

CHAPTER-1

Introduction and Literature Review



GENERAL OVERVIEW

The environment is being greatly exploited and manipulated in order to create a more comfortable and easy lifestyle for the ever-growing population of mankind. Thus, the world has evolved into a modern but unnatural polluted environment. Though, our activities involving rapid industrialization (mining, electroplating, chemical products syntheses, etc.), energy and electricity generation by massive consumption of coal and other fossil fuels, transport, waste disposal and modern practice of agriculture (which involves the massive use of chemicals) are obviously yielding enormously to some of our desires, particularly in terms of technological growth and advancement far beyond what an unaltered environment could offer, however, this comes with a consequence known as environmental pollution (i.e., the introduction of potentially harmful substances, be it in form of chemicals, energy or organisms into the natural environment). But still, we relish the numerous comforts that have emerged and would not want to give them up. This fact has made the problem of environmental pollution a destiny which cannot be completely avoided but can only be restricted, controlled, minimized or remediated to some extent.

Based on the primary environmental component of contact, environmental pollution can be categorized into air, soil and water pollution. Once the pollutants are released into the environment, they can be transported via different pathways from one environmental medium to another. This creates the possibility of one type of pollution leading to another. For instance, pollutants in the air could come in contact with soil via drifting down as fallouts. Likewise, pollutants in the soil can be transported to the underground and surface waters via several hydrological cycles (a typical example of non-point source water pollution). These possibilities render the marine environment the most likely sink for unlimited numbers of

environmental pollutants. The pollutants intoxicate man via feeding relationships with some of the poisoned aquatic organisms or direct consumption of the contaminated waters. Water remediation studies against these pollutants are thus, of great importance because the applications could limit the threat which they pose to man and the environment as a whole.

❖ **Sources of Water Pollution**

Despite the fact that our planet Earth has far more abundant water than land, more than 99% of the Earth's water is unusable by human and many other living organisms. This is because less than 3% of the Earth's water is freshwater, most of which is inaccessible. Unaccessible because over 68% of it is found in ice caps and glaciers and about 30% found in groundwater. Just about 0.3% of the Earth's freshwater is found in the surface water of lakes, rivers and swamps readily available form man and all other living organisms. This must be one of the reasons why 40% of the world's population face water shortage and this is more obvious in Asian and African countries. It is estimated that by 2025, the figure is expected to increase to more than 2.5 times the present population [1, 2].

Apart from the human population explosion against the little available freshwater for consumption, industrial water pollution is another factor that is aggravating the problem of non-availability good water for consumption. Direct consumption of the scarcely available freshwater could be very dangerous to human health due to contaminations from different sources. Not only humans can be the sufferers, but the water contaminants could also poison the natural inhabitants of the aquatic environment or/and make their natural home inhabitable for them (Figure 1.1).

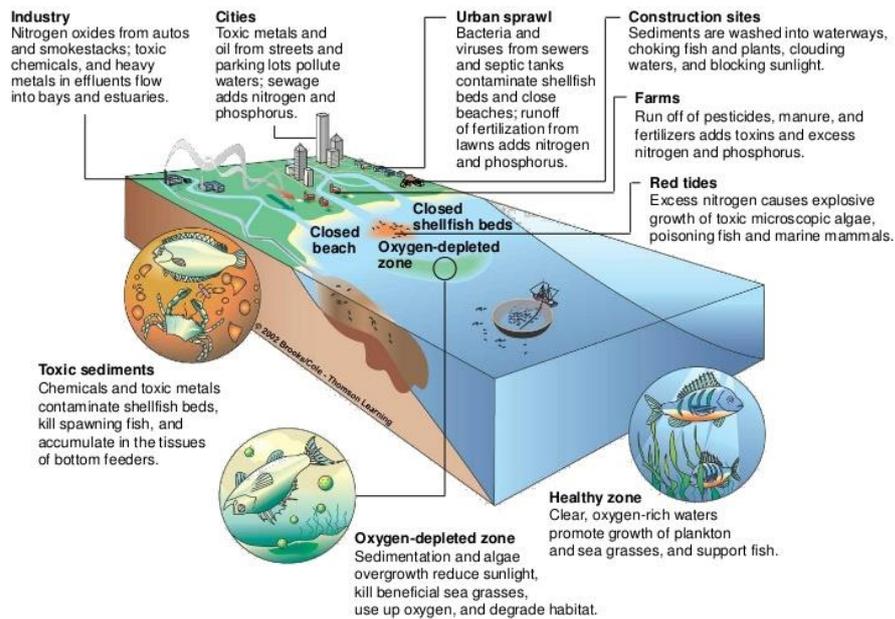


Figure 1.1 Sources of water pollution; the damaging effects on aquatic organisms

Water pollution could be a point or non-point (diffused) source. Point source occurs when there is a single identifiable and localized source of pollution. Otherwise, it is a diffused source. Highlighted below are the different ways by which water or the aquatic environment could get contaminated [3].

- Water pollution could be as a result of natural disasters. For instance, when a hurricane happens, it usually involves water contamination from sewage, petrochemical spills from ruptured boats or automobiles. Larger scale aquatic pollution could result if coastal rigs or refineries are involved. A volcanic eruption is another good example of a natural disaster that could cause water pollution.
- Water pollution can be caused by surface runoff. This is common in areas where there are dumpsites or/and where crops production involves the application of manures, fertilizers and pesticides. During heavy rainfall, the topsoil laden with chemicals and several kinds of other contaminants could be washed down to nearby rivers.

- Careless disposal of plastic wastes on land is another means by which water can be contaminated. These plastic materials can be transported by the action of wind and water into the aquatic environment, accumulate and constitute a significant portion of marine debris.
- Aquatic environment can be polluted via different activities of ships such as the discharge of cargo residues from bulk carriers into waterways and estuaries.
- Deep-sea mining, the mining activities that take place on the ocean floors, is another means of water pollution.
- Atmospheric deposition is another pathway to water pollution. This is usually by the settling of air-borne on the land and water. These pollutants can include dust, particulates of pollutants and even gaseous pollutants.
- Industrial activities also play an important role in the contamination of water resources. Chemical industries such as those of dyes, polymers, paints, pesticides, foods and drugs, and many others produce industrial wastewaters that are usually discharged into water bodies. Discharge of these industrial effluents is one of the major causes of water pollution.

Water pollution could also be traced to legal and illegal deposition of wastes in landfills. The solid wastes in the landfills under the influence of heat could break down or decompose, and via different pathways, especially underground leaching, most probably enhanced by rainfall, could be transported to surface and ground waters. This mostly happens in poorly maintained or failed landfills [4].

Industrial activities as well cause the release of acidic gases such as sulfur dioxide, nitrogen dioxide and carbon dioxide into the atmosphere. This can cause water acidification, especially in industrial zones [5].

Concentrated Animal Feeding Operations (CAFO) could also contribute to aquatic pollution. Most animal wastes from CAFOs are stored in very large open lagoons (liquid manure) and contain millions of gallons of wastewater. The liquid manure is typically sprayed on cropland and pastures in order to make the soils fertile. However, the over-application of the liquid manure and the improper management of the lagoons can leach nutrients and other substances into waterways and could end up contaminating the surrounding freshwaters [6].

Coastal development which is usually caused by the human population explosion is another means by which water can be polluted. Coastal construction and development can cause chronic sedimentation, sewage effluent, industrial discharge, and changes in water flow and runoff, which can adversely affect the quality of freshwater [7].

❖ **Harmful Effects of Water Pollution**

The aquatic environment is naturally characterized by biological riches that surpass that of forests and wildernesses but this large biodiversity is under threat. Apart from overfishing, water pollution is another main factor that contributes to the straining of the marine biodiversity, and directly or indirectly affects mankind.

Highlighted below are some of the consequences of the introduction of pollutants into the aquatic environment [8].

- Nutrients runoffs from fertilized farm fields, animal feedlots and urban areas can create harmful algal blooms. The algal blooms produce toxins that can be fatal to fishes and marine mammals.
- Coastal development causes disturbance and degradation of the aquatic environment, alters water quality and quantity, and causes loss of habitat and death of the native marine organisms. Generally,

coastal development brings about the decline in the diversity of aquatic species.

- Oil spillage in water bodies could make seabirds and otters lose their ability to float and stay warm, causing drowning and death of these species. The components of crude oil, polyaromatic hydrocarbons persist in the marine environment for years and toxic to some other marine lives such as fishes even at ppb concentration level. Chronic exposure to PAHs affects development, increase susceptibility to diseases and jeopardize reproductive cycles in many marine species.
- Ballast water from ships into a marine ecosystem could introduce invasive species. Invasive species are non-native species such as algae and larval forms of invertebrates whose introduction pose threat to the new environment. [9].
- Ocean acidification is a pervasive stressor that could affect marine organisms and cause profound ecological shifts. Ocean acidification can affect or kill lower marine invertebrates which have a lower capacity to compensate for the disturbances in extracellular ion, acid-base status and sensitivity of metabolism towards such disturbances. [10, 11].
- Heavy metals from deep sea mining could have negative impacts on the reproduction of aquatic organisms. Young [12] gave an account of the demonstration of the impact of copper contamination in the spawning of corals. The demonstration showed that even at lower concentrations of copper, the larvae produced by the corals were significantly reduced. The depletion of coral reefs could be devastating in the marine environment because they provide nurseries and protection for myriad marine life.
- The disposability of plastics and their low recycling rates contribute to a significant rise in the amount of plastic wastes produced globally. Those that are transported into the marine environment by

rivers, wind, tides, rainwater, storm drains, sewage disposal and flood events could undergo fragmentation into smaller pieces by photochemical, mechanical and biological processes. The plastic contaminants and the associated toxins can be biomagnified in the food chain. When this takes place, it can affect negatively the health of food webs which includes human as an apex predator [13].

❖ **Industrial Water Pollution**

Virtually all manufacturing activities consume a significant amount of water at some point in the production process. The water used for these industrial processes are discharged out of the production processes, but they do not exist in the same state which they formerly existed. The waters in most cases, now contain a significant amount of toxic chemicals which could even be non-biodegradable and are consequently expelled into the aquatic environment (Figure 1.2). These toxic chemicals have a tendency to trouble or destabilize the ecosystem.



Figure 1.2 Illustration of effluent discharge from a typical industrial facility

- **Industrial Wastewater Pollution Load**

Industries generate wastes, in form of effluents and sometimes in form of solids, which if not properly managed, could constitute a threat to the environment after discharge. The nature and constituents of the effluents discharged by these industries are dependent on what they produce. Substances such as cyanides could be a constituent of an effluent originating from industries producing pesticides, cadmium could be a constituent of effluents originating from companies producing batteries and accumulators, chromium could be a constituent of effluent from plating and tanning industries, and many more [14].

The specific health effects of industrial water pollution may vary depending on the constituents of the polluted water and may even be difficult to predict. This is because while some of the chemicals/pollutants discharged into river waters may follow the rule of simple dilution whereby they can only be transported over long distances without any change, some may undergo different kinds of transformation like microbial degradation or interaction with some other pollutants or chemicals in the water forming some complicated products whose environmental impacts may not be anticipated.

The sugar industry for instance, like any other manufacturing industry, generates quite a number of chemical wastes (Table 1.1) from its various units of operation (Table 1.2), particularly large volume of waste of organic nature and discharged onto land or into nearby watercourses, usually small streams, practically without pre-treatment. The discharge of the untreated effluents could result in the rise of BOD, and consequent depletion of oxygen, and hence disrupt the ecological area of living organisms [15].

This makes source control with adequate water treatment facilities very important in order to avoid imaginable and unimaginable consequences that could pose a serious threat to the ecosystem [16].

Table 1.1 Characteristic of wastewater generated from a typical sugar plant

Parameter	Concentration
BOD	1250 mg/L
COD	2250 mg/L
pH	5 – 7
Temperature	25 – 35 °C
Total Suspended Solids	600 mg/L
Total Dissolved Solids	2000 mg/L
Total Volatile Solids	1300 mg/L
Oil and Grease	60 mg/L
Sulphates	500 mg/L
Nitrogen	10 mg/L
Phosphorus	60 mg/L
Chlorides	60 mg/L
Calcium	180 mg/L
Magnesium	80 mg/L

Table 1.2 Quantity of effluent generation in various units of a sugar factory

Process	Effluent (Cubic metre/day)
Millhouse	50 – 80
Boling house	150 – 200
Boiler house (blow down)	40 – 50
Pump cooling water	80 – 100
Sulphur furnaces	14 – 20
Lime hydrator	14 – 16
Excess condensate	20 – 30
Final effluent	400 – 500
Spray pond overflow	400 – 500

The industrial wastewaters contribute significantly to pollution discharges in highly urbanized and industrial areas and these discharges contribute great environmental impact due to the nature and concentration of the pollutants involved:

Migo et al. [17] gave an instance of the impact of mining operations at Sta. Cruz town in the Philippines where generated nickel laterite concentrated mud killed some of the town residents. Fish sites, river systems, coasts, farmlands were also silted and rendered unproductive. Another instance of fish killing in Lian River in Batangas was mentioned and this was caused by disposal of distillery wastewaters into the aquatic environment which resulted to increase in the BOD and COD values up to 50,000 ppm and 100,000 ppm respectively.

Wright et al. [18] examined the impact that industrial effluent discharge could have on a wastewater site. Their multivariate analysis of macroinvertebrate assemblage revealed that mining and industrial wastewater sites were ecologically dissimilar to the reference sites used. The macroinvertebrate community assemblage in mining and industrial waste sites were significantly lower compared to the reference sites. This is an indication of pollution-induced environmental impairment and significant loss of biodiversity in the aquatic environment.

Wang 2016 [19] examined the effect of industrial water pollution on the residents of diverse cities in China. They studied the general mental and physical health of their subjects and were able to conclude that industrial water pollution influenced and deteriorated both the mental and physical health of the subjects.

- **Pollution Scenario of Hazira Industrial Zone, India**

The scenario of Hazira gives a picture of how industrial activities could result in contaminated water bodies. Hazira is a town in Surat Metropolitan

Region located on the bank of Tapti River. The town is recognized as the industrial hub of India because it is a base for numerous industrial facilities, such as Reliance Industries; Essar; Kribhco; Larson and Toubro; NTPC; ONGC; Adani; Shell India; GSPC; and many more. These industries, both large and scales discharge effluents: treated in the case of large scale industries; and untreated in the case of small scale industries (due to lack of resources such as finances, technicality and personnel to treat their wastewater) directly into the water bodies, most especially Tapti River [20]. Various researches have been carried out on the river and they point to the fact that it is polluted and constitutes a threat to the health of the environment [21-23].

LITERATURE REVIEW

❖ **Organic Pollutants**

Among water pollutants are a category of numerous organic aromatic compounds whose toxic effects could be more devastating than their inorganic counterparts. They are the more common pollutants that are usually the components of industrial effluents. These pollutants can intoxicate man via feeding relationship with some of the poisoned aquatic organisms or by direct consumption of the contaminated water. These organic pollutants, particularly those unsaturated or the aromatic ones, apart from direct intoxication in the form in which they are introduced into the environment, have the tendency to undergo different reactions in the aquatic environment to form products whose environmental consequences could be unpredictable. Among the set of these organic pollutants are Aniline, p-Nitroaniline and Nitrobenzene that are that are commonly used as raw materials or intermediates for the production of a wide range of consumer products.

• **Aniline Water Pollution and Toxicity Effect**

Aniline is a clear to slightly yellow liquid with a characteristic odour. It is soluble in water and does not readily evaporate at room temperature. Aniline is a very important industrial raw material and intermediate used in the production of wide range of synthetic chemical products such as dyes, plastics, pharmaceuticals, resins, marking inks, perfumes, shoe polishes, polyurethanes, rubber additives, pesticides and many other chemicals of current domestic and industrial interest [24-26].

As an industrial chemical, the solubility of aniline in water represents a serious risk for possible water pollution, as that would create a challenge of

uneasy removal from industrial effluent that would soon be discharged to the environment [27].

Aniline is a ubiquitous chemical, which aside from capable of being introduced directly into the environment via industrial effluent, is a common degradation product of dyes, drugs, pesticides and possibly other chemical products synthesized from aniline or has aniline as their constituents, that are discharged into the aquatic environment. In addition, aniline is a metabolite of microbial transformation of nitroaromatic compounds and aniline-based pesticides [28].

The presence of aniline in wastewater even in very low concentrations can be harmful to aquatic life. And in a human being, could react easily in the blood to convert haemoglobin (a protein that normally transports oxygen in the blood) to methaemoglobin (a stable oxidized form of haemoglobin), inhibiting the transportation of oxygen to body tissues for respiration. This condition is known as methaemoglobinemia and the severity depends on how much of the pollutant the victim is exposed to and how long [25]. The acute aniline poisoning in human could cause dizziness, headache, irregular heartbeat, convulsions, coma and death may occur while long-term exposure to lower levels of aniline may also cause symptoms similar to those experienced in acute high-level exposure [29].

Aniline is a recognized carcinogen to human bladder, ureter, and renal pelvis, intestines, lungs, liver, and prostate [30]. It also has the general ability to inhibit enzyme activities in man which could cause various physiological disorders [27]. Aniline is mutagenic, so its release into the environment tantamounts to the introduction of a mutagen into the environment [26].

The general human population may be exposed to aniline by eating food or drinking water that contains aniline [29]. Though this amount may be very small due to the fact that most of the aniline introduced into the water

bodies could be broken down by bacteria and other micro-organisms, care still has to be taken during water treatment to eliminate aniline in order to prevent ailments and deaths. For this reason, wastewaters containing aniline must be properly treated before their discharge to the water bodies. There should also be interest in removing it from contaminated sites and water meant for township consumption.

- **p-Nitroaniline Water Pollution and Toxicity Effect**

P-nitroaniline belongs to a class of aromatic amines, an important class of ionizable organic compounds. It is also an important chemical intermediate which serves as a basic building block for numerous synthetic chemical products. It is used for the manufacture of p-phenylenediamine, antioxidants, antiozonants, gasoline gum inhibitor, corrosion inhibitors, textile dyes, pigments, pesticides, antiseptic agents, medicines for poultry, pharmaceuticals and so on [31, 32].

Due to its wide application in the synthesis of chemical products, it is unavoidable for it to enter the environment through various channels such as improper treatment of waste stream from industries where it is either manufactured or used as intermediates for the production of other chemical products. The presence of p-nitroaniline in water even at very low concentration level would be harmful to aquatic life and human health [33-35].

Acute effects of p-nitroaniline which may occur immediately or shortly after exposure can also result in methemoglobinemia. Just like aniline, high-level exposure may interfere with the ability of the blood to carry oxygen causing headache, dizziness, and a blue colour to the skin and the lips. It can cause trouble breathing, collapse and even death [36].

A case of p-nitroaniline intoxication and consequently the death of a 15-year-old boy was reported [37]. The boy was found in a non-responsive

state with seizures and later died due to the oral intake of p-nitroaniline. The blood was analysed and a substantial amount of MetHb was found. MetHb intoxication and its metabolites such as p-phenylenediamine were established as the cause of the death.

Chronic effects of p-nitroaniline are well known in terms of its haematotoxicity, splenotoxicity and hepatotoxicity, and nephrotoxicity. Also, it may decrease fertility in males and females, and repeated exposures may cause a low blood count (anaemia). Nowadays, p-nitroaniline has been listed as a primary pollutant by many countries due to its toxicity, potential carcinogenic and mutagenic effects [36, 38-40].

In addition to its aromatic nature, the presence of a nitro group in its molecular structure further enhances its stability against physical degradation, chemical and biological oxidative degradation more than aniline. And meanwhile, anaerobic degradation produces nitroso and hydroxylamine compounds which are known carcinogens [34, 38]. This means the cleansing of water contaminated by p-nitroaniline cannot be left alone for the natural processes which involve microbial degradation. Extra effort is required by man to at least, minimize the threat that this pollutant in the little freshwater available for consumption, poses to the health of the environment.

- **Nitrobenzene Water Pollution and Toxicity Effect**

Nitrobenzene belongs to the group of aromatic nitro compounds which are commonly used in industrial processes. Nitrobenzene specifically is an important raw material as well as a product of industry. It is widely used in lubricating oils refinement, soaps and shoe polishes production. It has also been widely used in the manufacture of pesticides, dyes, explosives, plastics, pharmaceuticals and intermediates in chemical synthesis in chemical industries for years [1, 41-43].

Nitrobenzene is a very toxic chemical and it is soluble in water. Its vast application in industries suggests a high tendency of surface water and groundwater contamination due to industrial effluent discharge; thus, poisoning water resources. A further concern lies in the fact that it is a persistent or weakly biodegradable pollutant which means that it may not be reliably eliminated by biological process. This means whenever it is introduced into the aquatic environment, the poisoning effect would last longer compared to the more easily biodegradable water pollutants. Prevention or removal of weakly biodegradable pollutants such as nitrobenzene in water is very important for the protection of our environment. Even at low concentration, nitrobenzene may present high risks to ecological and human health. And because of its great pollution potential, nitrobenzene is listed as a priority pollutant by the USEPA [44-46].

Nitrobenzene can be detected in ambient air and drinking water, so exposure means are through water consumption, inhalation and skin penetration. Nitrobenzene is found in fishes and can be transferred to human beings via consumption. Acute inhalation, oral or dermal exposure to nitrobenzene in humans also cause methemoglobinemia. This causes fatigue, weakness, dyspnea, headache and dizziness. And at higher concentrations, it causes depressed respiration, bluish-grey skin, disturbed vision, and coma. Chronic exposure may also cause methemoglobinemia. Liver, spleen, kidneys and the central nervous system can also be damaged. Nitrobenzene is a possible mutagen and is reasonably anticipated to be a human carcinogen [47, 48].

❖ **Organic Pollutants Removal from Contaminated Water**

Water treatment process selection is a complex task involving the consideration of many factors which include the availability of space for the treatment, reliability of treatment process, the type of wastewater, the

equipment to be used, waste disposal constraints, desired water quality, and the capital and operating cost of the wastewater treatment process adopted.

A number of methods are available with varying degree of success for the treatment of water contaminated with organic pollutants. Such methods include biodegradation method, several advanced oxidation methods, solvent extraction or liquid-liquid extraction (LLE) method and adsorption method.

- **Biodegradation Method**

This method employs the use of micro-organisms in most cases, aerobic and anaerobic bacteria for the degradation of organic pollutants in contaminated water. The process applies bio-augmentation technology which involves the culturing of the micro-organisms and adding into the contaminated water for the purpose of breaking down specific water pollutants. The principle lies in the fact that some micro-organisms depend on carbon source for energy to carry out some physiological activities, growth and reproduction. Thus, the application of this method involves a careful selection of microbes, especially bacteria that may thrive on using specific organic pollutants as their carbon and energy source, breaking them down and assimilating them for life activities. For our target pollutants: aniline; p-nitroaniline and nitrobenzene, this method has proven to have some shortcomings. Several kinds of literature have been reviewed in order to establish those possible shortcomings. The highlights are given below.

The application of anaerobic sludge for the degradation of aniline in contaminated water by Shen et al. [26] did not remove COD concentration completely despite the disappearance of aniline from the contaminated water. This suggests that some species are formed during the degradation process and are resistant to further degradation. Hence constituting the chemically oxidizable species.

The application of *Acinetobacter calcoaceticus* for the degradation of aniline as carried out by Zhang et al. [49] produced ammonia. This observation is the same as that of another microbial degradation carried out by O'Neill et al. [50]. In fact, they described the released ammonia as a measure or indication of aniline mineralization in the wastewater.

Gorontzy et al.'s aniline degradation by treating contaminated water with methanogenic bacteria, sulphate reducing bacteria and clostridia in anaerobic conditions [51] transformed the aniline into its amino derivatives with nitroso or hydroxylamines.

In the degradation process of p-nitroaniline using *Shrenotrophomonas spp.* as carried out by Queresh et al. [52], the release of nitrite and ammonium ions which were supposed to confirm p-nitroaniline mineralization were not observed. As such, they did not rule out the possibility of the conversion of p-nitroaniline to stable intermediates such as N-oxidation products or acylated products.

A high rate of aerobic biodegradation of p-nitroaniline was reported by Saupe [53] but with the production of nitrates and ammonia as the products of the mineralization.

Silambarasan and Vangnai's [54] degradation of p-nitroaniline using *Acinetobacter spp* under aerobic condition yielded aniline, 1,2,4-benzenetriol and other compounds as metabolites.

The degradation of nitrobenzene in contaminated water by *Pseudomonas pseudoalcaligenes* as carried out by Nishino and Spain [41] was accomplished with the aid of enhancement factors such as enzyme assays, coenzymes and ferrous ion catalyst which were employed for the degradation of nitrobenzene to 2-aminophenol and ring cleavage to 2-aminomuconicsemialdehyde, which subsequently degraded to release ammonia.

Nishino and Spain [55] also reported the oxidative mineralization of nitrobenzene using *Comamonas spp.* This as well involved the use of enzyme assays to catalyse the degradation steps. Nitrobenzene was catabolysed to catechol with the release of nitrite. The catechol further degraded by ring cleavage. However, the consequential products of the cleavage were not confirmed by the authors.

Xie et al. [56] observed that their anaerobic bacteria converted nitrobenzene to aniline and no further degradation took place. It was even suggested that the determination of aniline concentration could help estimate the removal rate of nitrobenzene. The halt in the degradation process was attributed to the toxicity of nitrobenzene which might have caused the suppression of the microbial activity against further degradation.

The literature highlights gather up the problems that could be associated with the biological or microbial methods of removing our target pollutants: aniline; p-nitroaniline and nitrobenzene from contaminated waters. At least a problem occurs irrespective of the extent of mineralization. For the cases of incomplete mineralization, is always formation of intermediates which are as well toxic in nature. Complete mineralization of nitrobenzene and p-nitroaniline may require more complex procedures due to the more persistence character that they possess due to the presence of the nitro group in their molecular structures. And when the complete mineralization of the pollutants occurs, ammonium and nitrate ions are usually formed. These are also water pollutants, though may pose a less immediate threat than the initial pollutants

Another problem is that of reusability of microbes. The microbes could become less active during the degradation process due to the toxicity of the pollutants (one of the reasons for incomplete mineralization). Hence, there may be a need for subsequent rounds of re-culturing the microbes.

The release of ammonia during degradation is a shortcoming. This is because ammonia gas, being water soluble due to the hydrogen bond its molecules can form with those of water, can be present in the microbial treated water in high levels. According to EPA, discharging effluents containing too much of ammonia can impact the aquatic environment as ammonia is difficult for aquatic organisms to sufficiently excrete, leading to a toxic buildup in internal tissues and blood, and potentially death.

The possibility of other mineralization products such as nitrites and nitrates should also be of concern. These are sources of nitrogen whose buildup in the aquatic environment can cause eutrophication and algal blooms at suitable conditions.

- **Advanced Oxidation Processes (AOP)**

Advanced oxidation processes encompass the water treatment technologies whose techniques are based on the in situ generations of a very strong oxidant, in most cases hydroxyl radical in sufficient concentration and utilizing it for the oxidative degradation or mineralization of organic water pollutants. These techniques capitalize on the extremely high reactivity of the hydroxyl radicals, and once the radicals are formed, they start a non-selective attack on numerous organic pollutants, and radical cycle propagation commences. Then the formation of intermediates which are further broken down to water, carbon dioxide and inorganic ions. Depending on the mechanism that leads to the generation of the hydroxyl radical, AOP basically comprises four methods: Chemical AOP; Photochemical AOP; Sonochemical AOP; and Electrochemical AOP [57-59].

- i. Chemical AOP**

Very common is the use of Fenton's reagents. The reagents for this consists of a Fe^{2+} and hydrogen peroxide. The ferrous ion catalyses the

decomposition of the hydrogen peroxide into a hydroxyl radical, and this usually occurs in acidic medium. Another form of chemical AOP is the peroxonation process which involves the coupling or interaction between two strong oxidizing agents, ozone and hydrogen peroxide for the generation of hydroxyl radical.

ii. Photochemical AOP

This is the generation of a stream of hydroxyl radicals via photolysis of water using vacuum UV radiation (wavelength less than 190nm) that can degrade organic contaminants in the water. Similarly, the action of UV radiation on the powerful oxidants such as ozone and hydrogen peroxide could yield the stream of hydroxyl radicals. The action of UV radiation on water or any strong oxidizing agent for the generation of hydroxyl radicals is known as photolysis. Meanwhile, in some cases, UV active catalysts such as TiO_2 could be involved in the system for better and faster generation of the hydroxyl radicals (photocatalytic process). In such cases, UV could excite the catalyst for the decomposition of an oxidizing agent or even water containing the pollutants into streams of hydroxyl radicals.

iii. Sonochemical AOP

This AOP technique involves the use of ultrasound waves (frequencies greater than 16 kHz) to produce hydroxyl radicals needed for the degradation of refractory organic pollutants. Just like photo-radiation, ultrasonic waves could break down water molecules into hydroxyl radicals which could initiate the degradation of the organic pollutants present. Ultrasound could also be used in conjunction with strong oxidizing agents such as ozone or/and hydrogen peroxide for the generation of the streams of highly reactive hydroxyl radicals.

iv. Electrochemical AOP

This involves an electrochemical process for the in-situ generation of hydroxyl radicals. Hydroxyl radicals are directly formed at the anode surface by the oxidation of water with high oxygen evolution overvoltage anodes such as PbO_2 , doped SnO_2 , IrO_2 or DSA (dimensionally stable anodes). Whereas at the cathode, hydrogen gas is produced and is not involved in the oxidation of the pollutants. Therefore, the electrochemical method used in wastewater treatment mainly focuses on anodic oxidation.

The AOPs have well been researched upon and have proven to be potent and rapid means of removing or mineralizing our target pollutants which include aniline, p-nitroaniline and nitrobenzene nearly completely from contaminated water [60-67]. But be that as it may, they exhibit some shortcomings. Compared to other water treatment techniques, the costs of AOPs are relatively high. This is because they require the use of high-tech or sophisticated equipment and the continuous supply of the chemicals for the in-situ and continuous generation of the streams of hydroxyl radicals. And additionally, the generation of the hydroxyl radicals is driven by external energy sources such as electric power or UV radiation [68]. Also, to maximize the degradation of pollutants, combination of AOP techniques may be required [60]. Above all, the design, operation and maintenance require the services of qualified and competent engineers. This association of factors may make AOP deployment less affordable in some developing countries.

Generation of secondary pollutants is also a shortcoming for AOPs as regards our target pollutants. For instance, there is the possibility of nitrates generation in the degradation of nitrobenzene. The nitrates could constitute a nutrient source that can contribute to algal blooms in the aquatic environment. For aniline degradation, generation of ammonia is a possibility. Ammonia is toxic to some aquatic organisms, though less toxic

than the original pollutant. Also, there is the possibility of carbon dioxide saturation in AOP treated effluents. Discharge of such effluents into the aquatic environment may cause toxicity effect on some aquatic organisms via acidification.

- **Solvent Extraction or Liquid-Liquid Extraction (LLE) Method**

This removal or separation is based on 'like dissolves like' principle, that is it depends on the relative solubilities of the target pollutants in two immiscible liquids one of which is the contaminated water and the other an organic solvent. The process involves the agitation of a predetermined organic solvent with the contaminated water, then there is a net transfer of the organic pollutants species from the contaminated water into the organic solvent phase. The agitated mixture is allowed to settle into two distinct phases by the action of gravity and they are separated from each other. The organic solvent that would be rich in the target organic pollutant(s) is the extract, which could be recycled reuse. The contaminated water that would now be depleted of the organic pollutant(s) is the raffinate [69, 70].

The solvent extraction method has also proven to be effective [71-74] but the process is not as simple as it seems. Ordinarily considering that both the pollutants and the solvents are organic in nature may not necessarily separate the pollutant from the aqueous medium. It is therefore essential to consider the distribution coefficients and the activity coefficients of the pollutants in the solvent prior selection and application. A further complication that may happen is the secondary pollution of water after the extracts (organic phase rich in the pollutants) have been separated from the aqueous phase. The organic extractants are mostly poisonous and may pollute the water again and this may create a further effluent treatment problem.

- **Adsorption**

When fluid and a solid material come in contact with each other, there may be an interaction between the solutes of the fluid and the surface of the solid material. The solutes may accumulate at the media interface, distributed selectively between the fluid and the solid phases. This phenomenon is known as adsorption. It may also be described as the enrichment of the solutes in a fluid medium in the region between two bulk interfaces (i.e. interfacial layer), one being a solid and the other being fluid (liquid or gas). In a typical adsorption process, foreign material in a gaseous or liquid form becomes attached to or concentrated on the surface of a solid. Thus, adsorption is a surface phenomenon and does not happen without a surface (or more generally, a phase boundary including a liquid surface)

In an adsorption process, the solutes that are about to be adsorbed or adsorbable substance in the fluid phase is referred to as adsorptive. The substance, solute or fluid that is in an adsorbed state or being enriched at the solid-fluid interface or being adsorbed on the surface of solid material is known as an adsorbate. The solid material on which the adsorption occurs i.e. the solid surface on which there is accumulation or enrichment of the adsorbate is known as an adsorbent. Hence, an adsorption process of water treatment involves the application of a suitable adsorbent to accumulate target pollutants to its surface, and therefore, removing or reducing the concentration of the pollutants in the aqueous medium.

- **Adsorption Interaction**

In adsorption processes, molecules of the adsorptive can attach to the surfaces of the adsorbents by two kinds of interaction: **physisorption** which is otherwise known as physical adsorption and **chemisorption** which can be described as chemical adsorption. These interactions occur as a result of two types of forces: dispersion-repulsion forces (a.k.a. London or

van der Waal's forces) and electrostatic forces, which result as a result of molecule or surface group having a permanent electric dipole or quadrupole moment or net electric charge. The interactions which do not depend on the polar nature of the adsorbent or adsorptive and are therefore regarded as non-specific. Other kinds of adsorbate-adsorbent interactions associated with physisorption are hydrogen bonding and ion exchange processes. Other bonds or interactions associated with chemisorption are covalent and coordinate displacements [75-77]. Table 1.3 summarizes the differences between physisorption and chemisorption. However, a golden rule to differentiate between a physisorption and chemisorption interaction between an adsorbate and an adsorbent is the formation of a chemical bond. If the interaction involves chemical bonding, it is chemisorption. Otherwise, it is physisorption.

Table 1.3 Differences between physisorption and chemisorption

Physisorption (van der Waals)	Chemisorption
There is a relatively low degree of specificity	Dependent on the reactivity of the adsorbent and the adsorptive
Low adsorption heat: 10 – 40 KJ/mol	High adsorption heat: 20 – 400 KJ/mol
At high relative pressures, physisorption generally occurs as multilayer	Chemisorbed molecules are linked to reactive parts of the surface and the adsorption is necessarily confined to a monolayer
A physisorbed molecule keeps its identity and on desorption, return to the fluid phase in its original form. Physisorption is well suited for re-generable process	If a chemisorbed molecule undergoes reaction or dissociation, it loses its identity and cannot be recovered by desorption. Chemisorption destroys the capacity of the adsorbent

Physisorption is always exothermic but the energy involved is generally much larger than the energy of condensation of the adsorptive. However, it is appreciably enhanced when physisorption takes place in very narrow pores	The energy of chemisorption is the same order of magnitude as the energy change in a comparable chemical reaction.
Equilibrium is usually attained fairly rapidly, but equilibrium may be slow if the transport process is rate determining	Activation energy is often involved. And at low temperature, the system may not have sufficient thermal energy to attain thermodynamic equilibrium.
Temperature has a negative effect on physisorption	Temperatures to some extent have a positive effect, especially in adsorption processes that involve activation energy

➤ **Adsorbent**

Adsorbents are natural or synthetic solid materials having an amorphous or crystalline structure. They are usually characterized by a surface boundary on the bulk of the solid material. This surface boundary is the outer or topmost layer of the solid material where the bulk properties of the solid material are no longer sufficient to describe the systems properties. At this region, the interaction forces among the particles responsible for bulk properties of the solid change. They become asymmetric (Figure 1.3) since the outermost bonds are unsaturated, resulting in unbalanced forces of attraction and a peculiar chemical reactivity on the surface [78]. The surface then becomes capable of adsorbing foreign atoms or molecules.

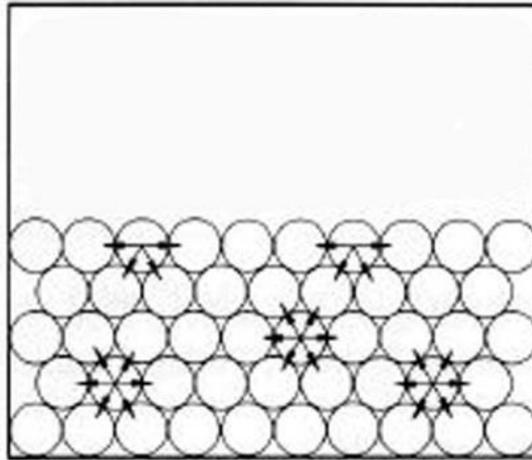


Figure 1.3 An adsorbent with asymmetric forces at the surface

In adsorption, the accumulation of solutes per unit surface area of the adsorbent is small, thus highly porous solids with very large internal area per unit volume are more desirable. And under certain conditions, there is an appreciable enhancement in the concentration of a particular component adsorbed, and the overall effect is dependent on the extent of the interfacial area. For this reason, all industrial adsorbents have large specific surface areas (generally well in excess of $100 \text{ m}^2/\text{g}$) and are therefore highly porous or composed of very fine particles [76, 79, 80].

➤ **Adsorption from Solution**

There may be competitive adsorption between the solvent and the solute. In this case, the apparent adsorption of a solute at the liquid-solid interface is usually evaluated by measuring the decrease in its concentration when brought in contact with the adsorbent. Thus, the percentage decrease in the concentration of the solute could be used as a measure of adsorption performance. Meanwhile, for the quantitative evaluation of an adsorbent capability, adsorption isotherms are applied. They are expressed as a function obtained at a constant temperature expressing an equilibrium amount of the adsorptive adsorbed at a certain concentration (general activity) of the adsorptive in the liquid (general bulk) phase. Adsorption isotherm starts from zero activity up to the maximum. To obtain reliable

experimental data, sufficient time for reaching an equilibrium between the adsorptive and the adsorbate is an unavoidable condition [81, 82].

➤ **Mechanism of Adsorption from Solution**

Solid-liquid adsorption is a multi-step process which could involve: the first step which is the transport of the adsorbate from the bulk of the solution to the surface of the adsorbent and the interaction with the adsorption sites; and pore filling or diffusion of the adsorbate into the interior of the particles of the porous adsorbent's surface. The concentration of adsorptive and agitation may affect the second step of the adsorption process. The third step is dependent on the nature of the sorbate molecules, such as polarity or anionic and cationic structures. The fourth step is usually considered as the rate determining stage in the sorption process, which certainly should affect the sorption of sorbate on the sorbents.

The adsorption of a solute from an aqueous solution may be affected by temperature, nature of the adsorbate and adsorbent, the presence of other solutes and atmospheric and experimental conditions such as pH, the concentration of the adsorptive, contact time, adsorbent particle size, adsorbent dose.

➤ **Adsorption Method of Water Treatment**

Adsorption is being applied at the industrial level for the removal of pollutants from wastewater. Adsorption method is fast, simple, inexpensive, efficient, economically viable and socially acceptable. It is universal in nature and it is being applied for the removal of soluble and insoluble contaminants at high efficiency. Furthermore, it does not add unwelcome by-product to the system. In real application of adsorption for water treatment, the contaminated water is shaken with a suitable adsorbent (Figure 1.4) and one or more pollutants in the wastewater get fixed through

physical and chemical bonds on the surface until a stage of equilibrium is reached between the contaminants in the wastewater and the contaminants that have been adsorbed onto the surface of the adsorbent. The development and optimization of adsorption parameters can be carried out by batch or column process in the laboratory. The adsorption technology is then applied at the pilot and industrial scales by using large columns [83-85].

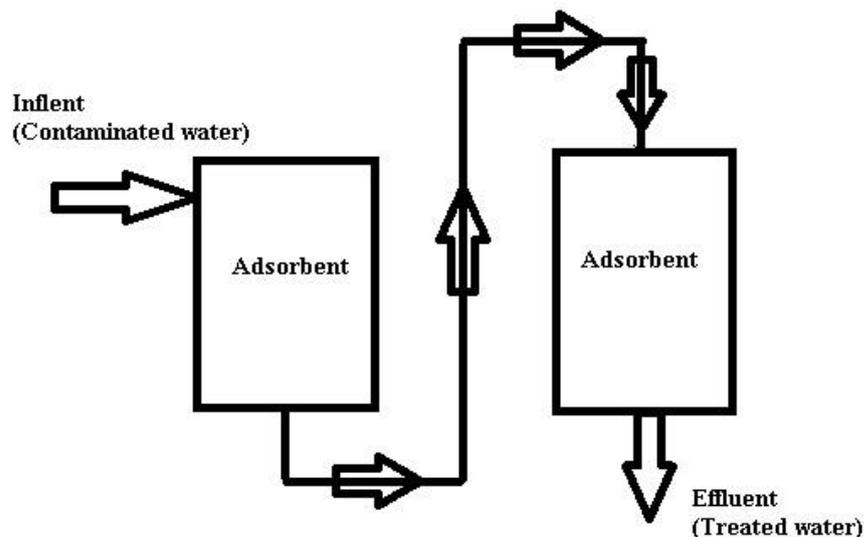


Figure 1.4 Layout of adsorption for the wastewater treatment system

Adsorption technique is also most commonly implemented for the removal or low concentrations of non-degradable organic compounds from groundwater. It is applied for the preparation of drinking water. Furthermore, it is being applied as tertiary water cleansing after the application of other treatment methods such as biological purification technique [86].

In the application of adsorption for wastewater treatment, the study of adsorption kinetics is very important for understanding the adsorption mechanism pathways in order to express the dependence of the surface properties of the adsorbent to adsorption performance and to design columns on the laboratory, pilot and industrial scales [84].

➤ **Adsorbents Used for Wastewater Treatment**

There is a broad range of adsorbents that are being used in the practices of the removal of contaminants from water. They are categorised into five [87]:

- i. Natural materials such as sawdust, wood, fuller's earth or bauxite
- ii. Natural materials treated to develop their structures and properties such as activated carbons, activated alumina or silica gels
- iii. Manufactured materials such as polymeric resins, zeolites or aluminosilicates
- iv. Agricultural solid wastes and industrial by-products such as date pits, fly ash or red mud
- v. Biosorbents such as chitosan, fungi or bacterial biomass

From this range of adsorbents, only four have dominated the commercial application for wastewater treatment. They are commercial activated carbons, zeolites, silica gel, commercial activated alumina. Activated carbon is the oldest and has been the first choice and most widely used adsorbent for the treatment and recycling of municipal and industrial wastewater to a potable water because of its good adsorption capacity owing to small particle size, active free valencies, large porous surface area, controllable pore structure, thermo-stability, interesting acid-base properties and their chemical nature which can be easily modified by chemical treatment in order to vary their properties. Activated carbons are very efficient for the removal of a broad type of organic and inorganic pollutants dissolved in aqueous media. In spite of all these desirable qualities, its usage on the large scale is too much costly due to the cost of production and regeneration. Similarly, the likes of zeolites, silica gel and commercial activated alumina are also not cheap, so their widespread use is restricted. Small and medium-sized enterprises (SMEs) cannot employ such adsorbents due to the high cost. Thus, there is a growing demand to find

relatively efficient, low-cost and easily available adsorbent for the removal of pollutants from wastewater. This has attracted scientists to develop low-cost adsorbents by using a wide range of carbonaceous and other precursors. Many starting materials for this purpose are agricultural by-products, industrial by-products and biomasses that are abundant in nature. The application of the agricultural and industrial waste products contributes towards waste management, recovery and reuse. Many of these alternative feedstocks have been proposed and used for the preparation of activated carbon; a lot of biomasses and some inorganic precursors have been tested at the laboratory level (Table 1.4) and have been established to produce potentially cheaper adsorbents compare with the commercial activated carbon for the removal of contaminants from water.

Table 1.4 Collection of several reviews on potential low-cost adsorbents for the removal of pollutants from wastewater

Adsorbent	Contaminant(s)	References
Peanut husk charcoal, fly ash and natural zeolites	Cu^{2+} , Zn^{2+}	[88]
MNP-OPP from orange peel powder	Cd^{2+}	[89]
Rice husk, fly ash	Fe^{2+} , Pb^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+}	[90]
Natural zeolites	NH_4^+ , Cu^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Ni^{2+} , Cr^{3+} , Co^{2+} , Mn^{2+}	[91]
Bamboo charcoal	Cd^{2+}	[92]
Peanut hull hydrochar	Pb^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+}	[93]
Rice husk, olive pomace, orange waste and compost biochars	Cu^{2+}	[94]
Fly ash, blast furnace slag,	Zn^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} ,	[95]

sludge and dust, red mud, lignin, black liquor waste of paper industry, waste hydroxide from the fertilizer industry	Cr ³⁺ , Cr ⁶⁺ , Cu ²⁺ , Ni ²⁺ , Hg ²⁺ , As ³⁺ , Cs ⁺	
Sugarcane pulp residue and biochar	Cr ³⁺	[96]
Cashew nutshell	Congo red dye	[97]
Chitosan-clay composite	Methylene blue dye	[98]
Walnut shell	Malachite green dye	[99]
Pinecone powder/acid treated	Congo red dye	[100]
Wood apple (<i>Feronia acidissima</i>) shell	Basic dyes: methylene blue, crystal violet	[101]
Coffee residues	Remazol brilliant blue RN, remazol red 3BS, remazol yellow gelb 3RS, basic blue 3G, remacryl red TGL, basic yellow 37	[102]
Rejected tea	Methylene blue	[103]
Pyrolysed straws of canola, soya bean and peanut	Methyl violet	[104]
Barley husk	Phenol red	[105]
Bamboo biochar	Metal-complex dye: Acid-black 172	[106]
Biochar/AlOOH nanocomposite	Methylene blue, phosphate, Arsenic	[107]
Seashell powder	Malachite green	[108]
MgO-biochar	Phosphate, nitrate	[109]
Bagasse fly ash	Orange-G, Methyl violet	
Zeolite, sepiolite	Reactive azo dyes: Black 5; Red 239; Yellow 176	[110]

Pinewood and pine bark chars	Fluoride	[111]
Waste rubber tire	Methoxychlor, atrazine and methyl parathion	[112]
Bamboo and coconut shell carbon	Dieldrin and chlorpyrifos	[113]
Poultry litter, wheat straw and swine solids biochars	Bisphenol A, 17 α -ethinyl estradiol, phenanthrene	[114]
<i>Citrullus colocynthis</i> seed ash; <i>Aloe vera</i> and mesquite (<i>Prosopsis</i>) leaves; stevensite; cellulose acetate/ <i>Amygdalus pendunculata</i> shell carbon; Linz Donawitz (LD) slag	Phenol	[115-119]
Jute stick char	4-nitrophenol	[120]
Brazilian peat	p-nitrophenol	[121]
Pine cone biomass powder	Phenol, 2-chlorophenol, 4-chlorophenol	[122]
Cu-impregnated pumice and zeolite	Pentachlorophenol	[123]
Jute fibres; chitosan-activated carbon complex; diatomite; <i>Aloe vera</i> leaves waste carbon; <i>Prosopis juliflora</i> carbon; lignin; pine sawdust	Aniline	[124-130]
Kaolinitic clay and <i>Jatropha curcas</i> seed coat; (carbonized) cotton stalk; bamboo charcoal	p-nitroaniline	[34, 39, 131, 132]
Activated sludge; maize and rice stems; cotton fibres	Nitrobenzene	[42, 133, 134]

➤ **Industrial ash, a potential resource for the production of cheap adsorbents**

Industrial ash is a solid waste that is usually generated by industries that make use of biomass as their source material for energy and electricity generation. Such industries involve electric power generation companies. The ash is generated as a result of coal combustion in thermal power plants.

Industrial Bagasse Fly Ash

Another of such industry that generates substantial ash as its waste is the sugar-producing industry. In the functioning of this industry, sugarcane is crushed and cane juice is extracted and processed into sugar. As a means of minimising the cost of energy generation, the sugarcane bagasse that is left is burned in a boiler (Figure 1.5) to produce steam utilized in the factory process and also to power turbines in order to produce electrical energy which supplies the energy needs of the factories. The solid waste material that is left behind after the combustion of the sugarcane bagasse is the industrial (bagasse) fly ash.

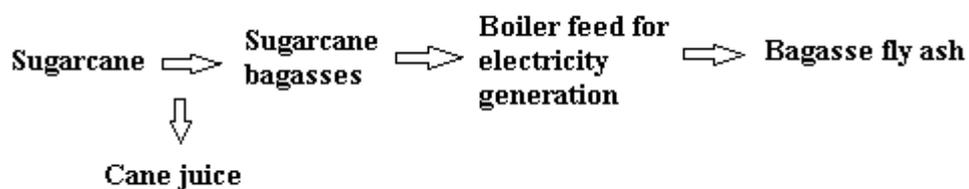


Figure 1.5 Schematic illustration of the generation of bagasse fly ash

Over the years, industrial ashes have been constituting problems to the environment due to the difficulties that are associated with the management. Landfilling is expensive and land intensive, deposition in ash ponds is risky as any breach in the dam system could cause massive spill capable of damaging nearby homes and fouling close by rivers and depositing them on the land surface could pose a direct threat to human

health. These problems have stirred up the idea of fly ash reuse. Despite various applications such as a constituent of construction materials like cement, blocks and tiles; constituents of fire-proof materials and ceramics; a soil stabilizer; and a metal releaser, less than 25% of the totality of the annual global fly ash produced is reused. Thus there is room for progress and new ideas in the reuse in order to further minimize the frequency of disposal, conserve land and also reduce the costs of landfills and ash ponds [15, 135-142].

The industrial ashes usually contain silica and alumina which are the major constituents of volcanic lava, a molten mineral matrix for the formation of zeolites. Zeolites are naturally occurring minerals, porous in nature and are used as adsorbents. The classical definition of zeolite is a crystalline porous aluminosilicate. However, some relatively recent discoveries of materials virtually identical to classical zeolites, but consisting of oxide structures with elements other than silicon and aluminium have stretched the definition [143-145]. Also, they have linked tetrahedral structure which creates the potential of various possible ways of stacking. The size and shape of the beautifully stacked regular array form pores and channels which have a major effect on the properties of these materials which gives them the potential of being used for sorption purposes.

Literature has pointed out the several methods by which industrial ashes could be transformed into materials containing zeolite composites, such that they improve the overall properties of the material such as surface area and porosity, and hence could make it suitable for the sequestration of pollutants from contaminated water. These methods are basically the simulation of the natural ways of zeolites formation. They involve the alkali/alkaline treatment of the industrial ashes at elevated temperatures in order to dissolve the Al-Si containing ash into a solution for the crystallization of zeolite phases. Methods such as **Alkaline Hydrothermal Treatment, Microwave Alkaline Hydrothermal Treatment and Fusion**

Techniques are being used to achieve this purpose [146]. The alkaline hydrothermal and the alkaline microwave hydrothermal methods are similar in that they both involve the interaction of the industrial ash and an alkaline solution at elevated temperatures. In both methods, the collapse of the fly ash crystalline phases, the release and dissolution of Si and Al, and the nucleation of the zeolite phases take place at a single phase and at the same reaction conditions. The only differences between the two are the source of the heat energy that is supplied for the zeolitization process and the means of transfer to the reaction system. In the alkaline hydrothermal method, the thermal energy required for the zeolitization process is generated outside the reaction vessel and transferred by conduction and convection. For the microwave hydrothermal process, the interaction of microwave energy with the aqueous medium of the reaction system is the heat source for the zeolitization process. The microwave energy is directly transmitted by radiation to the water molecules in the microwave-transparent reaction vessel, the magnetic field created by the microwave radiation causes the rapid dipole rotation (spinning) of the water molecules due to their polar nature, and leads to the generation of heat energy [147] that is required for the zeolitization process. The advantages of the Microwave Hydrothermal method over the conventional hydrothermal method are rapid heating, time and energy saving, and a higher degree of zeolitization [148]. The Fusion method involve a series of separate steps: the high temperature alkali treatment of industrial ash in muffle furnace in order to collapse the ash crystalline phases and release the Si and Al content; the ageing stage which is the dissolution of the released Si and Al into an aqueous medium and their interaction for zeolites nucleation; and the crystallization of the zeolite phases. Also, several more recent works had been reported on the modifications of the basic syntheses procedures for the zeolitization of industrial fly ash, by the incorporations some organic and inorganic constituents into the syntheses systems in order to

produce cheap and more efficient adsorbents for the sequestration of organic and inorganic pollutants from contaminated waters [143, 144, 149].

AIM AND OBJECTIVES

Several methods which could be used to remove our target pollutants: aniline; p-nitroaniline and nitrobenzene from contaminated water have been discussed in this chapter. However, literature has pointed to the adsorption method as the simplest and the least problematic in terms of the generation of secondary water pollutants. And in recent decades, research on the preparation of low-cost adsorbents for the removal of varieties of pollutants from contaminated water has intensified, particularly focusing on the utilization of agricultural and industrial wastes which possess very little economic value. Research in this direction has great potential for lowering the cost of wastewater treatment. And create an additional route of safely managing these wastes rather than allowing them to constitute a nuisance to the environment. Hence, a goal of studying the removal of aniline, p-nitroaniline and nitrobenzene from contaminated water using adsorbents prepared from bagasse ash, a sugar industry waste that has a great potential of constituting a nuisance to the environment was defined for this research. In order to achieve this goal, the work was directed towards the following objectives:

- i. To synthesize the adsorbents: Calcium Fused Zeolitic Bagasse Fly Ash (CaFZBFA) and Magnesium Fused Zeolitic Bagasse Fly Ash (MgFZBFA), both by Fusion Approach and having the incorporations of Ca(II) and Mg(II); and Calcium Microwave Zeolitic Bagasse Fly Ash (CaMZBFA) and Magnesium Microwave Zeolitic Bagasse Fly Ash (MgMZBFA), both by Microwave Alkaline Hydrothermal Method and having the incorporations of Ca(II) and Mg(II).
- ii. To evaluate the adsorption performances of the adsorbents towards the pollutants from their respective aqueous solutions.

- iii. To characterize the adsorbents by their mineralogical constituents, surface morphologies, surface functional groups, thermogravimetric properties, and surface areas and porosities.
- iv. To investigate the effect of syntheses methods on the properties of the adsorbents and the adsorption performances.
- v. To investigate the possible mechanisms for the adsorption processes via adsorption isotherm models, kinetics models and thermodynamic studies.

REFERENCES

1. Bhatkhande, D.S., et al., Photocatalytic and photochemical degradation of nitrobenzene using artificial ultraviolet light. *Chemical Engineering Journal*, 2004. **102**: p. 283–290.
2. NAT. Earth's freshwater. [cited 2018 8 May]; Available from: <https://www.nationalgeographic.org/media/earths-fresh-water/>.
3. SU_Ports. Pollution. [cited 2018 6 July]; Available from: <http://www.seinemaritime.net/suports/uploads/files/Pollution%20E-book%20Part%201%20Overview.pdf>.
4. Briggs, D., Environmental pollution and the global burden of disease. *British Medical Bulletin*, 2003. **68**: p. 1-24.
5. Eyu, D.G. and Aliu, A.O., Environmental pollution and mitigation- An overview. *ARPN Journal of Engineering and Applied Sciences*, 2013. **8**(8).
6. Marks, R. Cesspools of shame: How factory farm lagoons and sprayfields threaten environmental and public health. [cited 2018 6 July]; Available from: <https://www.nrdc.org/sites/default/files/cesspools.pdf>.
7. RRN. Coastal development. 2018 [cited 2018 6 July]; Available from: <http://www.reefresilience.org/coral-reefs/stressors/local-stressors/coastal-development/>.
8. Panetta, L.E., America's living oceans: Charting a course for sea change. 2003, Pew Oceans Commission.
9. Potters, G., *Marine pollution*. 2013: Oxford University Press.
10. Kroeker, K.J., et al., Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms. *Ecology Letters*, 2010. **13**: p. 1419–1434.

11. Portner, H.-O., Ecosystem effects of ocean acidification in times of ocean warming: a physiologist's view. *Mar Ecol Prog Ser*, 2008. **373**: p. 203–217.
12. Young, E. Copper decimates coral reef spawning. 2003 [cited 2018 28 April]; Available from: <https://www.newscientist.com/article/dn4391-copper-decimates-coral-reef-spawning/>.
13. Reisser, J., et al., Marine plastic pollution in waters around Australia: Characteristics, concentrations, and pathways. *PLoS ONE*, 2013. **8**(11).
14. eniscuola. Water pollution. [cited 2018 26 April]; Available from: http://www.eniscuola.net/wp-content/uploads/2011/02/pdf_water_pollution.pdf.
15. Sugar Industry: Process Description and Wastewater Treatment. [cited 2019 7 February]; Available from: <http://www.environmentalpollution.in/waste-management/sugar-industry-process-description-and-wastewater-treatment/2846>.
16. Dsikowitzky , L., et al., Complex organic pollutant mixtures originating from industrial and municipal emissions in surface waters of the megacity Jakarta—an example of a water pollution problem in emerging economies. *Environ Sci Pollut Res*, 2017.
17. Migo, V.P., et al., Industrial water use and the associated pollution and disposal problems in the Philippines, in *Water policy in the Philippines; Global issues in water*. 2018, Springer International Publishing AG.
18. Wright , I.A. and Ryan, M.M., Impact of mining and industrial pollution on stream macroinvertebrates: importance of taxonomic resolution, water geochemistry and EPT indices for impact detection. *Hydrobiologia*, 2016.

19. Wang, Q. and Yang, Z., Industrial water pollution, water environment treatment, and health risks in China. *Environmental Pollution*, 2016.
20. Bansal, N., Industrial development and challenges of water pollution in coastal areas: The case of Surat, India. *IOP Conf. Ser.: Earth Environ. Sci.* , 2018. **120** (012001).
21. Dubey, M. and Ujjania, N.C., Water quality and pollution status of Tapi river, Gujarat, india. *International Journal of Pure and Applied Zoology*, 2013. **1**(3): p. 261-266.
22. Shah, B.A., et al., Impacts of industrial and agricultural chemical wastes on freshwater resources. *JSM Chem*, 2018. **6**(1): p. 1052.
23. Shah, B.A., et al., Assessment of heavy metals in sediments near Hazira industrial zone at Tapti River estuary, Surat, India. *Environ Earth Sci*, 2013. **69**: p. 2365–2376.
24. Aoki, K., et al., Microbial metabolism of aniline through a meta-cleavage pathway: Isolation of strains and production of catechol 2,3-dioxygenase. *Agricultural and Biological Chemistry*, 1990. **54**(1): p. 205-206.
25. Han, Y., et al., Electrochemically enhanced adsorption of aniline on activated carbon fibers. *Separation and Purification Technology*, 2006. **50**: p. 365–372.
26. Shen, J., et al., Enhanced biodegradation of aniline under anoxic condition. *Advanced Materials Research*, 2012. **356-360** p. 25-30.
27. Dvorak, L., et al., Removal of aniline, cyanides and diphenylguanidine from industrial wastewater using a full-scale moving bed biofilm reactor. *Process Biochemistry*, 2014. **49**: p. 102–109.
28. Osaki, Y., et al., The microbial degradability of aniline in river water and an attempt to use the level of the biodegradability as an indicator of water pollution. *Eisei Kagaku*, 1990. **35**(7): p. 411-417.

29. ATSDR. Aniline. [cited 2018 7 May]; Available from: <https://www.atsdr.cdc.gov/toxfaqs/tfacts171.pdf>.
30. Lewis(Sr.), R.J., Hazardous chemicals desk reference. 2008, Hoboken, New Jersey: John Wiley & Sons, Inc.
31. Nair, R.S., et al., Subchronic inhalation toxicity of p-nitroaniline and p-nitrochlorobenzene in rats. *Fundamental and Applied Toxicology*, 1986. **6**: p. 618-627.
32. Sun, J.-H., et al., A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process. *Journal of Hazardous Materials*, 2007. **148**: p. 172–177.
33. Huang, J., Wang, X., and Huang, K., Adsorption of p-nitroaniline by phenolic hydroxyl groups modified hyper-cross-linked polymeric adsorbent and XAD-4: A comparative study. *Chemical Engineering Journal*, 2009. **155**: p. 722–727.
34. Li, K., et al., Adsorption of p-nitroaniline from aqueous solutions onto activated carbon fiber prepared from cotton stalk. *Journal of Hazardous Materials*, 2009. **166**: p. 1180–1185.
35. Zhu, L., et al., Effects of ionizable organic compounds in different species on the sorption of p-nitroaniline to sediment. *Water Research*, 2005. **39**: p. 281–288.
36. NJDEP. Hazardous substance fact sheet. [cited 2018 12 May]; Available from: <http://nj.gov/health/eoh/rtkweb/documents/fs/1548.pdf>.
37. Bakdash, A., et al., Lethal poisoning with p-nitroaniline. *T+K*, 2006. **73**(2): p. 61.
38. Lai, C., et al., Simultaneous degradation of P-nitroaniline and electricity generation by using a microfiltration membrane dual-chamber microbial fuel cell. *International Journal of Hydrogen Energy*, 2017: p. 1-9.
39. Li, K., Lib, Y., and Zheng, Z., Kinetics and mechanism studies of p-nitroaniline adsorption on activated carbon fibers prepared from

- cotton stalk by $\text{NH}_4\text{H}_2\text{PO}_4$ activation and subsequent gasification with steam. *Journal of Hazardous Materials*, 2010. **178**: p. 553–559.
40. Zheng, K., et al., Enhanced adsorption of p-nitroaniline from water by a carboxylated polymeric adsorbent. *Separation and Purification Technology*, 2007. **57**: p. 250–256.
41. Nishino, S.F. and Spain, J.C., Degradation of nitrobenzene by a *Pseudomonas pseudoalcaligenes*. *Applied and Environmental Microbiology*, 1993. **59**(8): p. 2520-2525.
42. Pan, J. and Guan, B., Adsorption of nitrobenzene from aqueous solution on activated sludge modified by cetyltrimethylammonium bromide. *Journal of Hazardous Materials*, 2010. **183**: p. 341–346.
43. Qin, Q., Ma, J., and Liu, K., Adsorption of nitrobenzene from aqueous solution by MCM-41. *Journal of Colloid and Interface Science*, 2007. **315**: p. 80–86.
44. Reungoat, J., et al., Adsorption of nitrobenzene from water onto high silica zeolites and regeneration by ozone. *Separation Science and Technology*, 2007. **42**(7): p. 1447-1463.
45. Sun, Z., et al., Magnetically motive porous sphere composite and its excellent properties for the removal of pollutants in water by adsorption and desorption cycles. *Adv. Mater.*, 2006. **18**: p. 1968–1971.
46. Wei, W., et al., Removal of nitrobenzene from aqueous solution by adsorption on nanocrystalline hydroxyapatite. *Desalination*, 2010. **263**: p. 89–96.
47. EPA. Nitrobenzene. [cited 2018 8 May]; Available from: <https://www.epa.gov/sites/production/files/2016-09/documents/nitrobenzene.pdf>.
48. PubChem. Nitrobenzene. [cited 2018 9 May]; Available from: <https://pubchem.ncbi.nlm.nih.gov/compound/nitrobenzene#section=Analytic-Laboratory-Methods>.

49. Zhang, S., et al., Performance of enhanced biological SBR process for aniline treatment by mycelial pellet as biomass carrier. *Bioresource Technology*, 2011. **102**: p. 4360–4365.
50. O'Neill, F.J., et al., Bacterial growth on aniline: Implications for the biotreatment of industrial wastewater. *Wat. Res.*, 2000. **34**(18): p. 4397-4409.
51. Gorontzy, T., Kuver, J., and Blotevogel, K.-H., Microbial transformation of nitroaromatic compounds under anaerobic conditions. *Journal of General Microbiology* 1993. **139**: p. 1331-1336.
52. Qureshi, A., et al., Degradation of 4-nitroaniline by *Stenotrophomonas* strain HPC 135. *International Biodeterioration & Biodegradation*, 2007. **60**: p. 215–218.
53. Saupe, A., High-rate biodegradation of 3- and 4-nitroaniline. *Chemosphere*, 1999. **39**: p. 2325-2346.
54. Silambarasan, S. and Vangnai, A.S., Biodegradation of 4-nitroaniline by plant-growth promoting *Acinetobacter* sp. AVLB2 and toxicological analysis of its biodegradation metabolites. *Journal of Hazardous Materials* 302, 2016. **302**: p. 426–436.
55. Nishino, S.F. and Spain, J.C., Oxidative Pathway for the Biodegradation of Nitrobenzene by *Comamonas* sp. Strain JS765. *Applied and Environmental Microbiology*, 1995. **61**(6): p. 2308–2313.
56. Xie, T., et al., Degradation of nitrobenzene-containing wastewater by a microbial-fuel-cellcoupled constructed wetland. *Ecological Engineering*, 2018. **112**: p. 65–71.
57. Oturan, M.A. and Aaron, J.-J., Advanced oxidation processes in water/wastewater treatment: Principles and applications. A review. *Critical Reviews in Environmental Science and Technology*, 2014. **44**: p. 2577–2641.

58. Swaminathan, M., Muruganandham, M., and Sillanpaa, M., Advanced oxidation processes for wastewater treatment. *International Journal of Photoenergy*, 2013.
59. Wang, J.L. and Xu, L.J., Advanced oxidation processes for wastewater treatment: Formation of hydroxyl radical and application. *Critical Reviews in Environmental Science and Technology*, 2012. **42**(3): p. 251-325.
60. Brillas, E., et al., Aniline mineralization by AOP's: anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes. *Applied Catalysis B: Environmental*, 1998. **16**: p. 31-42.
61. Chen, Y., et al., Electrochemical degradation of nitrobenzene by anodic oxidation on the constructed TiO₂-NTs/SnO₂-Sb/PbO₂ electrode. *Chemosphere* 2014. **113**: p. 48–55.
62. Jiang, Y., Petrier, C., and Waite, T.D., Effect of pH on the ultrasonic degradation of ionic aromatic compounds in aqueous solution. *Ultrasonics Sonochemistry*, 2002. **9**: p. 163–168.
63. Liu, X.-B., et al., Electrochemical degradation of nitrobenzene. *Current Organic Chemistry*, 2012. **16**: p. 1967-1971.
64. Nitoi, I., et al., UV–VIS photocatalytic degradation of nitrobenzene from water using heavy metal doped titania. *Journal of Industrial and Engineering Chemistry*, 2014.
65. Qin, Y., et al., Degradation and mineralization of aniline by O₃/Fenton process enhanced using high-gravity technology. *Chinese Journal of Chemical Engineering*, 2018.
66. Sun, J.-H., et al., Oxidative decomposition of p-nitroaniline in water by solar photo-Fenton advanced oxidation process. *Journal of Hazardous Materials*, 2008. **153**: p. 187–193.
67. Zheng, K., et al., 4-nitroaniline degradation by TiO₂ catalyst doping with manganese. *Journal of Chemistry*, 2015.
68. Mazille, F. Advanced oxidation process. [cited 2018 28 May]; Available from: <https://www.sswm.info/sswm-university->

[course/module-6-disaster-situations-planning-and-preparedness/further-resources-0/advanced-oxidation-processes.](#)

69. Kiezyk, P.R. and Mackay, D., Wastewater treatment by solvent extraction. The Canadian Journal of Chemical Engineering, 1971. **49**.
70. Rajan, A., Sreedharan, S., and Babu, V., Solvent extraction and adsorption technique for the treatment of pesticide effluent. CiVEJ, 2016. **3**(2).
71. Chai, W., et al., Extraction of aniline from wastewater: equilibria, model, and fitting of apparent extraction equilibrium constants. RSC Adv., 2016. **6**: p. 6125.
72. Li, C.-H., Recovery of aniline from wastewater by nitrobenzene extraction enhanced with salting-out effect. Biomedical and Environmental Sciences, 2010. **23**: p. 208-212.
73. Wu, X., et al., Liquid-liquid extraction of low-concentration aniline from aqueous solutions with salts. Ind. Eng. Chem. Res., 2010. **49**: p. 2581–2588.
74. Yun, C.H., Prasad, R., and Sirkar, K.K., Membrane solvent extraction removal of priority organic pollutants from aqueous waste streams. Ind. Eng. Chem. Res. , 1992. **31**: p. 1709-1717.
75. Bajpai, A.K. and Rajpoot, M., Adsorption techniques- A review. Journal of Scientific and Industrial Research, 1999. **58**: p. 844-860.
76. LeVan, M.D., Carta, G., and Yon, C.M., Adsorption and ion exchange. 1999, The McGraw-Hill Companies, Inc.
77. Ranke, W. Adsorption and desorption. [cited 2018 8 June]; Available from: http://www.fhi-berlin.mpg.de/acnew/departement/pages/teaching/pages/teaching_wintersemester_2008_2009/Wolfgang_Ranke_Adsorption_081128.pdf.
78. Bhatnagar, A. and Sillanpaa, A., Utilization of agro-industrial and municipal waste materials as potential adsorbents for water

- treatment—A review. *Chemical Engineering Journal*, 2010. **157**: p. 277–296.
79. MedicalPrep. Adsorption. [cited 2018 10 June]; Available from: <https://www.emedicalprep.com/study-material/chemistry/surface-chemistry/adsorption/>.
80. Rouquerol, F., Rouquerol, J., and Sing, K., Adsorption by powders and porous solids: Principles, methodology and applications. 1999, London, UK: Academic Press.
81. Kralik, M., Adsorption, chemisorption, and catalysis. *Chemical Papers*, 2014.
82. Ruthven, D.M., Principles of adsorption and adsorption process. 1984, United States of America: John Wiley and Sons Inc.
83. Ali, I. and Gupta, V.K., Advances in water treatment by adsorption technology. *Nat Protoc*, 2006. **1**(6): p. 2661-7.
84. Largitte, L. and Pasquier, R., A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. *Chemical Engineering Research & Design*, 2016. **109**: p. 495-504.
85. Visa, M. and Popa, N., Adsorption of heavy metals cations onto zeolite material from aqueous solution. *Journal of Membrane Science & Technology*, 2015. **5**(01): p. 133.
86. EMIS. Adsorption Techniques. [cited 2018 10 February]; Available from: <https://emis.vito.be/en/techniekfiche/adsorption-techniques>.
87. Crini, G., et al., Adsorption-oriented processes using conventional and non-conventional adsorbents for wastewater treatment, in *Green Adsorbents for Pollutant Removal*. 2018, Springer International Publishing AG.
88. AbdelSalam, O.E., Reiad, N.A., and ElShafei, M.M., A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *Journal of Advanced Research*, 2011. **2**: p. 297–303.

89. Gupta, V.K. and Nayak, A., Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe₂O₃ nanoparticles. *Chemical Engineering Journal*, 2012. **180**: p. 81–90.
90. Hegazi, H.A., Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC Journal* (2013) 9, 276–282, 2013. **9**: p. 276–282.
91. Wang, S. and Peng, Y., Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal*, 2010. **156**: p. 11–24.
92. Wang, F.Y., Wang, H., and Ma, J.W., Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent—Bamboo charcoal. *Journal of Hazardous Materials*, 2010. **177**: p. 300–306.
93. Xue, Y., et al., Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests. *Chemical Engineering Journal*, 2012. **200–202**: p. 673–680.
94. Pelleria, F.-M., et al., Adsorption of Cu(II) ions from aqueous solutions on biochars prepared from agricultural by-products. *Journal of Environmental Management*, 2012. **96**: p. 35–42.
95. Ahmaruzzaman, M., Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Advances in Colloid and Interface Science*, 2011. **166**: p. 36–59.
96. Yang, Z., et al., Cr(III) adsorption by sugarcane pulp residue and biochar. *J. Cent. South Univ.*, 2013. **20**: p. 1319–1325.
97. Kumar, P.S., et al., Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination*, 2010. **261**: p. 52–60.
98. Auta, M. and Hameed, B.H., Chitosan–clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption

- of methylene blue. *Chemical Engineering Journal*, 2014. **237**: p. 352–361.
99. Dahri, M.K., Kooh, M.R.R., and Lim, L.B.L., Water remediation using low cost adsorbent walnut shell for removal of malachite green: Equilibrium, kinetics, thermodynamic and regeneration studies. *Journal of Environmental Chemical Engineering* 2014. **2**: p. 1434–1444.
100. Dawood, S. and Sen, T.K., Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: Equilibrium, thermodynamic, kinetics, mechanism and process design. *Water Research*, 2012. **46**: p. 1933-1946.
101. Jain, S. and Jayaram, R.V., Removal of basic dyes from aqueous solution by low-cost adsorbent: Wood apple shell (*Feronia acidissima*). *Desalination* 2010. **250**: p. 921–927.
102. Kyzas, G.Z., Lazaridis, N.K., and Mitropoulos, A.C., Removal of dyes from aqueous solutions with untreated coffee residues as potential low-cost adsorbents: Equilibrium, reuse and thermodynamic approach. *Chemical Engineering Journal* 2012. **189–190**: p. 148– 159.
103. Nasuha, N., Hameed, B.H., and Din, A.T.M., Rejected tea as a potential low-cost adsorbent for the removal of methylene blue. *Journal of Hazardous Materials*, 2010. **175**: p. 126–132.
104. Xu, R., et al., Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues. *Bioresource Technology* 102 2011. **102**: p. 10293–10298.
105. Alebachew, N., Yadav, O.P., and Lokesh, Removal of phenol red dye from contaminated water using barley (*hordeum vulgare* L.) husk-derived activated carbon. *Sci. Int*, 2017. **5**(1): p. 7-16.
106. Yang, Y., et al., Evaluation of adsorption potential of bamboo biochar for metal-complex dye: equilibrium, kinetics and artificial neural network modeling. *Int. J. Environ. Sci. Technol.*, 2013.

107. Zhang, M. and Gao, B., Removal of arsenic, methylene blue, and phosphate by biochar/AlOOH nanocomposite. *Chemical Engineering Journal*, 2013. **226**: p. 286–292.
108. Chowdhury, S. and Saha, P., Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: Equilibrium, kinetic and thermodynamic studies. *Chemical Engineering Journal*, 2010. **164**: p. 168–177.
109. Zhang, M., et al., Synthesis of porous MgO-biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions. *Chemical Engineering Journal*, 2012. **210**: p. 26–32.
110. Ozdemir, O., et al., Comparison of the adsorption characteristics of azo-reactive dyes on mesoporous minerals. *Dyes and Pigments*, 2004. **62**: p. 49-60.
111. Mohan, D., et al., Fluoride removal from water using bio-char, a green waste, low-cost adsorbent: Equilibrium uptake and sorption dynamics modeling. *Ind. Eng. Chem. Res.*, 2012. **51**: p. 900–914.
112. Gupta, V.K., et al., Pesticides removal from waste water by activated carbon prepared from waste rubber tire. *Water Research*, 2011. **45**: p. 4047-4055.
113. Thuy, P.T., Anh, N.V., and Bruggen, B., Evaluation of two low-cost-high-performance adsorbent materials in the waste-to-product approach for the removal of pesticides from drinking water. *Clean – Soil, Air, Water* 2012. **40**(3): p. 246–253.
114. Sun, K., et al., Sorption of bisphenol A, 17 α -ethinyl estradiol and phenanthrene on thermally and hydrothermally produced biochars. *Bioresource Technology*, 2011. **102**: p. 5757–5763.
115. Hamdaoui, M., et al., Improvement of phenol removal from aqueous medium by adsorption on organically functionalized Moroccan stevensite. *J. Mater. Environ. Sci.*, 2018. **9**(4): p. 1119-1128.

116. Malakootian, M., et al., Phenol removal from aqueous solution by adsorption process: Study of the nanoparticles performance prepared from alo vera and mesquite (*Prosopis*) leaves. *Scientia Iranica*, 2018.
117. Salari, S., et al., Evaluation of removal efficiency of phenol from synthetic aqueous solutions by *Citrullus colocynthis* seed ash. *Environmental Health Engineering and Management Journal*, 2018.
118. Sarkar, C., Basu, J.K., and Samanta, A.N., Microwave activated LD slag for phenolic wastewater treatment: Multi-parameter optimization, isotherms, kinetics and thermodynamics. *Chemical Engineering Transactions*, 2017. **57**: p. 277-282.
119. Xiong, Q., et al., A cellulose acetate/*Amygdalus pedunculata* shell-derived activated carbon composite monolith for phenol adsorption. *RSC Adv.*, 2018. **8**: p. 7599.
120. Ahmaruzzaman, M. and Gayatri, S.L., Batch adsorption of 4-nitrophenol by acid activated jute stick char: Equilibrium, kinetic and thermodynamic studies. *Chemical Engineering Journal*, 2010. **158**: p. 173–180.
121. Jaeger, S., et al., Removal of p-nitrophenol from aqueous solution using Brazilian peat: Kinetic and thermodynamic studies. *Water Air Soil Pollut*, 2015.
122. Kumar, N.S., Asif, M., and Al-Hazzaa, M.I., Adsorptive removal of phenolic compounds from aqueous solutions using pine cone biomass: kinetics and equilibrium studies. *Environmental Science and Pollution Research*, 2018.
123. Rahmani, A.R., et al., A comparative study on the removal of pentachlorophenol using copper-impregnated pumice and zeolite. *Journal of Environmental Chemical Engineering*, 2018.
124. Gao, D.-W., et al., High-capacity adsorption of aniline using surface modification of lignocellulose-biomass jute fibers. *Bioresource Technology*, 2015.

125. Huang, R., et al., Simultaneous adsorption of aniline and Cr(VI) ion by activated carbon/chitosan composite. *J. App. Polym. Sci.*, 2014.
126. Jiang, L., et al., Preparation of a novel manganese oxide-modified diatomite and its aniline removal mechanism from solution. *Chemical Engineering Journal*, 2016.
127. Khaniabadi, Y.O., et al., Low-cost sorbent for the removal of aniline and methyl orange from liquid-phase: Aloe Vera leaves wastes. *Journal of the Taiwan Institute of Chemical Engineers*, 2016: p. 1-9.
128. Kumar, M. and Tamilarasan, R., Modeling studies: Adsorption of aniline blue by using *Prosopis juliflora* carbon/Ca/alginate polymer composite beads. *Carbohydrate Polymers*, 2013. **92**: p. 2171– 2180.
129. Lin, X., et al., Removal of aniline using lignin grafted acrylic acid from aqueous solution. *Chemical Engineering Journal* 2011. **172**: p. 856– 863.
130. Zhou, Y., et al., Removal of aniline from aqueous solution using pine sawdust modified with citric acid and β -cyclodextrin. *Ind. Eng. Chem. Res.*, 2014. **53**: p. 887–894.
131. Azeez, S.O. and Adekola, F.A., Sorption of 4-nitroaniline on activated kaolinitic clay and *Jatropha curcas* activated carbon in aqueous solution. *Jordan Journal of Chemistry*, 2016. **11**(2): p. 128-145.
132. Wu, G., Wu, G., and Zhang, Q., Adsorptive removal of p-nitroaniline from aqueous solution by bamboo charcoal: kinetics, isotherms, thermodynamics, and mechanisms. *Desalination and Water Treatment*, 2016.
133. Wang, S., et al., Use of low cost crop biological wastes for the removal of nitrobenzene from water. *Desalination*, 2010. **264**: p. 32–36.
134. Wu, Y., et al., Novel hydrophobic cotton fibers adsorbent for the removal of nitrobenzene in aqueous solution. *Carbohydrate Polymers* 2017. **155**: p. 294–302.

135. Huang, T.Y. and Chuieh, P.T., Life cycle assessment of reusing fly ash from municipal solid waste incineration. *Procedia Engineering*, 2015. **118**: p. 984-991.
136. James, J. and Pandian, P.K., A short review on the valorisation of sugarcane bagasse fly ash in the manufacture of stabilized/sintered earth blocks and tiles. *Advances in Materials Science and Engineering*, 2017. **2017**: p. 1-15.
137. Lokeshappa, B. and AnikKumar, D., Disposal and management of fly ash, in *International Conference on Life Science and Technology*. 2011, IACSIT Press, Singapore.
138. Martison, E. EPA coal ash rule still not done. 2014 [cited 2018 26 January]; Available from: <https://www.politico.com/story/2014/03/epa-coal-ash-rule-104967>.
139. Querol, X., et al., Synthesis of zeolites from coal fly ash: An overview. *Int J Coal Geol*, 2002. **50**(1-4): p. 413-423.
140. Raleigh, N.C. Duke Energy Corporation agrees to \$6 million fine for coal ash spill, North Carolina says. 2016 [cited 2018 26 January]; Available from: <https://www.cbsnews.com/news/duke-energy-corporation-agrees-6-million-fine-coal-ash-spill-north-carolina>.
141. Rauf, N., Damayanti, M.C., and Pratama, S.W.I. The influence of sugarcane bagasse ash as fly ash on cement quality. in *AIP*. 2017.
142. Teixeira, S.R., Pena, A.F.V., and Miguel, A.G., Briquetting of charcoal from sugar-cane bagasse fly ash (SBFA) as an alternative fuel. *Waste Management*, 2010. **30**: p. 804–807.
143. Abebe, A.A., Confiscation of aromatic compounds by microwave synthesized electrolyte treated and Si/Al enhanced mesoporous zeolitic materials originated from sugar industry detritus, in *Department of Chemistry*. 2016, Veer Narmad South Gujarat University.
144. Pandya, D.D., Impounding of phenols by zeolitic composites tailored from agricultural debris bagasse fly ash: Response surface

- methodology and column dynamics, in Department of Chemistry. 2017, Veer Narmad South Gujarat University.
145. Mistry, C.B., Hydrothermally modified agricultural detritus into zeolitic material with and without electrolyte media: Potential sorbents for uptake of metal ions, in Department of Chemistry. 2014, Veer Narmad South Gujarat University.
146. Patel, K.G. and Srivastava, V.K., Recent advances in the synthesis of zeolite from fly ash, in International Conference on Multidisciplinary Research & Practice.
147. Education.com. Soapy Science: How microwaves affect matter. 2013 [cited 2019 20 January]; Available from: <https://www.scientificamerican.com/article/bring-science-homes-soap-microwave/>.
148. Yuan, C., Hong-juan, W., and Zhi-ning, X., Advances in microwave assisted synthesis of ordered mesoporous materials. Trans. Nonferrous Met. Soc. China 2009. **19**: p. 656 - 664.
149. Patel, H.J., Amputation of phenolic pollutants by microwave assisted surface activated zeolitic composites derived from power station solid waste: Kinetics and column design, in Department of Chemistry. 2017, Veer Narmad South Gujarat University.