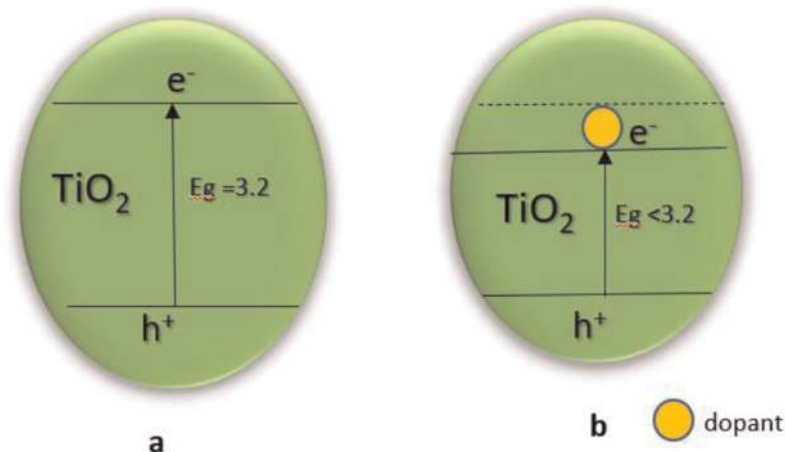


Figure 5.
The simple illustration of a) un-doped TiO₂, and b) doped TiO₂.

oxidizing power. Iron oxide nanoparticles have been prepared by using citrus extract for confinement of the particle growth. This method has produced in the nanoparticles providing a larger surface, an advance to result in effective degradation of some dyes [49]. The nanocomposite of graphene oxide bound with metal by using biomass as a template has also been reported [48]. This oxidizing agent has been proven to show effective degradation of the organic pollutants. Furthermore, the use of part of plants as reducing agents as well as a template for oxidizing agent nanomaterial has also been developed. One of the examples is graphene-supported silver nanocomposite [50]. The reducing agent from the biomass, replacing the toxic chemical can be categorized as the green reducing agent. The use of citrus and biomass waste as a template and reducing agent replacing the hazardous chemicals, allow the method as a greener one, due to the agreement with the principle no. 1, no. 5 and no. 12.

4. Conclusions

Several chemical analysis and pollutant removal methods are believed as very important and required by many fields. Some of the methods are recognized not obey some of the principles of the Green Chemistry. The greening methods of chemical analysis and chemical pollutant removal are essential, which can be conducted by reducing the quantity (mass and volume), substituting the toxic chemicals with the harmless or less toxic chemicals, modifying, and replacing them with the greener methods.

Conflict of interest


The authors declare no conflict of interest.

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